Applications Of Classical Electrodynamics And Statistical Mechanics To Problems In Energy Transfer And Fluorescence.

A thesis presented

by

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to

The Committee on the Degree of Doctor of Philosophy in Physical Chemistry

in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the subject of Physical Chemistry

Harvard University
Cambridge, Massachusetts
December, 1993
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The material in Chapter 3 is a revised and corrected version of an article by Andrew C. Pineda and David M. Ronis which appeared in the Journal of Chemical Physics and is © 1985 by Andrew C. Pineda, David M. Ronis, and the American Physical Society.
The problems of electronic dipole-dipole energy transfer ( Förster transfer) between dye molecules and fluorescence from dye molecules are studied using classical electrodynamics and the methods of statistical mechanics. In all the problems we study, we shall be modeling the dye molecules as classical Drude oscillators. We shall for the most part be concerned with the effects of geometry on these processes. In the case of energy transfer, we shall also study matters in the limits of steady-state and flashed excitation of the system.

The problem of energy transfer is studied in small spherical droplets whose dimensions are comparable to the wavelength of the light emitted by the dipoles and in systems of macroscopic dimensions. Depending upon the specific problem, we define a set of classical quantities that play roles similar to the quantum mechanical observables which measure excitation transfer. We consider the system of dye molecules to be a system of interacting classical point dipoles, some of which can be excited by external sources (donors) and some of which cannot (acceptors), whose classical equations of motion are subjected to a set of random initial conditions by which the quantum mechanical processes by which the system is excited are mimicked. We then compute the quantities of interest, which turn out to be bilinear in the classical dipole moments or their first time-derivatives, in terms of a density expansion using the binary collision operator formalism. The quantities we compute are expressed in terms of various one- and two-particle propagators for which approximate algebraic and integral equations are derived from the binary collision expansion using a diagrammatic resummation technique.
In the droplet case, it becomes important to consider the Mie resonances of the sphere since the resonances couple large, distantly separated regions in space. In light of this interaction various simplifications of the theory described above are made. For example, ordinary Förster transfer is neglected. The theory for the droplet case is studied in the limit of steady state excitation and compared with experimental results. When the model is studied for the Coumarin — Rhodamine-6G system in glycerol solution, excellent agreement is obtained with the observed anomalous density dependence which can be interpreted as arising from the broadening of Mie resonances as the density of dye molecules is increased.

In the bulk case, only short distances are important as discussed by Förster. In our theory, we start out using an interaction that includes a long-range, radiative, component in addition to a short-range, near field component. In the steady state limit, we show that the theory decomposes into a sum of short-range and long-range components. The long-range contribution is found to be negligible owing to induced loss which may be interpreted as being due to the renormalization of the dielectric constant of the medium, i.e., the extinction theorem. We then study the system for the case of flashed excitation, using only the short range interaction, and try to determine if our classical system will exhibit diffusive behavior. The propagators are found to exhibit unusual frequency behavior reminiscent of Davydov splitting in molecular crystals. Comparisons are made with more traditional approaches which use transition rates based on Fermi’s Golden Rule and embed them in Master equations for the excitation density.

The problem of fluorescence quenching in dye molecules near rough metal surfaces is considered in terms of a classical electrodynamic near field calculation of the interaction of a single Drude oscillator with a single prolate hemispherical bump on a flat metal surface. We include the effects of electromagnetic coupling between the surface bump and the bulk metal in contrast with other works. Fluorescence lifetimes are calculated for silver metal in the flat
plane and bump geometries and the bump lifetimes are found to be two to four orders of magnitude smaller. Avoided crossing behavior is predicted for the shortest bump-molecule densities.
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For my parents, Josefa Carballo Pineda and Andrew Garcia Pineda.
"Desocupado lector: sin juramento me podrás creer que quisiera que este libro, como hijo del entendimiento, fuera el más hermoso, el más gallardo y más discreto que pudiera imaginarse; pero no he podido yo contravenir al orden de naturaleza; que en ella cada cosa engendra su semejante."

"Idle reader, without doubt you may believe that I wish that this book, as a child of the intellect, were the most beautiful, most excellent, and most graceful that could be imagined, but I have not been able to contravene the order of nature in which each thing engenders its image."

— Miguel de Cervantes Saavedra, in

*El ingenioso hidalgo Don Quixote de la Mancha* (1605)
Acknowledgements.

In writing these acknowledgements, it is appropriate to look back at those who have made important contributions to both my life and this thesis. I would first like to thank my parents, Andrew and Josefa, for their all their love, support, and sacrifice as well as their commitment to my education and the education of my brother and sister. Although my mother did not live to see this thesis completed, I know she would have been proud.

I would like to thank my advisor, Professor David Ronis, for all the time and insight he has provided me with over the years. His door was always open, and his patience seemingly inexhaustible as we hammered out various aspects of this work. I should also thank David’s wife, Margaret, and his children for all those times I kept him in his office for late night discussions.

I also have to thank Professor William Klemperer for his sincere interest in my work and in my future. I must also thank him for the many enjoyable hours working with him teaching undergraduate quantum chemistry.

I have had the good fortune to work side by side with many wonderful and talented people during my sojourn in graduate school. Their friendship have helped to make the rigors of graduate life bearable, and yes, even enjoyable. I was blessed to have had such outstanding people as my officemates at Harvard and during my stay at McGill University in Montréal. Mariana Vertenstein and Tom Morton, were ever cheerful, supportive, and open to discussions ranging from science and computing to really important stuff like basketball, swimming and life. Jian-Yang Yuan, the post-doctoral fellow with whom I shared my office at McGill, was a great sounding board for ideas and full of curiosity. We engaged in many far-ranging debates on subjects scientific, and political. Equally important to me was the friendship of fellow students Yannis Drossinos, Sheema Khan, Brian Treadway, Susie Atlas, Carla Roberts and many others from the Karplus, Herschbach and Klemperer groups with whom I shared many lunch-
time discussions, ice cream runs, and foosball games as well as late nights in the computer room. They will all be sorely missed.

I gratefully acknowledge the support of the National Science Foundation which awarded me a Minority Graduate Fellowship for the initial portion of my tenure at Harvard. I would be remiss if I did not also thank Lois Brown and Arizona State University who provided me with access to the Internet computer network while I completed the writing of this thesis at home.

Finally, I would also like to thank my nephews, Carlos, Stephen, and Zachary, and new niece, Josefa, for reminding me about what is really important.
Introduction.
Introduction.

We treat problems in energy transfer and fluorescence in this thesis by the application of classical electrodynamics and the methods of statistical mechanics. Our approach throughout will be to model molecular dipoles as classical Drude oscillators and then to use classical electrodynamics to study their interactions with each other or with a variety of surfaces. Classical electrodynamics has a long history of successful use in the treatment of enhanced fluorescence near flat metal surfaces, near small metallic particles, and near metal surfaces with small protrusions, so one might expect that its extension to the problems we consider here should also have a reasonable chance of meeting with success. In the first chapter, we shall present a classical electrodynamic, many-body theory for energy transfer between donor and acceptor pairs of dye molecules dissolved in micron-sized droplets. The model is studied in the limit of steady-state excitation of the system and anomalous concentration effects are predicted. In the second chapter, the model is applied to systems of macroscopic dimensions. The anomalous concentration effects found previously disappear. The macroscopic theory is also examined in the time domain in the limit of pulsed excitation and is compared with standard models, based upon the Master equation, for the diffusion of the excitation from the initially excited molecule. Finally, in the third chapter, we present a purely classical electrodynamic near-field calculation of the interaction of a molecular dipole with a rough metal surface. The effects of surface roughness are studied by examining the interaction of a Drude oscillator with a metal surface that is flat except for a prolate hemispheroidal bump.

The work we present in chapter 1 was motivated by some experiments by Folan, et al., in which enhanced energy transfer between donor-acceptor pairs of dye molecules was observed for molecules dissolved within an electrostatically levitated aerosol particle. The experimenters measured the ratio of the luminescence from rhodamine-6G (acceptor) at 560 nm to the luminescence of coumarin-1 (donor) at 465 nm as a function of density. In the droplet, the
luminescence ratio was measured and presented as a function of density for fixed mole ratios of donor and acceptor for acceptor concentrations from 1µM to 30µM. The experimenters measured the luminescence ratio down to about 0.1µM, but their values below 1µM were noisier, and hence not presented in the figure in their paper. In the range reported in the figure, the observed luminescence ratio varied weakly with acceptor concentration. Vis-à-vis the behavior below 1µM, it was noted that in the vicinity of 0.1µM, the luminescence ratio took a sharp drop. For purposes of discussion and comparison, we have analyzed the data presented by Folan, et al., for the 1µM to 30µM range using a simple power law expression and have found that in this regime the luminescence ratio scales as $p^{-0.16\pm0.08}$. In bulk Förster transfer, the luminescence ratio scales as $p^1$.

Since the dimensions of the aerosol particles studied were small, of the order of 10 µm, the molecules dissolved in the particle were strongly coupled to the Mie resonances of the sphere, leading to unusual behavior for the energy transfer as a function of concentration. Mie effects have been shown to lead to enhanced decay rates for excited molecules located near small metal spheres and to enhanced stimulated visible emission from dye molecules dissolved within small droplets. Druger, et al., applied the standard Förster theory to the problem using the Mie theory to obtain the interaction for two point dipoles embedded in a dielectric sphere. Their approach was to evaluate the averaged two-particle transition rates using Fermi’s Golden Rule. The luminescence ratio was interpreted as a measure of the branching ratio for the excitation

$$\Gamma = \frac{W_{tr}'/W_{rad}'}{1 + W_{tr}'/W_{rad}'}$$

(1)

where $W_{tr}'$ is the averaged transfer rate and $W_{rad}'$ is the averaged radiation rate. The ratio of rates $W_{tr}'/W_{rad}'$ is simply proportional to the acceptor concentration with the constant of proportionality depending upon the Mie resonances and upon the properties of the molecules. The
weak concentration dependence noted above then arises when $W_{tr}'/W_{rad}' \gg 1$. The important feature here is that the transition between strong and weak dependence depends upon a number $X \equiv \frac{W_{tr}'}{pW_{rad}'}$ that is a two-particle property, i.e., it does not depend upon the concentrations of the molecules. In chapter 1, we present a different model for this process. We describe this system using classical electrodynamics. The dipoles are modeled using the classical equations of motion

$$\vec{p}_i'(\omega) = \vec{\alpha}_i(\omega) \cdot \vec{E}_i'(\omega)$$

(2)

where $\vec{\alpha}_i(\omega)$ is the molecular polarizability function for molecule $i$ and $\vec{E}_i'(\omega)$ the electric field at molecule $i$ due to fields from other molecules, the molecule's own field reflected back from surfaces, and finally external sources. After expressing the electric field at molecule $i$ in terms of dipole moments and sources, we are able to solve the equations of motion using a binary collision expansion. We express the luminescence ratio in terms of a classically analogous quantity, the ratio of the dissipation occurring in the acceptors to the total radiation of the dipoles to infinity. The binary collision expansion of the equations of motion is used to derive density expansions for the acceptor dissipation rate and the total radiation rate, which are resummed using the method used by Zwanzig for finding the density expansion of transport coefficients of gases. We will extract similar concentration effects from our model, however, the physical interpretation of the observed saturation effect is vastly different. In our model, the effect arises because the changing dye concentration leads to a broadening of the Mie resonances of the droplet, which can be interpreted as being due to a renormalization of the dielectric constant of the droplet.

In chapter 2, the theory presented in chapter 1 is applied to macroscopic systems. For the sake of completeness, we first re-examine the steady-state theory of chapter 1 using the bulk interaction. Two limits of the interaction are considered: (1) the full interaction (near-
field and far-field) obtained by solving Maxwell’s equations in the bulk, and (2) the near-field interaction only. This allows us to examine the effects of the resummations performed in the first chapter. We find that in the steady-state, the resummations have the effect of renormalizing the dielectric constants.

We also apply the theory in the limit of pulsed excitation of the system. In this case, we are interested in examining whether an excitation initially on a donor molecule propagates away in a diffusive manner. This problem was studied by Haan and Zwanzig using an approach based upon a Master equation for the probability distribution of the excitation. They studied a system of $N$ molecules randomly distributed in a volume $\Omega$. The probability that an excitation is on the $j$th molecule at time $t$ was written as $p_j(\mathbf{R},t)$ where $\mathbf{R}$ denotes the configuration \{\(r_1, r_2, \ldots, r_N\}\. The time evolution of the probability distribution is governed by a Master equation

$$\frac{dp_j}{dt} = -\frac{p_j}{\tau} + \sum_k \left[ w_{jk} p_k - w_{jk} p_j \right]$$

(3)

where the transition rates are given by the orientationally averaged Förster expressions

$$w_{jk} = \frac{1}{\tau} \left( \frac{R_0}{R_{jk}} \right)^6.$$  

(4)

They study the behavior of the average density of excitation defined by

$$P(N,\Omega,\mathbf{R},t) = \langle \sum_j \delta(\mathbf{r}_j - \mathbf{R}) p_j(\mathbf{R},t) \rangle$$

(5)

in terms of a generalized diffusion coefficient, $\hat{D}(\mathbf{k}, \varepsilon)$, defined by the transformed Green’s function

$$\hat{G}(\mathbf{k}, \varepsilon) = \left[ \varepsilon + k^2 \hat{D}(\mathbf{k}, \varepsilon) \right]^{-1},$$

where $\hat{G}(\mathbf{k}, \varepsilon)$ is the Fourier-LaPlace transform of the Green’s function defined by

$$P(N,\Omega,\mathbf{R},t) = \int d\mathbf{R}' G(N,\Omega,\mathbf{R},\mathbf{R}',t) P(N,\Omega,\mathbf{R}';0).$$

(6)
and in terms of the mean squared displacement

\[ <r^2(t)> = \int d\vec{r} \int d\vec{r}' P(\vec{r}, t). \]

Haan and Zwanzig were only able to obtain the first few terms of the density expansion of the Green’s function. By means of a conjecture, they were able to show that if the limiting behavior is diffusive, then the diffusion coefficient is

\[ D = \hat{D}(0; 0) = 0.324 \frac{R^2}{\tau} \left( \frac{4\pi R^3}{3} \right)^{4/3}. \]  
(7)

Later, Gochanour, Andersen, and Fayer re-examined the problem using diagrammatic methods, considering an infinite number of terms in the density expansion.\(^{11}\) They developed a self-consistent approximation method that allowed them to investigate the nature of the propagation of the excitation at long times and high concentrations. They were able to show that the propagation was initially non-diffusive, but that it ultimately became diffusive on a time scale that depended upon the concentration. For low densities, the propagation becomes diffusive after many decay lifetimes of the molecules in the system and for high densities, the propagation becomes diffusive within a single decay lifetime. The diffusion constant in the long time limit was again shown to scale as \( \rho^{4/3} \). This was verified experimentally.\(^{12}\) Later workers, extended this work to other systems, e.g., 1-D and 2-D disordered systems, randomly substituted lattices, and systems containing randomly distributed traps, where other scalings were obtained.\(^{13}\)

Our approach to the problem is to define an excitation density in terms of the dipole moment density in the system. We then compute the dipole moment density using the methods we applied previously to the calculation of the acceptor dissipation rate and total radiation rate. In chapter 2, we consider an approximation in which we expand out the density dependence in the propagators and make a conjecture similar to that of Haan and Zwanzig in order to obtain a diffusive limit. In an appendix to chapter 2, we lay the framework for an examination of the
problem without expanding out the density dependence. For technical reasons, we were not able to complete the latter treatment, so it is discussed in the context of a suggestion for future work.

In chapter 3, we use classical electrodynamics to study the fluorescence quenching of dye molecules above rough metal surfaces. We employ a near-field calculation of the interaction of a single Drude oscillator with a single prolate hemispheroidal bump on an otherwise flat metal surface. Prock, Chance, and Silbey successfully used classical electrodynamics to obtain the decay rates of excited molecules as a function of distance from perfectly flat surfaces. Whitmore, Robota, and Harris have verified the classical theory for molecule-surface distances from 10 Å to 400 Å for a few dye/flat metal surface systems. Kim, Leung, and George, examined classical decay rates in the presence of a spherical surfaces. Gersten and Nitzan also examined this problem, treating the flat part of the metal as a perfect metal. Our work builds upon the work of Gersten and Nitzan by treating the bumps and the flat portions of the metal in the same fashion.
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Classical Model For Energy Transfer In Microspherical Droplets.

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ABSTRACT

A classical electrodynamic model for energy transfer between donor and acceptor molecules in which the molecules are modeled as Drude oscillators is presented for dye solutions in micron-sized droplets. The model incorporates multiparticle scattering effects by means of a binary collision expansion. Enhanced energy transfer rates and nontrivial concentration effects appear due the Mie resonances of the droplet. The theory is discussed in light of the experiments of L. M. Folan, S. Arnold, and S. D. Druger [Chem. Phys. Lett. 118, 322 (1985)].

MS code no. 1993 PACS numbers:

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§ I. Introduction.

Recently, there have appeared studies of energy transfer or sensitized luminescence in mixtures of dye molecules in small micron-sized droplets. The dye mixtures consist of two types of molecules typically termed donors and acceptors immersed in a solvent such as glycerol, or glycerol and water. The donor molecules have an emission band that overlaps an absorption band of the acceptors. Hence, when the donors are excited at a frequency outside of the absorption band of the acceptor molecule, light may be emitted in the emission band of the acceptors as a result of the absorption of photons emitted by the donors. It is well known that the range of this transfer process in the bulk is of the order of 50–100 Å. It is found that the transfer process in the micron-sized droplet is greatly enhanced over that in the bulk by as much as a factor of 100 for the lowest concentrations. Moreover, the amount of the transfer, defined as a ratio of the luminescence of the acceptors to the luminescence of the donors, is found to depend very weakly on concentration. In 10μ spheres the transfer is found to scale like ρ^{0.16±0.08} where ρ denotes the concentration or number density.* In macroscopic systems, the transfer is found to scale as ρ. The anomalous concentration behavior occurs because of optical resonances in the droplet which have the effect of strongly coupling distantly separated pairs of molecules, by which we mean molecules with separations much larger than 100 Å.

The quantum mechanical theory of energy transfer in bulk dye mixtures is due to Förster and has been extended to the droplet case by Druger, et al. These theories are both two-______________

* The exponent was obtained by least-squares fitting Fig. 3 in Folan, et. al. The ±0.08 uncertainty was obtained in two ways: (1) drawing lines using the error bars appearing in the figure; and (2) fitting using the data points and using the standard formula for the error in the slope, cf. E. L. Crow, F. A. Davis, and M. W. Maxfield, Statistics Manual, (Dover Press, New York, 1960), p. 160 where the s_b = ±0.08 is the standard error of the slope. If we assume that the errors in the log-log plot in Fig. 3 are normally distributed (with identical σ^2), then we can say something about the confidence limits corresponding to the ±0.08 interval obtained by using the error bars. We find that this is about a 70 percent confidence interval. The 90 percent confidence limits are as large as the fitted slope. The confidence limits can be reduced by about a factor of four by excluding the point at about [A] = 5μM.
particle theories in the sense that multiparticle scattering effects are not included in a systematic fashion, rather transition rates are determined according to Fermi’s golden rule and after weighting by the density of states inserted into phenomenological rate equations. Scattering effects are negligible in the bulk because only small numbers of particles are coupled by a short range interaction, but this may not necessarily be true in the case of a droplet in which large spatial regions, and hence large numbers of molecules, are strongly coupled at the resonant frequencies.

In this paper, we propose to study these multiparticle effects by analyzing a classical electrodynamic model of energy transfer between Drude oscillators using a density expansion similar to that of Haan and Zwanzig. In macroscopically large systems this naturally leads to a theory in which most contributions come from particles separated by short distances, but with a small long-range correction arising from scattering effects. In the droplet case, we shall see that there exists a long-range interaction which strongly couples large regions in the sphere, and that we can neglect the short-range contribution from the bulk interaction.

Section II describes the classical model in greater detail. In section III, density expansions for the rates are obtained by means of the binary collision expansion method and expressed in terms of propagators describing the averaged interaction of varying numbers of particles. Expressions for the required propagators in terms of a set of coupled integral equations are presented. The types of approximations employed for computing the propagators for spherical microdroplets are discussed in section IV. In section V, numerical results for micron-sized droplets are presented.

§ II. A Classical Model For Energy Transfer.

Before discussing the classical model of energy transfer we use in this paper, it is instructive to review how the energy transfer process would be described quantum mechanically. The
quantum mechanical picture of the energy transfer process involving a pair of molecules is depicted in Fig. 1. A donor molecule absorbs a photon of a given energy from the medium, non-radiatively dissipates some of the energy and then reemits a Stokes-shifted photon back into the medium. Depending upon the nature of the absorption bands for the donors and the acceptors, an acceptor molecule may then absorb the shifted photon and shift it to still longer wavelengths, or it may simply scatter it elastically. Experimentally, the energy transfer rate is determined by measuring the rate at which photons are Stokes-shifted by the acceptors (typically normalized to the rate at which photons are scattered by donors at the original frequency). Here we shall assume that this rate is proportional, with a proportionality constant that is independent of any properties of the medium, to the rate at which the initial acceptor state decays. Hence, in a purely classical treatment of the energy transfer, we need to calculate the power radiated to infinity at the unshifted frequency and the non-radiative decay rate out of the initial acceptor state(s).⁴ In macroscopic systems, the transfer process occurs by means of the near-field interactions of dipoles. In the droplet case, we will find that the contribution from the near-field interaction is in fact negligible.

The donor and acceptor states involved in the transfer process may be viewed as collections of classical oscillators with given polarizability functions which interact by means of their electrodynamic fields. In a Fourier representation, we may write the dipole moment of each molecule as \( \vec{p}_i(\omega) = \sum \vec{p}_{i,\nu}(\omega) \) with each oscillator component, \( \vec{p}_{i,\nu}(\omega) \), obeying an equation of the form

\[
\dot{\vec{p}}_{i,\nu}(\omega) = \vec{\alpha}_{i,\nu}^{NR}(\omega) \cdot [i \omega \vec{n}_{i,\nu}^{R} \vec{p}_{i}(\omega) + \vec{E}_{i}(\omega) + \vec{Q}_{i}(\omega)],
\]

where \( \vec{\alpha}_{i,\nu}^{NR}(\omega) \) is the part of the polarizability of the \( \nu \)th oscillator in molecule \( i \) arising from

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⁴ Note that in our classical model photons emitted or scattered the acceptors may be absorbed by a donor molecule different from that which emitted the initial photon. This process may not be possible in the quantum mechanical system.
non-radiative processes, including decay, $\vec{E}_i'(\omega)$ is the electric field experienced by the $i$th molecule due to the presence of dielectric interfaces and other molecules in the system and $\vec{Q}_{i,v}(\omega)$ is a random source for the oscillator component.

The random source function is used to mimic the processes by which the donor states are populated and in part depends upon the kind of experiment being performed. In pulsed experiments $\vec{Q}_{i,v}(\omega)$ may be interpreted as arising from random initial conditions for each molecule, while in CW experiments, it is related to the rate at which the upper states of the molecules are excited. Its stochastic properties will not be used directly as will be discussed in more detail below. Radiative damping effects are included via the $i \omega \gamma_i^R \vec{p}_i(\omega)$ term.\footnote{We model the radiative decay term as an exponential decay via the $i \omega \gamma_i^R \vec{p}_i$ term thus avoiding the theoretical difficulties (e.g., runaway solutions) associated with using the Abraham-Lorentz equation as a model for the radiation damping.}

An equation for the total dipole moment, $\vec{p}_i(\omega)$, is obtained by summing the equation above over the individual oscillator components, i.e.

$$\vec{p}_i(\omega) = \vec{\alpha}_i^{NR}(\omega) \cdot [i \omega \gamma_i^R \vec{p}_i(\omega) + \vec{E}_i'(\omega) + \vec{Q}_i(\omega)]$$

$$= \vec{\alpha}_i(\omega) \cdot [\vec{E}_i'(\omega) + \vec{Q}_i(\omega)],$$

(II.2.a)

(II.2.b)

where $\vec{\alpha}_i^{NR}(\omega) = \sum_v \vec{\alpha}_{i,v}^{NR}(\omega)$ is the total non-radiative polarizability,

$$\vec{Q}_i(\omega) \equiv [\vec{\alpha}_i^{NR}(\omega)]^{-1} \sum_v \vec{\alpha}_{i,v}^{NR}(\omega) \cdot \vec{Q}_{i,v}(\omega)$$

(II.3)

is a sum of the sources weighted by the non-radiative polarizabilities, and

$$\vec{\alpha}_i(\omega) = [\vec{\alpha}_i^{NR}(\omega)]^{-1} - i \omega \gamma_i^R \vec{p}_i(\omega)$$

(II.4)

is the total polarizability for the molecule $i$. The non-radiative polarizability functions in this work model damped Drude oscillators, hence they have Lorentzian lineshapes
\[ \vec{\alpha}_{i,\nu}^{NR}(\omega) = \frac{e_i^2 m_i \omega}{\omega_0^{2, \nu} - \omega^2 - i \omega \gamma_{i,\nu}^{NR}} = \frac{\alpha_{0,i,\nu}}{\omega_0^{2, \nu} - \omega^2 - i \omega \gamma_{i,\nu}^{NR}} \]  

(II.5)

where the constants \( \gamma_{i,\nu}^{NR} \), \( m_{i,\nu} \), \( \omega_{0,i,\nu} \), and \( e_{i,\nu} \) denote the non-radiative damping constant, the effective mass, the frequency and the effective charge for the \( \nu \)th oscillator associated with the \( i \)th molecule, respectively. We denote the ratio \( e_i^2 m_i \omega / \omega_{0,i,\nu} \) by \( \alpha_{0,i,\nu} \).

The electric field due to the presence of dielectric interfaces and due to other molecules may be written as a sum of two types of terms

\[ \vec{E}_i(\omega) = \vec{V}_{i}^{sc}(\omega) \cdot \vec{p}_i(\omega) + \sum_{j \neq i} \vec{V}_{ij}(\omega) \cdot \vec{p}_j(\omega). \]  

(II.6)

The first term gives the field at molecule \( i \) due to the reflection of its own fields from dielectric interfaces and the second term gives the contributions from the other molecules. For spherical droplets, \( \vec{V}_{i}^{sc}(\omega) \) and \( \vec{V}_{ij}(\omega) \) are both easily obtained by solving Maxwell’s equations for a point dipole embedded in a dielectric medium in terms of vector spherical harmonics.

In this paper, we shall study events in a CW or steady-state experiment. It is well known from the theory for solids that the rates computed for CW and pulsed (flashed) excitation differ.\(^6\) In our classical model, this arises from the statistical properties of the random source functions. We shall focus on the weighted sum of the sources defined in Eq. (II.3) since, as will be shown below, the quantities we wish to compute only depend upon it and its correlations; moreover, the behaviors of the individual oscillator components may be trivially extracted if desired. The dipole moments of donor molecules are created via radiationless transitions from the higher excited states of the donors; we shall assume that this process completely randomizes the initial phases and orientations of the donor dipoles, and hence, \( \vec{Q}_i(\omega) \) has random phase and orientation, i.e. it has zero mean. Since the acceptors are not excited by an external source we make the additional assumption that the frequency-frequency correlation functions involving one or two acceptors also vanish. Finally, the random phase and orientation assum-
tions imply that different Cartesian components of the same donor are uncorrelated as are the
sources for different donors. This discussion can be summarized in the following expression
for the correlation functions

\[
\langle Q_i^{\mu}(\omega) Q_j^{\nu}(\omega) \rangle = \begin{cases} 
\frac{\Omega_i(\omega)}{3} \delta_{i,j} \delta^{\mu,\nu} \delta(\omega - \omega') & i, j \in D \\
0 & \text{otherwise,}
\end{cases}
\]  

(II.7)

where \(\delta_{i,j}\) is a Kronecker-delta and the superscripts \(\{\mu, \nu\}\) denote the Cartesian components of
the vectors. The delta function in frequency is specific to a CW experiment and accounts for
the fact that averages of \(Q_i^{\mu}(t) Q_j^{\nu}(t)\) are stationary in time.\(^*\) Finally, we assume that the excitation
is uniform throughout the system; so that \(\Omega_i(\omega)\) does not depend upon the molecule’s po-
sition and as a result may be factored out of the average over molecular positions. This as-
sumes that the excitation of the system does not occur at frequencies which couple strongly to
the Mie resonances of the sphere.

In a Fourier representation, we write the equations of motion as

\[
\overrightarrow{p}_i(\omega) = \sum_j \overrightarrow{G}_{ij}(\overrightarrow{R}^N; \omega) \cdot \overrightarrow{Q}_j(\omega).
\]  

(II.8)

The \(3 \times 3\) matrix \(\overrightarrow{G}_{ij}(\overrightarrow{R}^N; \omega)\) is the \(ij\) block of the \(3N \times 3N\) propagator matrix \(\overrightarrow{G}(\overrightarrow{R}^N; \omega)\) which
depends upon the positions of all of the particles as well as the frequency.\(^2\) One can use Eqs.

\(^*\) This is to be expected in a CW experiment, since the populations of excited
donors are continually being replenished by the external source. On the other hand, in
a flashed experiment, in which the system is flashed at say time \(t_0\) one might expect
that \(\langle Q_i^{\mu}(\omega) Q_j^{\nu}(\omega) \rangle\) would be proportional to something like \(e^{i(\omega t_0 + \omega')}\) reflecting the
fact that in the time domain the correlation functions are proportional to delta functions
in time. Of course, in the latter case one could also make the dependence upon the in-
itial conditions explicit by reverting to LaPlace or Fourier-LaPlace (i.e., half-sided
Fourier) transforms.

\(^2\) For the calculation in the droplet, we have adopted the following Fourier conven-
tion

\[
f(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} f(\omega)
\]

Note that if instead one uses the convention

\[
f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} f(\omega)
\]
(II.1), (II.2.b), and (II.8) to show that

\[
\vec{p}_{i,v}(\omega) = \alpha_{i,v}^{NR}(\omega) \cdot \left[ \alpha_{i,v}^{NR}(\omega)^{-1} \cdot \sum_j \vec{G}_{ij}(\vec{R}^N : \omega) \cdot \vec{G}_j(\omega) + \vec{G}_{i,v}(\omega) - \vec{G}_v(\omega) \right].
\]  

For the acceptor molecules, the last two terms in the above expression may be omitted since their averages and correlation functions vanish. It is for this reason, that we need only consider the correlations of the weighted source functions. Eq. (II.2.b) represents three components of a $3N \times 3N$ matrix equation, whose solution may be cast in the form of Eq. (II.8) by employing Eq. (II.6).

The energy transfer rate is computed from the non-radiative rate of dissipation occurring in the acceptors at the absorption frequency of the acceptor. This typically requires a model for the dissipation in the acceptors. We consider the case in which the donors and acceptors may be treated as point-dipole Drude oscillators. In this event, the average dissipation rate for the acceptors, $\langle \tilde{W}_A(t) \rangle$, takes the form

\[
\langle \tilde{W}_A(t) \rangle = \sum_{i \in A, v} \frac{m_{i,v}^{NR}}{e_{i,v}^2} \langle |\vec{p}_{i,v}|^2 \rangle
\]  

\[
= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^2 \sum_{i \in A, v} \bar{\eta}_{i,v}^{NR} \langle |\vec{p}_{i,v}(\omega)|^2 \rangle
\]  

\[
= \frac{N_A N_D}{3\pi} \int_{-\infty}^{\infty} d\omega \omega^2 \Gamma_{A}^{NR}(\omega) \Omega_{D}(\omega) \langle Tr [G_{11}^+ (\omega) \cdot G_{11}^+ (\omega)] \rangle,
\]

where $\bar{\eta}_{i,v}^{NR} = m_{i,v}^{NR} / e_{i,v}^2$ and

\[
\Gamma_{A}^{NR}(\omega) = \sum_{\nu} \gamma_{A,\nu}^{NR} |\alpha_{A,\nu}^{NR}(\omega)|^2 / |\alpha_{\nu}^{NR}(\omega)|^2.
\]

Henceforth, we assign primed and unprimed integer labels to each donor and acceptor then all the rate equations expressed in terms of frequencies merely pick up an extra overall factor of $1/(2\pi)$. 
molecule, respectively.

In the single oscillator limit, the latter equation, Eq. (II.10.c), becomes

\[ <\tilde{W}_A(t)> = \frac{N_A N_D}{3\pi} \int_0^\infty d\omega \omega^2 \gamma_A^{NR} \Omega_D(\omega) <Tr \left[ \vec{G}^f_{11}^t(\omega) \cdot \vec{G}^r_{11}(\omega) \right]> . \]  

(II.11)

For the purpose of presenting our numerical results in the discussion section, we define the quantity, \( D_A(\omega) \), by the relation

\[ D_A(\omega) = \frac{V N_A}{3\pi} \omega^2 \gamma_A^{NR} <Tr \left[ \vec{G}^f_{11}^t(\omega) \cdot \vec{G}^r_{11}(\omega) \right]> , \]  

(II.12.a)

so that we have

\[ <\tilde{W}_A(t)> \equiv \rho_D \int_0^\infty d\omega \Omega_D(\omega) D_A(\omega) \]  

(II.12.b)

where \( \rho_D = N_D/V \) is the concentration (number density) of donor molecules in the system. \( D_A(\omega) \), in a loose sense, represents the contribution of the frequency region centered on \( \omega \) to the rate \( <\tilde{W}_A(t)> \). The sums in Eq. (II.10.a) are over acceptor molecules and internal oscillators. In Eq. (II.12), \( \gamma_A^{NR} \) is defined as \( \gamma_A^{NR} = \frac{m_A g_A^{NR}}{e_A^2} \), where the subscript \( A \) denotes an acceptor particle and \( N_A \) (\( N_D \)) is the number of acceptors (donors) in the medium. Eq. (II.10.c) is derived from Eq. (II.10.b) using Eq. (II.9). Finally, the full-sided frequency integration has been rewritten as a half-sided one because the integrand is explicitly even in \( \omega \). For notational convenience, particle labels referring to acceptor molecules are unprimed, while those referring to donors are singly primed.

The average rate at which energy is radiated to infinity, \( <\tilde{R}_{A+D\to \infty}(t)> \), is given by Poynting’s theorem

\[ <\tilde{R}_{A+D\to \infty}(t)> = \lim_{r \to \infty} \frac{1}{4} \int d\Omega \vec{n} \cdot \vec{S}(t) r^2 \]  

(II.13.a)
\[= \int_{-\infty}^{\infty} d\omega \sum_{i,j} \langle \hat{\mathcal{P}}_{ij}^\dagger(\omega) \cdot \hat{\mathcal{W}}_{ij}^{\text{rad}}(\omega) \cdot \hat{\mathcal{P}}_{ij}(\omega) \rangle \quad \text{(II.13.b)}\]

\[= \frac{1}{3} \int_{-\infty}^{\infty} d\omega \sum_{i,j} \sum_{k \in D} \Omega_k(\omega) \langle \text{Tr} \left[ \hat{G}_{jk}(\omega) \cdot \hat{\mathcal{W}}_{ji}^{\text{rad}}(\omega) \cdot \hat{G}_{ik}(\omega) \right] \rangle, \quad \text{(II.13.c)}\]

where \( \vec{S}(t) \equiv \frac{c}{4\pi} \hat{E}(t) \times \hat{H}(t) \) is the Poynting vector, \( \hat{n} \) is an outward unit normal, \( d\Omega \) represents an integration over the angles of the unit sphere. \( \hat{\mathcal{W}}_{ij}^{\text{rad}}(\omega) \) is obtained from the expressions for the fields far outside the sphere by solving Maxwell’s equations, and carrying out the integration over the angles. The details of the derivation of the expression for the matrix \( \hat{\mathcal{W}}_{ij}^{\text{rad}}(\omega) \) is presented in appendix A. In this paper, we shall analyze Eqs. (II.11) and (II.13) in for the case in which both donors and acceptors are each composed of a single oscillator. This is solely for the purpose of saving on computational effort. The essential physics should still be captured.

Again, for the purpose of presenting our numerical results in the discussion section, we define \( R^{\text{rad}}(\omega) \) by the relation

\[R^{\text{rad}}(\omega) \equiv \frac{2V}{3} \sum_{i,j} \langle \text{Tr} \left[ \hat{G}_{ji}^\dagger(\omega) \cdot \hat{\mathcal{W}}_{ji}^{\text{rad}}(\omega) \cdot \hat{G}_{ij}(\omega) \right] \rangle \quad \text{(II.14.a)}\]

so that we have

\[\langle \hat{R}_{A+D \rightarrow \omega}(t) \rangle \equiv \frac{1}{2} \rho_D \int_{-\infty}^{\infty} d\omega \Omega_D(\omega) R^{\text{rad}}(\omega), \quad \text{(II.14.b)}\]

\( R^{\text{rad}}(\omega) \) is the contribution of the frequency region around \( \omega \) to \( \hat{R}_{A+D \rightarrow \omega}(t) \).
§ III. Density Expansion Of The Propagators And Rates.

Here we shall consider the density expansion of the expressions for the energy transfer and radiation rates presented in section II. There we saw that the rates were all related to averages of the traces of various quantities which were bilinear in the propagators $\mathbf{G}_{ij}(\omega)$. In other words, all of the rate expressions contained quantities $\mathbf{K}_{ij}(\omega)$ of the form

$$K_{ij}(\omega) \equiv \langle \text{Tr} [\mathbf{G}_{i}^{\dagger}(\omega) \cdot \mathbf{K}_{ij}(\omega) \cdot \mathbf{G}_{j}(\omega)] \rangle$$

where the $3 \times 3$ matrix $\mathbf{K}_{ij}(\omega)$ depended solely upon the positions of the particles $i$ and $j$, and perhaps the frequency.

Recall that Eq. (II.8) may be cast in the form of a matrix equation

$$\left[ \mathbf{V}_{\alpha}(\omega) - \sum_{\alpha} \mathbf{V}_{\alpha}(\omega) \right] \cdot \mathbf{P}(\omega) = \mathbf{Q}(\omega),$$

where $\mathbf{V}_{\alpha}(\omega)$ is a $3N \times 3N$ matrix (where $N \equiv N_{A} + N_{D}$) containing those parts of Eq. (II.8) which are diagonal in particle indices (and hence it is block diagonal with each block a function of a single particle position) and the $\mathbf{V}_{\alpha}(\omega)$ are $3N \times 3N$ matrices which are non-zero only in the blocks involving the pair of particles $\alpha \equiv (i,j)$ and which in addition to the frequency depend only upon the pair of position variables. The vectors $\mathbf{P}(\omega)$ and $\mathbf{Q}(\omega)$ contain the molecular dipole moments, $\mathbf{P}_{i}(\omega)$, and random sources, $\mathbf{Q}_{i}(\omega)$, in the obvious order. Each pair of particles appears only once in the sum over $\alpha$. Finally, utilizing Eqs. (II.2.b), (II.6) and (II.8), we may identify the non-zero $3 \times 3$ blocks in the $3N \times 3N$ matrices $\mathbf{V}_{\alpha}(\omega)$ and $\mathbf{V}_{\alpha}(\omega)$ which appear in Eq. (III.2) as follows

$$[\mathbf{V}_{\alpha}(\omega)]^{ij} \equiv \mathbf{V}_{\alpha}^{ij}(\omega) = [\mathbf{V}_{\alpha}(\omega)]^{-1} - \mathbf{V}_{\alpha}(\omega)$$

and
\[ [\tilde{V}_a(\omega)]^{ij} \equiv \tilde{V}_a^{ij}(\omega) = \nabla_{ij}(\omega), \quad \text{for } i, j \in \alpha. \quad (III.3.b) \]

The formal solution of the Eq. (III.2) is

\[ \tilde{P}(\omega) = \tilde{G}(\tilde{R}^N; \omega) \cdot \tilde{Q}(\omega) \quad (III.4) \]

where \( \tilde{G}(\tilde{R}^N; \omega) \) is the \( 3N \times 3N \) matrix inverse of the quantity in brackets in Eq. (III.2).

As is well known, a naive density expansion for the quantities of interest may be obtained by employing the binary collision expansion for the \( 3N \times 3N \) propagator matrix \( \tilde{G}(\tilde{R}^N; \omega)^7 \)

\[ \tilde{G} = \tilde{G}_0 - \tilde{G}_0 \cdot \sum_{\alpha} \tilde{T}_\alpha \cdot \tilde{G}_0 + \tilde{G}_0 \cdot \sum_{\alpha=\beta} \tilde{T}_\alpha \cdot \tilde{G}_0 \cdot \tilde{T}_\beta \cdot \tilde{G}_0 - \cdots \quad (III.5) \]

where the binary collision matrices are defined by

\[ \tilde{T}_\alpha = -\tilde{V}_\alpha + \tilde{V}_\alpha \cdot \tilde{G}_0 \cdot \tilde{T}_\alpha = -\tilde{V}_\alpha + \tilde{T}_\alpha \cdot \tilde{G}_0 \cdot \tilde{V}_\alpha \]

\[ = -[\tilde{I} - \tilde{V}_\alpha \cdot \tilde{G}_0^{-1}]^{-1} \cdot \tilde{V}_\alpha = -\tilde{V}_\alpha \cdot [\tilde{I} - \tilde{G}_0^{-1} \cdot \tilde{V}_\alpha]^{-1} \quad (III.6) \]

and \( \tilde{G}_0 \equiv \tilde{V}_0^{-1} \). The binary collision matrix \( \tilde{T}_\alpha \) describes the full interaction of pairs of particles \( \alpha \equiv (i,j) \). Within each term, each summation is over all pairs of particles in the system except for the pair appearing in the summation immediately to its left, if any. We note the following properties of \( \tilde{G}_0 \) and \( \tilde{T}_\alpha \):

(i) \( \tilde{G}_0 \) is diagonal in particle labels;

(ii) the only non-zero blocks of the matrices \( \tilde{T}_\alpha \) are those in which only the particles from the pair \( \alpha \equiv (i,j) \) are involved (i.e., only \( \tilde{T}_{\bar{a}}^{\bar{i}}, \tilde{T}_{\bar{a}}^{\bar{j}}, \tilde{T}_{\bar{a}}^{\bar{j}}, \text{ and } \tilde{T}_{\bar{a}}^{\bar{j}} \)); and

(iii) in macroscopically large systems, in the limit \( r_{ij} \to \infty \) the binary collision matrices behave as \( \tilde{T}_{\bar{a}}^{\bar{j}} \sim -\tilde{V}_{\bar{a}}^{\bar{j}} \sim O(r_{ij}^{-1}) \) and \( \tilde{T}_{\bar{a}}^{\bar{j}} \sim O(r_{ij}^{-2}) \), in the limit \( r_{ij} \to 0 \) the binary collision matrices vanish.
As a consequence of (i) and (ii) many of the terms in the formal expansion above, Eq. (III.5), are zero. We shall identify them below as we discuss the diagrammatic representation of the series.

The expansion of the $3 \times 3$ dimensional submatrix $\hat{G}_{ij}$ of the $3N \times 3N$ matrix $\hat{G}$ which represents the interaction of the pair of particles $(i,j)$ may be represented diagrammatically. The basic elements appearing in the construction of a diagram are illustrated in Fig. 2 along with the expressions that correspond to them. A typical term from the class of terms in the expansion corresponding to the interaction of $N \leq N$ particles, and containing $M \geq N - 1$ factors of $\hat{T}$, and $M + 1$ factors of $\hat{G}_0$ is represented by a graph with $N$ labeled horizontal particle lines and $M$ vertical $T$ lines connecting pairs of particle lines. A vertical line connecting particle line $i$ with particle line $j$ represents a factor of $-\hat{T}_\alpha$ in the expansion, again $\alpha$ denotes the pair $(i,j)$. The horizontal lines between pairs of vertical lines or between a side and a vertical line correspond to a factor of $\hat{G}_0$.

The non-zero terms contributing to the expansion of $\hat{G}_{ij}$ with a given labeling of particles, a given set of factors of $T$, etc., may be put in one-to-one correspondence with the possible paths connecting particle $i$ on the left side of the graph with particle $j$ on the right side by associating the appropriate blocks of the $3N \times 3N$ matrices $\hat{G}_0$ and $\hat{T}_\alpha$ in order from left to right with each segment of the path. Of course, by "possible paths", we mean those paths which proceed monotonically from one side of the graph to the other without backtracking. For clarity, we label the endpoints of the path with crosses on the right and left hand sides of the diagram.

To each portion of the path on the particle line $i$ between two $T$ lines, or between a $T$ line and a side, one associates a factor of $\hat{G}_0^{ii}$. To a portion of a path passing from particle line $i$ on the left side of the $T$ line connecting the pair of particles $\alpha$ to particle line $j$ on the right side of the $T$ line, one associates a factor of $-\hat{T}_\alpha^{ij}$. Note that because of the sparse nature of
the matrix for $T_{\alpha\beta}$, a path yielding a non-zero contribution to the expansion must contact each $T$ line in the graph by passing through at least one connection of particle line and $T$ line.

Hence, the "disconnected" diagrams, i.e. those in which the particles connected by $T$ lines fall into disjoint subsets, give no contribution, cf. Fig. 3(a). Similarly, there will be no contribution from "branching" diagrams which are those diagrams which contain a section, defined as any portion of a diagram between two imaginary vertical lines cutting across the $G_0$ lines and containing 2 or more $T$ lines between them, in which disjoint subsets of particles are connected by one or more $T$ lines. The simplest example of a branching diagram appears in Fig. 3(b) where after the first $T_{ij}$ line the next two $T$ lines connect different sets of particles. From the definition of the binary collision expansion in Eq. (III.5), we see that diagrams in which the same pair of particles are connected two or more times in succession by $T$ lines do not appear.

Examples of the types of diagrams which may or may not appear in the expansions are given in Fig. 3 along with the expressions to which they correspond.

The first few terms of the expansion of $G_{ii}$ and $G_{ij}$ are shown in Figs. 4 and 5. As indicated in the figures, the terms in the expansion may be grouped into classes of connected diagrams involving 1 (in the case of $G_{ii}$), 2, 3, ..., $N$ particles. The expansions of the propagators include only the topologically distinct diagrams by which we mean that those diagrams which can be made the same by permuting only the unlabeled lines while preserving the connections appear only once. The contribution of a diagram containing unlabeled lines is determined by summing the unlabeled diagram over the possible labelings of the unlabeled lines, or equivalently, by multiplying any single labeling by the appropriate combinatoric factor.

The diagrammatic representation of the expansion of the quantities $K_{ij}$ follows in a similar fashion. A term (or terms) involving $N_i$ particles, $M_t$ factors of $T$, etc., coming from the expansion of the adjoint of the propagator to the left of the matrix $K_{ij}$ and $N_t$ particles, $M_t$ factors of $T$, etc., coming from the expansion of the propagator to the right is associated with a
diagram with \( N_l \) lines, etc., on the left side, \( N_r \) lines, etc., on the right side and a jagged line in between connecting particles \( i \) and \( j \), representing the matrix \( \mathbf{K}_{ij} \). If there are particles in common between the sets of \( N_r \) and the sets of \( N_l \) particles, they are either explicitly labeled as such or written as a continuous line across both sides of the diagram (for clarity the portion of the line between the two sides is presented as a dotted line in the figures in this paper). The rules associating submatrices with segments of the path from one side of the diagram to the other remain unchanged except that adjoint submatrices are used for the segments appearing on the left hand side of the diagram. (Of course, the allowed paths must go through the jagged line between lines \( i \) and \( j \).)

The diagrams contributing to \( K_{ij} \) at a given order \( N \) in density contain \( N \) unlabeled lines and must contain \( M \geq N + N' \) factors of \( T \) where \( N' \) denotes the number of unlabeled lines common to both sides of the diagram. The general form of the expansion that emerges from the binary collision expansion is a double expansion in both powers of density and powers of \( G_0T \). Fig. 6 illustrates this expansion for \( K_{ij} \) in the case in which \( i \neq j \) and \( j = 1 \), i.e., \( j \) is the initially excited donor. Note that at zeroth order in density, there are two terms which are \( O(G_0T) \) and \( O((G_0T)^2) \).

In order to characterize the nature of the expansion, we consider the set of functions \( G_{i_1t_2 \cdots i_M}^{ij} (\{\rho\};\omega) \) defined as

\[
G_{i_1t_2 \cdots i_M}^{ij} (\{\rho\};\omega) = V^M \int d\vec{r}_N \prod_{j=1}^{M} \delta(\vec{r}_{ij} - \vec{R}_j) P(\vec{R}_N) \\
\times \left\{ \text{connected diagrams of } \mathcal{T}_{ij}(\vec{R}_N;\omega) \right\} \right|_{i_1, i_2, \cdots, i_M \text{ as a subset}} \tag{3.37}
\]

where both particles \( i \) and \( j \) belong to the set of particles \( \{i_1, i_2, \cdots, i_M\} \), \( \{\rho\} \) denotes the set of concentrations (number densities) of the various species in the system, and \( P(\vec{R}_N) \) is the
configurational probability distribution for the molecules. In this paper, we shall take $P(R^N)$ to have the ideal value $V^{-N}$. This represents a quenched distribution of dye molecules. Hence, we are assuming that the phenomena of interest takes place on a time scale much shorter than spatial motion of the dye molecules.

Using the above functions, the general form of $K_{ij}$ in the case in which $i \neq j$ with $j = 1$ is

$$
K_{ij} = Tr \{ (G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j + (G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j \\
+ \sum_k \rho_k \int d\vec{r}_k [(G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j + (G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j] \cdot \cdots \}
$$

(III.8)

where the sum on $k$ is restricted to one particle typical of each species in the system. Fig. 6 shows the leading order diagrams which contribute to the expansion of $K_{ij}$. The diagrams boxed with a solid line come from the expansion of the term $(G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j$. The diagrams boxed with a dashed line come from the expansion of $(G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j$, and the remaining unboxed terms in the figure are obtained from the expansion of $\sum_k \rho_k \int d\vec{r}_k (G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j$. The first few terms of the expansion of $\sum_k \rho_k \int d\vec{r}_k (G_{ij}^j)^j \cdot K_{ij} \cdot G_{ij}^j$ are $O(p^3 T^4)$ and are not included in the figure owing to space limitations.

We note that the leading behavior of $G_{i_{i_1} \cdot i_m}^j((\rho);\omega)$ is

$$
G_{i_{i_1} \cdot i_m}^j((\rho);\omega) \sim O((G_0 T)^{M-1})
$$

so that if the order relation $(G_0 T) \sim o(1)$ holds, then the hierarchy of functions behave as

$$
G_{i_{i_1} \cdot i_m}^j((\rho);\omega) \sim o(G_{i_{i_1} \cdot i_m}^j((\rho);\omega))
$$

(III.9)

and the second term of Eq. (III.8) is negligible with respect to the first term. Potential problems with this ordering that might arise with this ordering due to the slow $r^{-1}$ decay of $T$ and

---

A function, $f(r)$, is $o(g(r))$ if $\|g(r)\| \ll |f(r)|$. 

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Chapter 1.

V for large distances do not pose a problem in the droplet case. In the bulk case, elastic or inelastic scattering events will renormalize the dielectric properties of the medium, thereby introducing loss and causing the fields to decay exponentially. In order to treat this decay properly, more extensive resummations might be necessary.

In the bulk, factors of $T$ decay as $O(r^{-1})$ for the off-diagonal blocks and as $O(r^{-2})$ for the on-diagonal blocks as $r \to \infty$. Hence, one expects higher powers of $\mathcal{T}$ to give contributions from progressively smaller fractions of the system volume (especially if pairs of particles are connected more than once). Therefore, one expects the ordering given above in Eq. (III.9) for the $G^i_{j_1 \cdot \cdot \cdot j_m}(\{\rho\})$. In the droplet case, we expect the same sort of behavior because $\mathcal{T}$ is large only in localized regions of the sphere, the main differences from the bulk being that the region is much larger than that in the bulk, and also often at a large spatial separation from the source.

Fig. 7 shows that $K_{ij}$ for $i \neq j$ with $i \neq 1$ and $j \neq 1$ is given by

$$K_{ij} \sim Tr \{ (G^i_{1,1})^f \cdot K_{ij} \cdot G^j_{1,1} + (G^i_{1,1})^f \cdot K_{ij} \cdot G^j_{1,1} \}
\quad + (G^i_{1,1})^f \cdot K_{ij} \cdot G^j_{ij} + (G^i_{1,1})^f \cdot K_{ij} \cdot G^j_{ij},$$

$$\quad + \sum_k \rho_k \int d^3 \vec{r}_k \left[ (G^i_{1,1})^f \cdot K_{ij} \cdot G^j_{ij} + \cdots \right] + O(\rho^2). \quad \text{(III.10)}$$

Fig. 8 shows the lowest order in density terms of the expansions of $K_{ii}$ when $i \neq 1$ and $i = 1$. The expansions of these quantities are particularly simple. For $i \neq 1$,

$$K_{ii} \sim Tr \{(G^i_{1,1})^f \cdot K_{ii} \cdot G^i_{1,1} + \sum_k \rho_k \int d^3 \vec{r}_k (G^i_{1,1})^f \cdot K_{ii} \cdot G^i_{1,1} + \cdots \}, \quad \text{(III.11.a)}$$
and for $i=1$, 
\[
K_{11} = - Tr \left\{ (G_{11}^{(1)})^t \cdot K_{11} \cdot G_{11}^{(1)} + \sum_k \rho_k \int d\vec{r}_k (G_{1k}^{(1)})^t \cdot K_{11} \cdot G_{1k}^{(1)} + \cdots \right\}. \quad (III.11.b)
\]

For the two component case under study, we introduce the following somewhat simpler notation
\[
G_{\alpha}^i (\vec{r}; \omega) \equiv G_{11}^{(1)} (\vec{r}_1 = \vec{r}; \omega), \quad (III.12.a)
\]
\[
G_{\beta}^i (\vec{r}; \omega) \equiv G_{11}^{(1)} (\vec{r}_1 = \vec{r}; \omega), \quad (III.12.b)
\]
and
\[
G_{\alpha \beta}^i (\vec{r}; \vec{r}'; \omega) \equiv G_{11}^{(11)} (\vec{r}_1 = \vec{r}_1 = \vec{r}'; \omega), \quad (III.12.c)
\]
etc. The functions $G_{\alpha}^i (\vec{r}; \omega)$ represent the propagation of a particle of species $\alpha$ located at position $\vec{r}$ due to its interaction with the medium and other particles. The function $G_{\beta \beta}^i (\vec{r}, \vec{r}'; \omega)$ represents the effect of a particle of species $\beta$ located at position $\vec{r}'$ on a particle of species $\alpha$ located at position $\vec{r}$. This enables us to write the expressions for the leading order contributions to $K_{ij}(\omega)$ as
\[
K_{ij}(\omega) = \frac{1}{V^2} \int d\vec{r} \int d\vec{r}' \left\{ \frac{1}{V} Tr \left[ G_{\beta}^i (\vec{r}; \omega) \cdot K_{\beta}^i (\vec{r}; \omega) \cdot G_{\beta}^i (\vec{r}; \omega) \right], \quad i = j = 1; \quad (III.13.a)
\]
\[
= \frac{1}{V^2} \int d\vec{r} d\vec{r}' \cdot Tr \left[ G_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \cdot K_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \cdot G_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \right], \quad i = j = 1; \quad (III.13.b)
\]
\[
= \frac{1}{V^2} \int d\vec{r} d\vec{r}' \left\{ Tr \left[ G_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \cdot K_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \cdot G_{\alpha \beta}^i (\vec{r}, \vec{r}'; \omega) \right], \quad i = 1 \text{ and } j = 1; \quad (III.13.c)
\]
etc., where
\[
K_{\beta}^i (\vec{r}; \omega) = K_{11}^{(1)} (\vec{r}_1 = \vec{r}; \omega), \quad (III.14.a)
\]
and
The question now arises as to what approximation to insert for \( G_{D}^{i} (\omega) \), \( G_{AD}(\omega) \), etc. By employing the binary collision expansion, we have implicitly done some resummations. The binary collision expansion itself, in part at least, takes into account that factors of \( \overrightarrow{G} \) that would appear in a naive Born expansion may not be small. Hence to a certain extent we have already accounted for the possibility that the interaction or the molecular polarizability may be large. Hence we now focus on the behavior arising from the factors of \( \overrightarrow{G} \). Based upon what we said earlier, the dominant terms at each order of density in \( K_{ij}(\omega) \) are those with the fewest number of \( \overrightarrow{G} \) lines especially since those with more \( \overrightarrow{G} \) lines must have at least one pair of particles connected by more than one \( \overrightarrow{G} \) line. These are the diagrams in which distinct sets of particles (except for the initial donor particle \( \tilde{1} \) and possibly particle \( i \) if \( i = j \)) appear on either side of the diagram. Furthermore, on each side of the diagram, loop diagrams such as the boxed terms, i.e., (d), (e), and (f) of \( \overrightarrow{G}_{ij} \) in Fig. 4 or the boxed terms of \( \overrightarrow{G}_{ij} \) in Fig. 5 do not appear. The terms which remain on either side of the diagram are the unboxed terms of either Fig. 4 or Fig. 5; in general this class of diagrams is called completely factorizable. Since the factorizable diagrams give the largest contributions at each order in density, their resummation will give the leading order behavior in density.

This indicates that reasonable approximations for \( G_{D}^{i} \) and \( G_{AD} \) might be obtained by dropping the loop diagrams from Figs. 4 and 5. This type of approximation is common in the theory of wave propagation in random media. With the aid of the diagrams, it is a straightforward task to resum the series expansions for the loopless averages. After the average over positions has been carried out, each unlabeled line in a diagram contributes a factor of density, along with an integration over the corresponding variable. When there are multiple species present, then separate terms are obtained by associating the densities of each species with each of the unlabeled lines. For example, diagram (b) of Fig. 4 yields the following expression:
\[- \rho_\text{D} \int d\mathbf{r}_2 \cdot \mathbf{T}_{12}^{1} \cdot - \rho_\text{A} \int d\mathbf{r}_1 \cdot \mathbf{T}_{11}^{1} \cdot \]

where \(\rho_\text{A}\) is the number density of acceptors and \(\rho_\text{D}\) is the number density of donors.

The series for the loopless self-propagator for the donors, \(G_{\text{D}}(\mathbf{r}; \omega)\), is simply a geometric series, and becomes
\[
G_{\text{D}}(\mathbf{r}; \omega) = \left( \left[ G_{0}^{-1}(\omega) \right]_{11} + \rho_\text{D} \int d\mathbf{r}_2 \cdot \mathbf{T}_{12}^{1} \cdot (\omega) + \rho_\text{A} \int d\mathbf{r}_1 \cdot \mathbf{T}_{11}^{1} \cdot (\omega) \right]^{-1}. \tag{III.15}
\]

A similar expression holds for the acceptor self-propagator.

The series for the loopless two-particle propagators, \(G_{\text{AA}}\), \(G_{\text{AD}}\), \(G_{\text{DA}}\), and \(G_{\text{DD}}\) are slightly more complicated. Instead of an algebraic equation, one obtains a set of coupled integral equations
\[
G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \omega) = - G_{\alpha}^{\beta}(\mathbf{r}; \omega) \cdot \mathbf{T}_{\alpha\beta}^{\text{loop}}(\mathbf{r}, \mathbf{r}'; \omega) \cdot G_{\beta}^{\gamma}(\mathbf{r}'; \omega) \\
- \sum_{\gamma} \rho_{\gamma} \int d\mathbf{r} \cdot G_{\alpha}^{\gamma}(\mathbf{r}; \omega) \cdot \mathbf{T}_{\alpha\gamma}^{\text{loop}}(\mathbf{r}, \mathbf{r}'; \omega) \cdot G_{\gamma}^{\beta}(\mathbf{r}'; \omega) \tag{III.16}
\]

Higher order approximations to \(G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \omega)\) of the form of Eq. (III.16) defined by the diagrams in Fig. 5 exist. By replacing the approximations for the self-propagators, Eq. (III.15), appearing in Eq. (III.16) by the full exact self-propagators, \(G_{\alpha}^{\beta}(\mathbf{r}; \omega)\), or any intermediate approximations to the self-propagator that are available since Eq. (III.16) also holds with the full \(G_{\alpha}^{\beta}(\mathbf{r}; \omega)\) replacing the approximate one when all loops which begin on one particle and end on another (the boxed diagrams in Fig. 5 are the simplest examples) are dropped from the full series in Fig. 5. However, such an approach may not be consistent since Eq. (III.16) is not exact in any case.

In the next section, we discuss the approximate numerical solution of Eqs. (III.15) and (III.16). In what follows we shall use the simpler of the two approximations to the two-
§ IV. Approximations For Spherical Microdroplets.

In this section, we obtain approximations to the self- and two-particle propagators introduced in the previous section and use them in the evaluation of the rates for energy transfer in a spherical microdroplet. To compute the propagators, one needs the \( \mathbf{T} \) matrices, which are functions of the molecular polarizabilities, and the \( \mathbf{V} \) matrices, which relate the electric fields in the system to their sources. The components of the matrix \( \mathbf{V}^{\infty}(\omega) \) giving the electric field that molecule \( i \) experiences due to the reflection of its own field from the boundary of the dielectric medium (in this case, a "microsphere") and the components of the matrix \( \mathbf{V}_{ij}(\omega) \) giving the electric field at molecule \( i \) due to molecule \( j \) are both easily obtained as expansions in vector spherical harmonics.\(^9\) \( \mathbf{V}^{\infty}(\omega) \) can be written as sum of scalar functions of \( \vec{r}_i \) and \( \omega \) multiplying the longitudinal tensor, \( \hat{r}_i \hat{r}_i \), and a transverse tensor, \( \mathbf{r} - \hat{r}_i \hat{r}_i \). Moreover, \( \mathbf{V}_{ij}(\omega) \) may be decomposed into a sum of a term which represents the interaction in a macroscopic system with the dielectric constant of the sphere and a term corresponding to the interaction with the sphere.

\( \mathbf{T} \) and \( \mathbf{V} \) are related by trivial algebraic equations.

\[
\mathbf{T}_{12}^{11} = - \left[ 1 - \mathbf{V}_{12}^{22} \cdot \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{21} \cdot \mathbf{G}_{0}^{21} \right]^{-1} \cdot \mathbf{V}_{12}^{22} \cdot \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{21}
\]

\[
= - \mathbf{V}_{12}^{12} \cdot \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{11} \cdot \left[ 1 - \mathbf{G}_{0}^{11} \cdot \mathbf{V}_{12}^{22} \cdot \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{21} \right]^{-1}
\]

(IV.1.a)

\[
\mathbf{T}_{12}^{22} = - \left[ 1 - \mathbf{V}_{12}^{22} \cdot \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{21} \cdot \mathbf{G}_{0}^{21} \right]^{-1} \cdot \mathbf{V}_{12}^{22}
\]

\[
= - \mathbf{V}_{12}^{12} \cdot \left[ 1 - \mathbf{G}_{0}^{22} \cdot \mathbf{V}_{12}^{21} \cdot \mathbf{G}_{0}^{21} \cdot \mathbf{V}_{12}^{11} \right]^{-1}
\]

(IV.1.b)
\[
\mathcal{T}_{12}^{21} = - \left[ 1 - \mathcal{V}_{12} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12} \cdot \mathcal{T}_{00} \right]^{-1} \cdot \mathcal{V}_{12}^{21}
\]

\[
T_{12}^{22} = - \left[ 1 - \mathcal{V}_{12} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12} \cdot \mathcal{T}_{00} \right]^{-1} \cdot \mathcal{V}_{12}^{21} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12}^{11}
\]

However, it is not so trivial matter to obtain the vector spherical harmonic expansion of \( \mathcal{T} \) from that of \( \mathcal{V} \). It is possible, however, to greatly simplify matters with a few physically reasonable approximations. We employ the leading order perturbative or "weak coupling" approximation in this paper. In this approximation, the various blocks of the matrix \( \mathcal{T}_{12} \) simplify to

\[
\mathcal{T}_{12} = \begin{bmatrix}
\mathcal{V}_{12} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12}^{21} & \mathcal{V}_{12}^{21} \\
\mathcal{V}_{12} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12}^{11} & \mathcal{V}_{12} \cdot \mathcal{T}_{01} \cdot \mathcal{V}_{12}^{12}
\end{bmatrix},
\]

where the dependence of \( \mathcal{V}_{j}^{(\omega)}(\omega) \) upon \( \mathcal{V}_{j}^{x}(\omega) \) has been kept, i.e.,

\[
\mathcal{V}_{j}^{(\omega)} = \left[ (\mathcal{\alpha}^{-1}) - \mathcal{V}_{j}^{x} \right]^{-1},
\]

and in Eq. (IV.2.a) only the non-zero blocks of the \( 3N \times 3N \) dimensional \( \mathcal{T}_{12} \) matrix are shown. In this work, the polarizability tensors for the molecules are assumed to be isotropic. Furthermore, the polarizability is assumed to have a simple Lorentzian lineshape.

While we initially chose the weak coupling approximation in order to obtain equations which were computationally tractable, its use can be justified. To this end, we have numerically compared the weak coupling expressions for \( \mathcal{T} \) with the exact \( \mathcal{T} \)'s at frequencies close to and far from the Mie resonance frequencies of the spherical droplet. In the resonant or very nearly resonant case, the \( \mathcal{V} \) matrices are large in magnitude, by which we mean that they are...
of a magnitude comparable to or greater than the bulk quasi-static interaction in the 10Å–100Å regime within a large fraction of the sphere volume, and one might expect the two sets of functions to differ significantly. However, we have found that both functions are very much alike over much of the sphere volume when parameters typical of those encountered experimentally are used. This is illustrated in Figs. 9 through 14. Figs. 9 through 11 show √Tr(V12 T V12) as a function of observer position for various values of the source radius for a particularly strong Mie resonance frequency and Figs. 12 through 14 do the same for √Tr(T12 T V12). The only visible differences between the figures for √Tr(V12 T V12) and √Tr(T12 T V12) occur for the largest source radius. The functions differ greatly in magnitude only in small regions of the space spanned by the position variables of the source and observer. The greatest differences occur only when the distance between the source and observer positions is extremely small where the bulk interaction dominates and when the source and observer are both located within a very thin shell near the sphere surface (say about 100Å for a 3.8 micron radius sphere). The latter is illustrated by Figs. 11 and 14 while the former occurs in a region much smaller than can be resolved in the figures. In both of these regimes we in fact overestimate Tr. This is because Tr goes to zero for V’s of sufficient magnitude. Figs. 10 and 13 illustrate the typical resonant interaction in the region in which |Tr| is large.

The differences can be also interpreted in terms of the mode decomposition of Tr and V into products of radial functions and vector spherical harmonics for the same particle radii. These functions appear in the general solution of the integral equation so it is instructive to study them. The radial functions obtained depend upon the species involved as well as upon a set 3 angular momentum quantum numbers \{J,J,l\} where the first varies from 1 to ∞ and the last two numbers may range from J−1 to J+1. The details of the decomposition is described more fully in appendix A.

In the non-resonant region, these radial functions are virtually indistinguishable. Figs. 15
through 17 illustrate the result of performing this decomposition of $\mathbf{T}$ and $\mathbf{V}$ in the resonant frequency region for the same particle radii that appear in Figs. 9 through 14. The figures include all 9 values of $l$ and $l'$ which are not so small as to be comparable to the roundoff error associated with the algorithm used to compute them.

What is found is that when the distances of the two particles from the sphere center are large the effect of all the matrix algebra in Eqs. (IV.1) is simply to boost the magnitudes of the non-resonant mode radial functions which appear in the vector spherical harmonic decomposition of $\mathbf{T}$ relative to their values in the decomposition of the weak coupling expression in Eq. (IV.2). The contribution of the resonant mode does not change much. Even so, the radial function of the resonant mode often remains by far the largest in magnitude and is given to a good approximation by its weak coupling value. Hence, in most cases notable differences between $\mathbf{T}$ and its weak coupling limit will appear only in the spatial nodes of the resonant mode contribution. Moreover, the contributions to the solution of the integral equation are expected to come from one resonant mode in the resonant frequency regions and from many modes in the non-resonant regions. We will therefore use Eq. (IV.2) as an approximation for the appropriate blocks of the $\mathbf{T}$ matrices.

In addition to the weak coupling approximation, there is another approximation that one can make to greatly simplify the solution of the integral equations, Eq. (III.16). As was noted earlier, the matrix $\mathbf{V}_{ij}(\omega)$ describing the interaction of two molecules can be decomposed into a sum of two parts: one, $\mathbf{V}_{ij}^{\infty}(\omega)$, corresponds to the interaction of the two molecules in an infinite medium with the dielectric constant of the droplet, and another, $\mathbf{V}_{ij}^{sc}(\omega)$ describes the effects of reflections from the dielectric boundary. When comparing the magnitude of $\mathbf{V}_{ij}^{sc}(\omega)$ with that of $\mathbf{V}_{ij}^{\infty}(\omega)$ in the resonant frequency region, we find that $\mathbf{V}_{ij}^{sc}(\omega)$ is much larger than the infinite medium contribution at intermolecular separations $r>50\AA$, which is a distance typical of ordinary Förster transfer in a bulk fluid. Moreover, the magnitude of $\mathbf{V}_{ij}^{sc}(\omega)$ is comparable, or
greater, than that of $\nabla_{ij}^\infty$ at short intermolecular distances ($r_{ij} \leq 50\AA$) in a large fraction of the sphere volume near the sphere surface. Given the fraction of the system volume in which $\nabla_{ij}^\infty(\omega)$ is very large, it is therefore reasonable to drop the infinite medium contribution entirely. Of course, this corresponds to the neglect of the standard Förster transfer mechanism, and will not be valid in macroscopic systems.

Let us now turn to the evaluation of Eqs. (III.15) and (III.16) for the propagator. In view of the approximations stated above, we only require expressions for $V_{ij}^{\infty}(\omega)$ and $V_{ij}^\infty(\omega)$. Because of the rotational symmetry of the system, the expression for $V_{ij}^{\infty}(\omega) (=V_{ij}^{\infty}(r_i^j;\omega))$ has a simple form

$$V_{ij}^{\infty}(\omega) = v^{\infty} \cdot (\hat{r}_i - \hat{r}_j) + v^{\infty} \cdot (\hat{r}_i \cdot \hat{r}_j),$$

(IV.3)

where the scalar functions, $v^{\infty} \cdot (r_i;\omega)$ and $v^{\infty} \cdot (r_j;\omega)$, have simple expansions in terms of spherical Bessel functions. The series expansion for $V_{ij}^\infty(\omega) (=V_{ij}^{\infty}(r_i^j;\omega))$ can also be written in a simple form

$$V_{ij}^\infty(\omega) = \sum_{J=1}^{\infty} \sum_{J=1}^{J} \sum_{l=-J}^{J} \sum_{M=-J}^{J} \eta_{JlM} \cdot (j_i(r_i^j) j_j(r_j^i) \hat{r}_i \cdot (\hat{r}_j)) \tilde{Y}_{JlM}(\Omega_i) \tilde{Y}_{JlM}^*(\Omega_j),$$

(IV.4)

where the radial functions are spherical Bessel functions and the $\tilde{Y}_{JlM}(\Omega)$ are the vector spherical harmonics as defined in Edmonds. The coefficients $\eta_{JlM}$ are simply related to the Mie coefficients for the system. Both the $\eta_{JlM}$ and the Mie coefficients are defined in appendix A, section C. One should also note that for the resonant modes the arguments to the Bessel functions are in the range where the Bessel functions are well approximated by their small argument power law forms, $j_l(x) \sim x^l/(2l+1)$. This implies that the dominant contributions to the energy transfer come from particles situated in a shell located near the surface of the sphere.

The matrix for $G_0(r;\omega)$ involves the matrices $\nabla_{ij}^{\infty}(\omega)$ and $\int d\hat{r}_j \hat{t}_{1/1}^{\infty}(\omega)$. With the above expressions for the $V$ matrices, it is a simple matter to use the orthogonality properties of the
vector spherical harmonics to obtain an expression for $G^j_0(\rho; \omega)$

$$G^j_0(\rho; \omega) = g^j_0 \{ (\hat{\rho} - \rho \hat{\rho}) + g^j_0 \hat{\rho} \rho \hat{\rho} \}, \quad (IV.5)$$

where the functions $g^j_0(r; \omega)$ and $g^j_0 \{ r; \omega \}$, defined in appendix A, are functions of the polarizabilities, densities and Mie coefficients. The form of Eq. (IV.5) is expected from rotational symmetry. A similar expression may be written for $G^i_A(r; \omega)$.

The integral equations, Eqs. (III.16), are easy to solve using the above approximations. The solution to the integral equations may be written as

$$G_{\alpha \beta}(\rho, \rho'; \omega) = \sum_{J=1}^{\infty} \sum_{J'=1}^{J+1} \sum_{l=J-1}^{J'} \sum_{M=-J}^{J} G_{\alpha \beta, Jl l \cdot M} (r, r'; \omega) Y^l_J(\Omega) Y^l_{J'}(\Omega'), \quad (IV.6)$$

Using the orthogonality properties of the vector spherical harmonics, the angular integrations are easily performed, leading to sets of coupled integral equations for the radial functions, $G_{\alpha \beta, Jl l \cdot M} (r, r'; \omega)$.

Furthermore, since we have dropped the infinite medium contribution to $V$, the resulting set of coupled radial integral equations is separable. The radial functions turn out to have the form

$$G_{\alpha \beta, Jl l \cdot M} (r, r'; \omega) = - \sum_{J_1=J-1}^{J+1} \sum_{l_1=J-1}^{J+1} \sum_{l_5=J-1}^{J+1} F^\alpha_{Jl l l_1} (r) \Gamma_{Jl l l_1 l_5}^{\alpha \beta} F^\beta_{Jl l l_1 l_5} (r'), \quad (IV.7)$$

where the radial functions are defined in appendix A. The coefficients, $\Gamma_{Jl l l_1 l_5}^{\alpha \beta}$, are obtained by solving simple matrix equations with dimension equal to three times the number of components in the system for each value of $J$.

With the above expressions, the various energy transfer rates can be computed after some straightforward algebra. Since the matrix $W$ in the radiation rates can be written in a form similar to $V$, they are also easily computed. The details are somewhat lengthy and are given in appendix A.
§ V. Discussion Of Results.

Even with all the simplifications of our problem arising from the approximations introduced above, the solution of the coupled integral equations in a droplet given in the previous section remains a very formidable numerical task. The solutions of the integral equations in the droplet may be expanded in terms of vector spherical harmonics. As we have mentioned previously, and cover in more detail in appendix A, section D, the three-dimensional coupled integral equations for the propagators have been reduced to a sequence of simpler one-dimensional coupled, separable, integral equations for functions of the radial distance, \( r \). Since the equations are separable, they may then be solved by taking overlaps with the appropriate radial functions, thereby obtaining a sequence of coupled linear equations of low dimensionality.

Since the standard, i.e., recursive, methods for computing the spherical Bessel functions required for computing the Mie coefficients and overlap functions yield the Bessel functions for many orders simultaneously, it was advantageous to perform the required overlap integrals for the full sequence of matrix equations in parallel using an adaptive, vector, Gaussian integration scheme.* The numerical calculations we present below include contributions from modes with \( J \) in the range \( 1 \leq J \leq 89 \). In the frequency range shown in the figures there are of the order of 120 Mie resonances with \( Q \)’s in the range from \( 10^4 \) to \( 10^{12} \).

Figs. 18 and 19 present plots of \( D_A(\omega) \) and \( R^{\text{rad}}(\omega) \) for a set of densities spanning ten orders of magnitude. The frequency range displayed correspond to wavelengths from 322\( \text{nm} \) to

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* Even so, the computation was extremely time-consuming; typically requiring many months of CPU time even on the fastest SPARC workstations and 80386 and 80486 class DOS and UNIX based PC’s in order to obtain a spectrum containing a sufficient number of points for it to be integrated with reasonable accuracy. This is because of the large number of narrow Mie resonances and the large variation (over many orders of magnitude) of the Mie coefficients, and hence the functions being computed, near these resonances. (Interestingly enough, since the most numerically intensive parts of the algorithm were not highly vectorizable, computations on an IBM mainframe were no faster than those on the workstations and PC’s.)
442nm. Naively, $D_A(\omega)$ is expected to scale with the acceptor density since the dissipation occurring in the acceptors should be proportional to the concentrations of both donor particles and acceptor particles. Similarly, for the micromolar densities which we are studying, $R^{\text{rad}}(\omega)$ should be largely independent of density since the leading contribution to the total radiation comes from the radiation emitted by the initially excited donors.

In order to present a spectrum which is more like that obtained experimentally and which, given the narrowness of many of the resonances ($Q \sim 10^3 - 10^{12}$), can be easily displayed, the data represented in Figs. 18 and 19 have been convolved with a Gaussian weighting function with a width that is typical of most spectrometers.

The overall magnitude of $D_A(\omega)$ does indeed increase with density, however the peaks corresponding to the resonances decrease in height and broaden considerably. Similarly, $R^{\text{rad}}(\omega)$ remains largely independent of density, except in frequency ranges near the Mie resonances. Again, the effect of increasing density is to broaden and decrease the magnitude of the peaks.

Fig. 20 examines the function $D_A(\omega)$ (not convolved with any weighting functions) in the vicinity of one of the strongest and narrowest of the Mie resonances. The figure shows the effects of varying the density over ten orders of magnitude. The peak corresponding to the resonance is observed to both shift and broaden as the density is increased, until the peak has more or less disappeared. The increase in the widths appears to be proportional to the density. One may simply interpret this as being due to the introduction of loss into the solvent as a consequence of the addition of the dye molecules. This loss may be understood as arising from both the elastic and inelastic scattering of the excitation by the molecules. The loss arising from the elastic scattering can be understood in terms of dephasing, whereas the loss due to inelastic scattering is due to the fact that the oscillators are all damped.
We have not been able to explain the "glitches" that appear in the figure at higher concentrations. While it is most likely that we have simply reached the limits of the low density theory and need to consider other classes of resummations in order to proceed to the higher densities, we cannot completely discount the possibility that these glitches appear simply because the calculation at those points is very sensitive to the machine precision because of the high Q’s involved. Indeed, inclusion of other resummations might reduce the sensitivity to machine precision by broadening the higher Q resonances.

Figs. 21 and 22 show the results of integrating the functions $D_A(\omega)$ and $R^{\text{ed}}(\omega)$ over frequency. These integrals are strictly proportional to the rates only in the limit in which the source correlation function $\Omega_{\text{ef}}(\omega)$ may be regarded as a constant over the frequency range of interest. However, since the Mie resonance frequencies in our figures are more or less uniformly distributed over the frequencies included, we expect that the density trends we observe should not depend strongly upon how the frequencies are weighted by $\Omega_{\text{ef}}(\omega)$.

The final integrals for the two cases plotted in Figs. 21 and 22 were handled in different manners. The degenerate case, in which the donor and acceptor particles have identical polarizability parameters, was integrated using roughly half as many points as the non-degenerate case by employing an integrator that was customized to integrating a function with many sharp peaks whereas the the non-degenerate case was integrated using the trapezoid rule after adding enough points to ensure that the variation of the functions being integrated was small. Also different frequency ranges were used for the degenerate and non-degenerate cases owing to the widths and amount of overlap of the polarizability functions in the two cases. Both methods

\footnote{All calculations were done in double precision (64 bits) on 32 bit machines hence the machine precision is about 15 decimal digits. Hence allowing for rounding errors, the Bessel functions which determine the Mie coefficients are probably good to at best 12 to 13 digits. The strongest resonances in these calculations have Q’s (i.e., $\omega^{\Delta\omega}$) in the $10^{10}$ to $10^{13}$ range. Hence, we expect some sensitivity to rounding errors to appear if the function being computed becomes very sensitive to the precise value of the resonant Mie coefficient. This possibility can only be ruled out in a reasonable amount of time on a higher precision machine.}
seem to predict the same trend; i.e., for the intermediate concentrations, the quantities calculated depend only weakly on concentration. For the lowest concentrations, the non-degenerate case results indicate that the behavior of the dissipation rate reverts to the naively expected scaling.

Figure 23 shows the ratios of the quantities in Figs. 21 and 22, since what is typically reported is the ratio of the quantity of the light emitted by the acceptors to the total amount emitted. (This ratio plays the role of the quantum yield in our model.) In the concentration range reported in the experiment cited in the introduction, we find that this ratio scales as \( \rho^{0.12} \) in excellent agreement with the experimental values \( \rho^{0.16 \pm 0.08} \). For much lower densities the ratio scales as \( \rho \), as expected. This effect is also observed experimentally. The theory of Druger, et. al., predicts similar behavior,\(^2(b)\) i.e., for low density the ratio scales linearly with density and as the density increases the dependence becomes progressively weaker, eventually saturating. However, the physical interpretation of the effect is completely different in the two theories. In Druger’s theory, the saturation effect arises entirely because of the ratio being computed. The ratio in that theory has the form

\[
\frac{\rho X}{1 + \rho X}
\]

(V.1)

where \( X \) is a ratio of two particle transition and radiation rates (integrated over appropriate densities of states, etc). The resonances do not broaden as the density is varied. The resonances simply determine the magnitude of the number \( X \) which in turn determines a range of \( \rho \) over which the system transitions from linear density scaling to very weak scaling. By contrast, in our theory, the behavior of the ratio is largely determined by the density behavior of the acceptor dissipation rate, which varies because resonances are broadening as the density is increased.
§ VI. Conclusions.

While our simple classical electrodynamic treatment of the problem of energy transfer in micron-sized droplets lacks many of the features of a fully quantum mechanical or quantum field theoretical treatment, nonetheless, it seems to be able to describe some of the multiple scattering, many-body aspects that result in nontrivial density dependences in droplets, in the Mie-resonant regions of the spectrum. By choosing a single or multiple oscillator model for each dye molecule, we were able to mimic some of the spectral features of these molecules and we were able to extract the experimentally obtained concentration dependences. Specifically, we have been able to show that the reported anomalous density dependence of energy transfer in droplets can be traced to the long-range coupling induced by the Mie resonances and to the effective loss induced in the medium by multiparticle scattering. The competition between these two effects leads to a saturation effect for sufficiently large densities.

§ VII. Acknowledgment.

A portion of this work was supported by the National Sciences and Engineering Research Council of Canada, by Le Fonds pour la Formation de Chercheurs et l’Aide à la Recherche du Québec and by the National Science Foundation. One of us, A.C.P., also wishes to thank the Chemistry Department of McGill University for their hospitality and Arizona State University for providing access to their computer network during the preparation of this manuscript.
§ Appendix A. Details Of The Droplet Calculation.

A) Notation.

A word about the notation for many of the functions we use is in order. In order to avoid confusion and ambiguity in what follows, we need to clarify the notation we used in the main body of the paper for these functions when the position arguments are explicitly listed. There are several reasons for this. In the various fields or propagators we need to compute, there is a need to distinguish source and observation points. There is also frequently a need to distinguish which particle types are present at the two locations. Finally, we wish to keep the notation as simple as possible.

Let us first focus on the matrices $\leftarrow\rightarrow T_{\alpha\beta}$. Recall that in the definition of the $\leftarrow\rightarrow T_{\alpha\beta}$ matrices given in the main body of the paper, the subscripts denote the pair of particles which are coupled by the matrix (which is $3N\times3N$ dimensional). We shall use letters in the subscripts to denote a generic particle of a particular species (e.g., $A$ for acceptors, and $D$ for donors). Primes on letters in subscripts will be used to distinguish between two generic particles of the same species. When numbers are used as subscripts and superscripts for functions, they are used to denote a specific particle and primes on numbers are used to differentiate among species (so that each species in the problem can have its particles numbered starting from 1). For the problem we study in this paper, there are only two types of molecules, donors and acceptors, and we will use primes for donor molecules.

So long as no positional arguments are included, the order of the labels in the subscripts is irrelevant. We can take advantage of this freedom when positional variables are explicitly written. We shall assign the positional variables, written as arguments to a function, sequentially to the function’s subscripts in a one-to-one fashion.
When superscripts are also attached to the $\mathbf{T}_{\alpha\beta}$, e.g., as in $\mathbf{T}_{\alpha\beta}^{\alpha\beta}$, then we are referring to a specific $3\times3$ dimensional sub-block of the larger $3N\times3N$ matrix. The various sub-blocks correspond to one particle or the other being in source and/or observer positions. There are only four non-zero $3\times3$ dimensional blocks in each $3N\times3N$ dimensional matrix, $\mathbf{T}_{\alpha\alpha}^{\alpha\alpha}$, $\mathbf{T}_{\alpha\beta}^{\alpha\beta}$, $\mathbf{T}_{\beta\alpha}^{\beta\alpha}$, and $\mathbf{T}_{\beta\beta}^{\beta\beta}$. The rightmost superscript label denotes the particle at the source position and the leftmost superscript label denotes the particle at the observation point.

Employing the rules given above, in a function such as $\mathbf{T}_{\alpha\beta}^{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \mathbf{r})$, $\mathbf{r}$ is the position variable of a particle of species $\alpha$ (or of a specific particle if $\alpha$ denotes a specific particle label) which is in the source position and $\mathbf{r}'$ is the position variable of a particle of species $\beta$ which is in the observer position.

**B) Useful Properties Of The Vector Spherical Harmonics.**

A number of identities are useful in doing the calculation. Since they prove to be ubiquitous, we define the quantities $A_{Jl}$ by the relation $\hat{r} \cdot \hat{y}_{JM}(\Omega) = A_{Jl} Y_{JM}(\Omega)$. The $A_{Jl}$ are given by

$$A_{Jl} = \begin{cases} \left( \frac{J + 1}{2J + 1} \right)^{1/2} & \text{for } l = J + 1 \\ \left( \frac{J}{2J + 1} \right)^{1/2} & \text{for } l = J - 1 \\ 0 & \text{otherwise.} \end{cases}$$ (A.1)

The following identities for the vector spherical harmonics may be proven from relations in Edmonds$^{11}$

$$\int d\Omega \; \mathbf{y}_{JM}^J(\Omega) \cdot \mathbf{y}_{JM}(\Omega) = \delta_{JJ} \cdot \delta_{MM}. \quad \text{(A.2.a)}$$

$$\int d\Omega \; \mathbf{y}_{JM}^J(\Omega) \cdot \hat{r} \cdot \mathbf{y}_{JM}(\Omega) = A_{Jl} \cdot A_{Jl} \cdot \delta_{JJ} \cdot \delta_{MM}. \quad \text{(A.2.b)}$$
\[
\int d\Omega \vec{F} \cdot \vec{Y}_{JM}^e(\Omega) \times \vec{Y}_{JM}^f(\Omega) = -i \delta_{JJ} \delta_{MM}.
\]

\[
\left[ \delta_{JJ} \left[ A_{J-1, J+1} \delta_{J+1} - A_{J+1, J} \delta_{J-1} \right] + \left[ A_{J-1, J+1} \delta_{J} - A_{J+1, J} \delta_{J} \right] \right] \delta_{JJ} \quad \text{(A.2.c)}
\]

and

\[
\sum_{M=-J}^{J} \vec{Y}_{JM}^e(\Omega) \cdot \vec{Y}_{JM}^f(\Omega) = \left[ \frac{2J+1}{4\pi} \right] \delta_{JJ} \delta(1Jl) \quad \text{(A.2.d)}
\]

where \(\delta(1Jl)\) is 1 for \(l \in [J-1, J, J+1]\) and zero otherwise. We also have the completeness relation

\[
\delta_{\Omega \Omega'} = \sum_{J=0}^{\infty} \sum_{l=-J}^{J} \sum_{M=-J}^{J} \vec{Y}_{JM}^e(\Omega) \vec{Y}_{JM}^f(\Omega').
\]

\textbf{C) Properties Of The Interactions} \(\vec{V}\) and \(\vec{T}\).

The propagator relating the dipole moment of a source located (at position \(\vec{r}'\)) inside a sphere of radius \(R\) to the electric field inside the sphere (at position \(\vec{r}\)) may be written as

\[
\vec{V}(\vec{r}, \vec{r}'; \omega) \equiv \vec{V}^s(\vec{r}, \vec{r}'; \omega) + \vec{V}^c(\vec{r}, \vec{r}'; \omega)
\]

where
\[\nabla \cdot \psi(r, \rho, \theta, \phi, \omega) = \frac{4\pi i \kappa_j}{\varepsilon_i} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ \nabla \times \left[ h_j^{(1)}(\kappa_j r) \bar{Y}_{ilm}(\Omega) \right] \right] + \kappa_j^2 \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ j_j^{(1)}(\kappa_j r) \bar{Y}_{ilm}(\Omega) \right] \bar{Y}_{ilm}^*(\Omega^{'}) \]

\[\nabla \times \left[ j_j^{(1)}(\kappa_j r) \bar{Y}_{ilm}(\Omega) \right] \bar{Y}_{ilm}^*(\Omega^{'}) \text{ for } R < r < R \]

and

\[\nabla \times \psi(r, \rho, \theta, \phi, \omega) = \frac{4\pi i \kappa_j}{\varepsilon_i} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ \eta^E_j \nabla \times \left[ j_j^{(1)}(\kappa_j r) \bar{Y}_{ilm}^*(\Omega) \right] \right] + \kappa_j^2 \eta^M_j \left[ j_j^{(1)}(\kappa_j r) \bar{Y}_{ilm}^*(\Omega) \right] \bar{Y}_{ilm}^*(\Omega^{'}) \]

where the quantities \(\eta^E_j\) and \(\eta^M_j\) are the Mie coefficients for the expansion of the fields inside the sphere corresponding to the TE and TM modes, respectively. The quantities \(\varepsilon_i\) and \(\varepsilon_o\) are the dielectric "constants" inside and outside the sphere. The \(\kappa_j\) and \(\kappa_o\) are given by \(\kappa_j \equiv \frac{\omega}{c} \sqrt{\varepsilon_j}\), etc. The Mie coefficients appearing in Eq. (A.4) are defined by

\[\eta^E_j \equiv \frac{\varepsilon_j h_j^{(1)}(\kappa_j R)[\kappa_o R h_j^{(1)}(\kappa_o R)]}{\varepsilon_i j_j^{(1)}(\kappa_i R)[\kappa_o R j_j^{(1)}(\kappa_o R)]} \text{ for } R < r < R \]

and
\[ \eta^M_j = - \frac{h_j^{(1)}(\kappa R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa R)[\kappa, Rj_j^{(1)}(\kappa, R)]'}{j_j(\kappa R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa R)[\kappa, Rj_j^{(1)}(\kappa, R)]'} . \]  

The prime on the bracketed expressions in the equations above denote differentiation of the expression with respect to the argument of the spherical Bessel function contained within it. For the case \( r = r' \), we abbreviate to just \( \vec{V}^{sc}(r, r; \omega) \) to just \( \vec{V}^{sc}(r; \omega) \).

The propagator relating the dipole moment of a source located at position \( r' \) inside a sphere of radius \( R \) to the electric field outside the sphere at position \( r \) may be written as

\[ \vec{V} (\vec{r}, \vec{r}'; \omega) = \frac{4\pi i}{\varepsilon_o} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left\{ r^E_l \left[ \nabla \times \left[ h_j^{(1)}(\kappa', r) Y_{l,m}(\Omega) \right] \right] \left[ \nabla \cdot \left[ j_j(\kappa', r') Y_{l,m}^*(\Omega) \right] \right]^T \right. 
\[ + \kappa^2 \eta^M_j h_j^{(1)}(\kappa, r) j_j(\kappa', r') Y_{l,m}^*(\Omega) \right\} \]  

and the corresponding Mie coefficients for the expansion of the fields outside the sphere due to sources inside are \( \xi^E_j \) and \( \xi^M_j \) and are given by the expressions

\[ \xi^E_j = \frac{\varepsilon_o}{\varepsilon_i} \left\{ \frac{j_j(\kappa, R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa, R)[\kappa, Rj_j^{(1)}(\kappa, R)]'}{j_j(\kappa, R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa, R)[\kappa, Rj_j^{(1)}(\kappa, R)]'} \right\} \]  

and

\[ \xi^M_j = \frac{\varepsilon_o}{\varepsilon_i} \left\{ \frac{j_j(\kappa, R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa, R)[\kappa, Rj_j^{(1)}(\kappa, R)]'}{j_j(\kappa, R)[\kappa, Rh_j^{(1)}(\kappa, R)] - h_j^{(1)}(\kappa, R)[\kappa, Rj_j^{(1)}(\kappa, R)]'} \right\} . \]

In writing the above expressions we have taken the magnetic permeabilities of the media to be unity.
Dropping the direct interaction terms in the expression for $\hat{\nabla}$ inside the sphere, we can write expressions for the requisite sub-blocks of the $3N \times 3N$ in the more convenient form

$$\hat{\nabla}_{g\delta} \left( \vec{r}, \vec{r}'; \omega \right) = \sum_{J=1}^{\infty} \delta_{J+1} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} \sum_{M} \eta_{JlM} \vec{J}_{JlM} \vec{J}^{JlM} \left( \Omega \right) \vec{J}^{Jl'M} \left( \Omega' \right)$$

(A.8.a)

and

$$\hat{\nabla}_{b\delta} \left( \vec{r}, \vec{r}'; \omega \right) = \sum_{J=1}^{\infty} \delta_{J+1} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} \sum_{M} \eta_{JlM} \vec{J}_{JlM} \vec{J}^{JlM} \left( \Omega \right) \vec{J}^{Jl'M} \left( \Omega' \right)$$

(A.8.b)

where we have defined the following expressions in terms of the Mie coefficients of the expansion inside the sphere

$$\eta_{J, J+1, J+1} = \frac{4\pi i \kappa_i^3}{\varepsilon_i} \frac{J}{2J+1} \eta^E$$

(A.9.a)

$$\eta_{J, J-1, J-1} = \frac{4\pi i \kappa_i^3}{\varepsilon_i} \frac{J+1}{2J+1} \eta^E$$

(A.9.b)

$$\eta_{J, J+1, J-1} = \eta_{J, J-1, J+1} = -\frac{4\pi i \kappa_i^3}{\varepsilon_i} \frac{J(J+1)}{2J+1} \eta^E$$

(A.9.c)

$$\eta_{J, J} = \frac{4\pi i \kappa_i^3}{\varepsilon_i} \eta^M$$

(A.9.d)

$$\eta_{J, J \pm 1} = \eta_{J, J \pm 1} = 0.$$

(A.9.e)

Note that the general form of $\hat{\nabla}$ and the fact that the $\eta_{JlM}$ obey

$$\eta_{JlM} = (-1)^{Jl} \eta_{JlM}$$

(A.10)

are both consequences of how the interactions must transform under rotations of the entire system. Using the notation above, we also write
\[ \nabla \cdot v(r; \omega) \equiv v^{x/c} \cdot \hat{r} + v^{x/c} \cdot \mathbf{r} \times \left( \mathbf{r} \times \hat{r} \right) \]  
\[ \text{(A.11)} \]

where

\[
4 \pi v^{x/c} \cdot \mathbf{r} = \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} (2J + 1) \eta_{Jl} \cdot j_{l} (\kappa_{l} r) \hat{r} \cdot (\kappa_{l} r) A_{Jl} A_{Jl'} \quad \text{and} \quad (A.12)
\]

and

\[
4 \pi v^{x/c} = \frac{1}{2} \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} (2J + 1) \eta_{Jl} \cdot j_{l} (\kappa_{l} r) \hat{r} \cdot (\kappa_{l} r) (\delta_{ll} - A_{Jl} A_{Jl'}) \quad \text{. (A.13)}
\]

General expressions for some of the \( \mathbf{\hat{r}} \) that are consequences of this rotational symmetry are

\[
\mathbf{\hat{r}}_{\alpha \beta}(\mathbf{r}'; \mathbf{r}; \omega) = \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} t_{\alpha \beta}^{a \beta} (r, r'; \omega) \mathbf{Y}_{Jl}^{f} (\Omega) \mathbf{Y}_{Jl'}^{f} (\Omega') \quad \text{. (A.14.a)}
\]

and

\[
\mathbf{\hat{r}}_{\alpha \beta}(\mathbf{r}'; \mathbf{r}; \omega) = \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{l'=-J}^{J} t_{\alpha \beta}^{a \beta} (r, r'; \omega) \mathbf{Y}_{Jl}^{f} (\Omega) \mathbf{Y}_{Jl'}^{f} (\Omega') \quad \text{. (A.14.b)}
\]

The functions \( \mathbf{\hat{r}}_{\alpha \beta}^{a \beta} \) are more complicated and may be obtained from the relation

\[
\nabla \cdot v^{x/c} = \sum_{b=0}^{1} \mathbf{\hat{r}}_{\alpha \beta}^{a \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \quad \text{or} \quad \nabla \cdot v^{x/c} = \sum_{b=0}^{1} \mathbf{\hat{r}}_{\alpha \beta}^{a \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta} \nabla b_{\alpha \beta}
\]

Fortunately, as we shall see in the following section of this appendix, we only require \( \mathbf{\hat{r}}_{\alpha \beta}^{a \beta}(\mathbf{r}'; \mathbf{r}; \omega) \) in the context of its integral over the \( \beta \) coordinates \( \mathbf{r}' \) and this is straightforward to obtain.

The rotational symmetry requirement shows that the radial functions given above are not all independent. Rather they are related according to

\[
t_{\alpha \beta}^{a \beta} (r, r'; \omega) = (-1)^{l' + l} t_{\alpha \beta}^{a \beta} (r, r'; \omega) \quad \text{. (A.15)}
\]

Simple approximations for the radial functions that meet these conditions are given by
\[ \tau^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r', \omega) = \zeta^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r') \]  
\[ \text{(A.16.a)} \]

and

\[ \tau^{\beta \alpha}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r', \omega) = \zeta^{\beta \alpha}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r') \]  
\[ \text{(A.16.b)} \]

where the coefficients \( \zeta^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}} \) are related by

\[ \zeta^{\beta \alpha}_{\alpha \beta; J_{III} \cdot J_{I}} = (-1)^{y + 1} \zeta^{\beta \alpha}_{\alpha \beta; J_{I} \cdot J_{I}}. \]  
\[ \text{(A.17)} \]

Numerical work we have performed suggests that it perhaps more correct to write our approximation as

\[ \tau^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r', \omega) = \zeta^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r') f_{J_{II}}(r) f_{J_{I}}(r') \]  
\[ \text{(A.18.a)} \]

and

\[ \tau^{\beta \alpha}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r', \omega) = \zeta^{\beta \alpha}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r') f_{J_{II}}(r) f_{J_{I}}(r) \]  
\[ \text{(A.18.b)} \]

where the functions \( \zeta^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}} \) have the same symmetry property as above and where for weak fields, i.e., as \( \eta_{J_{III}} \rightarrow 0 \) the new radial functions and coefficients have the limiting forms

\[ f_{J_{II}}(r) \rightarrow j_{I}(\kappa, r) \]  
\[ \text{(A.19)} \]

and

\[ \zeta^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}} \rightarrow -\eta_{J_{III}}. \]  
\[ \text{(A.20)} \]

For the cases we have been able to study numerically, the differences between the \( f_{J_{II}}(r) \) and the \( j_{I}(\kappa, r) \), are fairly minor.

We will use the more general ansatz for \( \tau^{\alpha \beta}_{\alpha \beta; J_{III} \cdot J_{I}}(r, r', \omega) \) given above in the formal work to follow in order to keep the expressions we derive as general as possible.
We also have need of the expressions for the fields outside the sphere

\[ \vec{E}(\omega) = \sum_{j} \vec{U}(\vec{r}, \vec{r}_j; \omega) \cdot \vec{p}_j(\omega) \]

(A.21)

and

\[ \vec{B}(\omega) = \sum_{j} \vec{U}(\vec{r}, \vec{r}_j; \omega) \cdot \vec{p}_j(\omega) . \]

(A.22)

In the expressions above, \( \vec{r} \) is outside the sphere and the \( \vec{r}_j \) are all contained within the sphere. In this case \( \vec{U} \) and \( \vec{U} \) have the expansions,

\[ \vec{U}(\vec{r}, \vec{r}_j; \omega) = \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{M=-J}^{J} \sum_{l'=J}^{J} \zeta_{j M} h_{j}^{(1)}(\kappa, r) j_{l} \cdot (\kappa, r') \vec{Y}_{j M}(\Omega) \vec{Y}_{j M}(\Omega) \]

(A.23)

and

\[ \vec{U}(\vec{r}, \vec{r}_j; \omega) = \sum_{J=1}^{\infty} \sum_{l=-J}^{J} \sum_{M=-J}^{J} \sum_{l'=J}^{J} \zeta_{j M} h_{j}^{(1)}(\kappa, r) j_{l} \cdot (\kappa, r') \vec{Y}_{j M}(\Omega) \vec{Y}_{j M}(\Omega) \]

(A.24)

where

\[ \zeta_{j J-1 J-1 M} = \frac{4\pi i \kappa^{2} \kappa_{\omega}}{\varepsilon_{o}} \frac{J+1}{2J+1} \zeta_{j}^{E} \]

(A.25.a)

\[ \zeta_{j J+1 J+1 M} = -\frac{4\pi i \kappa^{2} \kappa_{\omega}}{\varepsilon_{o}} \frac{[J+1]}{2J+1} \zeta_{j}^{E} \]

(A.25.b)

\[ \zeta_{j J J M} = \frac{4\pi i \kappa^{3}}{\varepsilon_{o}} \zeta_{j}^{M} \]

(A.25.c)

\[ \zeta_{j J+1 J+1 M} = \frac{4\pi i \kappa^{2} \kappa_{\omega}}{\varepsilon_{o}} \frac{J}{2J+1} \zeta_{j}^{E} \]

(A.25.d)

\[ \zeta_{j J-1 J+1 M} = \zeta_{j J J+1 M} = 0 \]

(A.25.e)

and
\[ u_{J J + 1 J M} = u_{J J - 1 J M} = u_{J J J M} = 0 \]  
(A.26.a)

\[ u_{J J - 1 J M} = \frac{4\pi i \kappa_i^2 \kappa_o c}{\omega \epsilon_o} \left[ \frac{J + 1}{2J + 1} \right] \xi^M_j \]  
(A.26.b)

\[ u_{J J - 1 J M} = -\frac{4\pi i \kappa_i^2 \omega}{c} \left[ \frac{J + 1}{2J + 1} \right] \xi^E_j \]  
(A.26.c)

\[ u_{J J J + 1 J M} = \frac{4\pi i \kappa_i^2 \omega}{c} \left[ \frac{J}{2J + 1} \right] \xi^E_j \]  
(A.26.d)

\[ u_{J J J + 1 J M} = -\frac{4\pi i \kappa_i^2 \kappa_o c}{\omega \epsilon_o} \left[ \frac{J}{2J + 1} \right] \xi^M_j. \]  
(A.26.e)

**D) Solution Of The Integral Equation.**

The integral equation we wish to solve is

\[
G_{\alpha \beta}(\vec{r}, \vec{r}'; \omega) = -G'_{\alpha}(\vec{r}; \omega) \cdot \frac{\omega}{i \omega}(\vec{r}, \vec{r}'; \omega) \cdot G_{\beta}(\vec{r}'; \omega) - \sum_{\gamma} \rho_{\gamma} \int d\vec{r}' G'_{\alpha}(\vec{r}; \omega) \cdot \frac{\omega}{i \omega}(\vec{r}, \vec{r}'; \omega) \cdot G_{\beta}(\vec{r}'; \omega). 
\]

(A.27)

In the situation we study there are only two species, donors and acceptors, which we label by \( D \) and \( A \), respectively.

The quantities \( G_A'(\vec{r}; \omega) \) and \( G_D'(\vec{r}; \omega) \) were defined diagrammatically in section §III and are given by

\[
G_{\alpha}(\vec{r}; \omega) = \left[ U_{\alpha}(\omega) \right]^{-1} + \rho_A \int d\vec{r} \cdot \frac{T_{11}}{i \omega}(\vec{r}, \vec{r}'; \omega) + \rho_D \int d\vec{r} \cdot \frac{T_{11}}{i \omega}(\vec{r}, \vec{r}'; \omega) \]  
(A.28.a)

and
\[ G_B^\prime (\vec{r}'; \omega) = \left[ \bar{G}_B^\prime (\omega) \right]^{-1} + \rho_D \int d\vec{r} \int d\vec{r}' G_{12}^\prime (\vec{r}, \vec{r}'; \omega) + \rho_A \int d\vec{r} \int d\vec{r}' G_{11}^\prime (\vec{r}, \vec{r}'; \omega) \] \quad (A.28.b)

where

\[ \left[ \bar{G}_B^\prime (\omega) \right]^{-1} = \left[ \bar{\alpha}_B (\omega) \right]^{-1} - \nabla \cdot (\vec{r}'; \omega) \] \quad (A.29.a)

\[ = \left[ \alpha_B (\omega) \right]^{-1} - \nabla \cdot (r ; \omega) \left( \vec{T} - \vec{\nabla} \right) + \left[ \alpha_B (\omega) \right]^{-1} - \nabla \cdot (r ; \omega) \vec{\nabla} \] \quad (A.29.b)

We define

\[ \rightarrow \bar{G}_B^\prime (\vec{r} ; \omega) \equiv \frac{1}{\rho} \left( \vec{T} - \vec{\nabla} \right) + \frac{1}{\rho} \vec{\nabla} \] \quad (A.30)

where we have written for the polarizability

\[ \bar{\alpha}_B (\omega) = \alpha_B (\omega) \] \quad (A.31)

and

\[ \left[ d\vec{r} \right] \rightarrow \bar{G}_{\alpha\beta} (\vec{r} ; \omega) \equiv \frac{1}{\rho} \left( \vec{T} - \vec{\nabla} \right) + \frac{1}{\rho} \vec{\nabla} \] \quad (A.32)

Note that we have separated \( \beta \) from \( \alpha \) with a comma in the above expression simply as a reminder of the fact that the position variables of \( \beta \) are those over which an integration has already been performed. We also have

\[ 4\pi \left[ \frac{1}{\rho} \right]_{\alpha\beta} (r ; \omega) = \sum_{J = -J}^{J} \sum_{M = -J}^{J} \sum_{l_1 = -J}^{J} \sum_{l_2 = -J}^{J} \sum_{J = -J}^{J} \sum_{l_2 = -J}^{J} \sum_{J = -J}^{J} \sum_{l_2 = -J}^{J} \eta_{j_1, j_2} \xi_{\alpha, \beta, j_1, J_1, J_2} A_{j_1} A_{j_2} \tilde{j}_{j_1} (\kappa, r) f_{j_2} (r) \]

\[ \int_{0}^{R} d\vec{r}' \left( \vec{T} \right) [A_{j_1} A_{j_2} g_{\alpha\beta} (r ; \omega)] \]

\[ + (\delta_{l_1, l_2} - A_{j_1} A_{j_2}) g_{\alpha\beta} (r ; \omega)] \tilde{j}_{j_1} (\kappa, r) f_{j_2} (r) \] \quad (A.33.a)

and
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\[ 4 \pi \delta_{\alpha \beta}(r : \omega) = \frac{1}{2} \sum_{J = 1}^{\infty} \sum_{M = -J}^{J} \sum_{l = 1}^{J} \sum_{l' = 1}^{J} \sum_{l'' = 1}^{J} \sum_{l''' = 1}^{J} \eta_{J l J l'} \eta_{\alpha \beta} g_{\alpha \beta, J l J l'} \]

\[ (\delta_{l J} - A_{ll, J J}) f_{J l J l}(r) \]

\[ \int_{0}^{R} d r' (r')^2 [A_{l', J} A_{l J}] g_{\alpha \beta, J l J l}^{0} (r', \omega) \]

\[ + (\delta_{l J} - A_{ll, J J}) g_{\alpha \beta, J l J l}^{0} (r', \omega) f_{J l J l}(r) . \] (A.34.b)

We determine the radial functions in the vector spherical harmonic expansion of various terms in the integral equations. We define the following

\[ \langle J' M' | \alpha | G_{\alpha \beta, J J M M} (r, r' ; \omega) \rangle = \int d \Omega d \Omega' \tilde{Y}_{J J}^{*} (\Omega) \cdot G_{\alpha \beta, J J M M} (r, r' ; \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega'). \] (A.35.a)

\[ = \int d \Omega d \Omega' \tilde{Y}_{J J}^{*} (\Omega) \cdot G_{\alpha \beta, J J M M} (r, r' ; \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega'). \] (A.35.b)

Taking overlaps of the other parts of the integral equation, we have

\[ \langle J' M' | \alpha | G_{\alpha \beta}^{*} (r, r' ; \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega) \cdot G_{\alpha \beta} (r', \omega) \rangle = \]

\[ = \sum_{J' = 1}^{\infty} \sum_{M' = -J'}^{J'} \sum_{l' = 1}^{J'} \sum_{l'' = 1}^{J'} \sum_{l''' = 1}^{J'} \sum_{l'''}^{J'} \eta_{J l J l'} \eta_{\alpha \beta} g_{\alpha \beta, J l J l'}^{0} (r', \omega) \int_{0}^{\infty} d r' (r') f_{J l J l'}(r) \]

\[ \int d \Omega \tilde{Y}_{J J}^{*} (\Omega) \cdot G_{\alpha \beta}^{*} (r, \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega') \int d \Omega' \tilde{Y}_{J J}^{*} (\Omega') \cdot G_{\alpha \beta} (r', \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega'). \] (A.36)

and

\[ \int d \Omega \tilde{Y}_{J J}^{*} (\Omega) \cdot G_{\alpha \beta}^{*} (r, \omega) \cdot \tilde{Y}_{J J}^{*} (\Omega') = \]

\[ = \delta_{J J} \delta_{M M} \left[ A_{J J} A_{J J} g_{\alpha \beta, J J}^{0} (r, \omega) + (\delta_{l l} - A_{J J} A_{J J}) g_{\alpha \beta, J J}^{0} (r, \omega) \right] . \] (A.37)
Defining new radial functions by
\begin{equation}
F_{J\ell+1}^{\alpha}(r;\omega) \equiv [A_{J\ell}A_{J\ell} \cdot g_{\ell+1}^{\alpha}](r;\omega) + (\delta_{J\ell} - A_{J\ell}A_{J\ell}) g_{\ell+1}^{\alpha}(r;\omega)] f_{J\ell+1}(r),
\end{equation}
we obtain
\begin{equation}
<J \ell M; \alpha| G_{\alpha}^{\ell}(\bar{r};\omega) \cdot \stackrel{\leftrightarrow}{\mathcal{T}}_{\ell}^{\alpha}(\bar{r},\bar{r}';\omega) \cdot G_{\beta}^{\ell}(\bar{r}',\omega) | J' \ell' M'; \beta> = \\
= \delta_{JJ'} \delta_{MM'} \sum_{l' = J-1}^{J+1} \sum_{l'' = J-1}^{J+1} F_{J\ell+1}^{\alpha}(r;\omega) \gamma_{\alpha\beta}^{l\ell l'\ell'} F_{J'\ell'}^{\beta}(r',\omega),
\end{equation}
and
\begin{equation}
<J \ell M; \alpha| \int dr^2 G_{\alpha}^{\ell}(\bar{r};\omega) \cdot \stackrel{\leftrightarrow}{\mathcal{T}}_{\ell}^{\alpha}(\bar{r},\bar{r}';\omega) \cdot G_{\beta}^{\ell}(\bar{r}',\omega) | J' \ell' M'; \gamma>
= \sum_{J = 0}^{\infty} \sum_{l' = J-1}^{J+1} \sum_{l'' = J-1}^{J+1} \int_0^{\infty} dr(r^*)^2
\end{equation}

\begin{equation}
<J \ell M; \alpha| G_{\alpha}^{\ell}(\bar{r};\omega) \cdot \stackrel{\leftrightarrow}{\mathcal{T}}_{\ell}^{\alpha}(\bar{r},\bar{r}';\omega) \cdot G_{\beta}^{\ell}(\bar{r}',\omega) | J' \ell' M'; \gamma>
= \sum_{l'' = J-1}^{J+1} \gamma_{\alpha\beta}^{l\ell l'\ell'} F_{J\ell+1}^{\alpha}(r) f_{J'\ell'}(r^*),
\end{equation}

and
\begin{equation}
<J \ell M; \alpha| G_{\alpha}^{\ell}(\bar{r};\omega) \cdot \stackrel{\leftrightarrow}{\mathcal{T}}_{\ell}^{\alpha}(\bar{r},\bar{r}';\omega) | J' \ell' M'; \gamma>
= \delta_{J\ell'} \delta_{MM'} \sum_{l'' = J-1}^{J+1} \gamma_{\alpha\beta}^{l\ell l'\ell'} F_{J\ell+1}^{\alpha}(r) f_{J'\ell'}(r^*).
\end{equation}

Eq. (A.41) shows that \( G_{\alpha\beta;J\ell+1,M'J'\ell'+1}(r,\bar{r}',\omega) \) can be written as
\begin{equation}
G_{\alpha\beta;J\ell+1,M'J'\ell'+1}(r,\bar{r}',\omega) = \delta_{J\ell'} \delta_{MM'} G_{\alpha\beta;J\ell+1,M}(r,\bar{r}',\omega).
\end{equation}

Inserting these expressions into the integral equation, and taking overlaps with the radial functions, \( f_{J\ell}(r) \), transforms the integral equation into a sequence of matrix equations, one for
each value of $J$, whose dimensionality is determined solely by the number of species in the problem. For the two species case, we are required to solve a $6 \times 6$ matrix inversion problem. If we define the overlap integral below

\[
\Theta_{J_{l_1}'}(r; \omega) \equiv \int_0^R dr r^2 f_{J_{l_1}}(r) F_{J_{l_1}'}(r; \omega)
\]  

(A.43)

we obtain as the solution

\[
G_{\alpha\beta, \gamma\delta}(r, r'; \omega) \equiv - \sum_{l_1=J-1}^{J+1} \sum_{l_2=J-1}^{J+1} F_{J_{l_1}}(r; \omega) \Gamma_{J_{l_1}J_{l_2}} \cdot F_{J_{l_2}'}(r'; \omega)
\]  

(A.44)

with

\[
\Gamma_{J_{l_1}J_{l_2}} = \zeta_{\alpha\beta, J_{l_1}J_{l_2}} - \sum_{l_3} \sum_{l_4} \sum_{l_5} \sum_{l_6} \rho_\delta \zeta_{\alpha\beta, J_{l_1}J_{l_2}} \left( K^J \right)^{-1} \delta l_2 l_3 \Theta_{J_{l_1}J_{l_2}} \zeta^{\gamma\beta}_{l_1 l_2 l_3}
\]  

(A.45)

where

\[
K^J_{\alpha\beta} = \delta_{\alpha\gamma} \delta_{\beta\gamma} + \rho_\gamma \sum_{l_1=J-1}^{J+1} \Theta_{J_{l_1}J_{l_1}'} \zeta_{\alpha\gamma, J_{l_1}J_{l_1}'}
\]  

(A.46)

the matrix inverse is defined by

\[
\sum_{\gamma} \sum_{l_1} K^J_{\alpha\gamma} \left( K^J \right)^{-1} \delta_{\alpha \gamma} \delta_{l_1} = \delta_{\alpha\beta} \delta_{l_1 l_2}
\]  

(A.47)

E) Computation Of Rates.

Now let us look at the total radiation rate,

\[
<\tilde{R}_{A+D \rightarrow \infty}(t)> = \lim_{r \rightarrow \infty} \int d\Omega \, \hat{n} \cdot \hat{S}(t) \, r^2
\]  

(A.48)

When the magnetic permeabilities of the two media are unity, we have
\[ S(t) = \frac{c}{4\pi} \vec{E}(t) \times \vec{B}(t). \] \hspace{1cm} (A.49)

We specify the Fourier transform convention we use in the time transforms, since the factor of \(2\pi\) that may or may not appear in the transform definition appears in the expression for the result, it is

\[ \vec{E}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \vec{E}(\omega). \] \hspace{1cm} (A.50)

As we are interested in the case in which the correlation of the dipole moments in frequency space is proportional to \(\delta(\omega + \omega')\), we may write

\[ <\hat{\mathbf{R}}_{A+D}^{\omega}(t)> = \sum_{i,j} \langle \vec{p}^i(\omega) \cdot \hat{W}^\text{rad}_{ij}(\omega) \cdot \vec{p}^j(\omega) \rangle \] \hspace{1cm} (A.51)

where \(\hat{W}^\text{rad}_{ij}(\omega)\) is defined by the expression

\[ \sum_{i,j} \vec{p}^i(\omega) \cdot \hat{W}^\text{rad}_{ij}(\omega) \cdot \vec{p}^j(\omega) = \]

\[ = \lim_{\epsilon \to \infty} \frac{c}{4\pi} \frac{1}{(2\pi)^2} \int d\Omega \hat{\mathbf{r}} \cdot \left[ \sum_i \hat{\mathbf{U}}(\mathbf{r}, \mathbf{r}^i; -\omega) \cdot \vec{p}^i(-\omega) \right] \times \left[ \sum_j \hat{\mathbf{U}}(\mathbf{r}, \mathbf{r}^j; \omega) \cdot \vec{p}^j(\omega) \right] r^2. \] \hspace{1cm} (A.52)

Performing the algebra we obtain
\[
\tilde{W}_{ij}^{\text{rad}}(\omega) = \frac{1}{\pi} \frac{|\kappa_j|^4 \omega}{|\kappa_o|^{2} \xi_o^* \sum_{j = 1}^{\infty} \sum_{l = j-1}^{j+1} \sum_{l' = -j+1}^{j-1} \sum_{M = -j}}
\]

\[
\begin{align*}
&\left\{ \delta_{l,j-1} \delta_{l',j-1} \kappa_o^* |\xi_j| \frac{J+1}{2J+1} - \delta_{l,j-1} \delta_{l',j-1} \kappa_o^* |\xi_j| \frac{2[J(J+1)]^{1/2}}{2J+1} \\
&+ \delta_{l,j} \delta_{l,j} \frac{|\kappa_i|^2}{\kappa_o} |\xi_j|^2 - \delta_{l,j+1} \delta_{l',j+1} \kappa_o^* |\xi_j|^2 \frac{2[J(J+1)]^{1/2}}{2J+1} \\
&+ \delta_{l,j+1} \delta_{l',j-1} \kappa_o^* |\xi_j|^2 \frac{J}{2J+1} \right\} [j_i (\kappa_j r_i)^T j_i (\kappa_j r_i) \tilde{\gamma}_{jJM}^i (\Omega_j) \tilde{\gamma}_j^{i'} (\Omega_j)].
\end{align*}
\] (A.53)
§ Appendix B. Details Of The Droplet Calculation Using Morse And Feshbach Vector Spherical Harmonics.

In most of the numerical work used to generate the figures in this paper we have employed the set of real vector spherical harmonics defined by Morse and Feshbach rather than those we have employed in the bulk of the paper. The two sets of functions are mathematically equivalent. However, the aspects of the problem relating to rotational symmetry are more clearly expressed using the more elegant representation of our model in terms of the complex vector spherical harmonic functions, \( \hat{Y}_{\ell M}^{\sigma} (\Omega) \). The latter representation is also a bit more useful for studying other approximation schemes since we at then least have the possibility of making use of some of the power of the vector addition rules familiar from quantum mechanics. In this appendix, we present many of our results in terms of the functions defined by Morse and Feshbach for the benefit of those who may wish to make use of, or possibly extend, any of the computer programs we have written.

A) Notation.

We use the real vector spherical harmonic functions \( \vec{P}_{ml}^{\sigma} (\Omega) \), \( \vec{B}_{ml}^{\sigma} (\Omega) \), and \( \vec{C}_{ml}^{\sigma} (\Omega) \) defined by Morse and Feshbach\(^{12}\) where \( \Omega \) represents the spherical angles \( \theta \) and \( \phi \). It is notationally convenient to write this set of functions in terms of a new function \( \vec{A}_{\nu}^{\sigma} (\Omega) \) defined by the equation

\[
\vec{A}_{\nu}^{i} (\Omega) = \begin{cases} 
\vec{P}_{ml}^{\sigma} (\Omega) & i = 1 \\
\vec{B}_{ml}^{\sigma} (\Omega) & i = 2 \\
\vec{C}_{ml}^{\sigma} (\Omega) & i = 3 
\end{cases} \quad (B.1)
\]

where we use the single greek subscript \( \nu \) merely as a shorthand for the three variables \([l, m, \sigma]\).
The functions $\vec{A}_\nu$ possess the following useful properties:

$$\int d\Omega \vec{A}_\nu^T(\Omega) \cdot \vec{A}_\nu(\Omega) = \frac{\delta_{\nu,\nu} \delta_{\omega,\omega} 4\pi}{l(l+1)D_\nu} \tag{B.2}$$

and

$$\hat{r}^T \cdot \vec{A}_\nu(\Omega) = \delta_{\nu \nu} \vec{A}_\nu(\Omega) \tag{B.3}$$

where the function $D_\nu$ is

$$D_\nu = \delta_{\nu,\nu} = \frac{(2 - \delta_{m,0}) (2l + 1) (l - m)!}{l (l + 1) (l + m)!} \tag{B.4}$$

We shall also find it more natural to use the radial functions defined by $f_\nu^k(r)$ by

$$f_\nu^k(r) = \begin{cases} \frac{j_1(\kappa r)}{\kappa r} & k = 1, \\ \frac{[\kappa r j_1(\kappa r)]'}{\kappa r} & k = 2, \\ j_1(\kappa r) & k = 3, \end{cases} \tag{B.5}$$

where the prime on the quantity in the brackets in the $k = 2$ case denotes differentiation with respect to the argument of $j_1$.

**B) Expressions For $\hat{\nabla}_{ij}(\omega)$ And $\hat{W}_{ij}^{rad}(\omega)$.**

The method of obtaining expansion of $\hat{\nabla}_{ij}(\omega) = \hat{\nabla}(\vec{r}_i, \vec{r}_j; \omega)$ in terms of vector spherical harmonics has been presented elsewhere.\(^{13}\) Briefly, the expansion of $\hat{\nabla}$ when the source is located inside the droplet is constructed by adding a solution of the source free Maxwell’s equations to the solution of Maxwell’s equations for an infinite medium with the dielectric constant of the droplet and a point dipole source. The solution outside the droplet is written as a solution of the source free Maxwell equation corresponding to outgoing waves. The solutions are matched by applying the appropriate boundary conditions on the surface of the sphere.

When the source and observation points are both inside the sphere, $\hat{\nabla}$ may be written in
terms of the vector solutions of the wave equation:

\[
\vec{V} (\vec{r}, \vec{r}'; \omega) = \vec{V}^\omega (\vec{r}, \vec{r}'; \omega) + \vec{V}^\infty (\vec{r}, \vec{r}'; \omega)
\]  

(B.6)

where the \(\vec{V}^\omega (\vec{r}, \vec{r}'; \omega)\) is the bulk contribution given by

\[
\vec{V}^\omega (\vec{r}, \vec{r}'; \omega) = \frac{i \kappa_j^3}{\epsilon_j} \sum_\nu D_\nu \left\{ \bar{M}_v^1 (\kappa_j \vec{r}) \bar{M}_v^1 (\kappa_j \vec{r}') + \bar{N}_v^1 (\kappa_j \vec{r}) \bar{N}_v^1 (\kappa_j \vec{r}') \right\}
\]

for \(r > r'\) \(\quad (B.7)\)

and \(\vec{V}^\infty (\vec{r}, \vec{r}'; \omega)\) is a solution of the source free wave equation which may be interpreted as the field scattered from the sphere boundary to \(\vec{r}\) from \(\vec{r}'\) and is given by

\[
\vec{V}^\infty (\vec{r}, \vec{r}'; \omega) = \frac{i \kappa_j^3}{\epsilon_j} \sum_\nu D_\nu \left\{ \eta_\nu^E \bar{M}_v^1 (\kappa_j \vec{r}) \bar{M}_v^1 (\kappa_j \vec{r}') + \eta_\nu^E \bar{N}_v^1 (\kappa_j \vec{r}) \bar{N}_v^1 (\kappa_j \vec{r}') \right\}
\]

(B.8)

and the sum is \(\sum_\nu \sum_\ell \sum_m \sum_\sigma \sum_e\).

The functions \(\bar{M}_v^1 (\kappa_j \vec{r}) \{\bar{M}_v^3 (\kappa_j \vec{r})\}\) and \(\bar{N}_v^1 (\kappa_j \vec{r}) \{\bar{N}_v^3 (\kappa_j \vec{r})\}\) are combinations of spherical Bessel functions (spherical Hankel functions) with the real vector spherical harmonics which are transverse solutions of the vector wave equation. The quantities \(\eta_\nu^E\) and \(\eta_\nu^M\) are Mie coefficients corresponding to \(TE\) and \(TM\) modes respectively. They are given by

\[
\eta_\nu^E = - \frac{[\kappa_e / \kappa_j] h_{l}^{(1)}(\kappa_j R)[\kappa_e \kappa_j]}{[\kappa_e / \kappa_j] h_{l}^{(1)}(\kappa_j R)[\kappa_e \kappa_j]} \quad \text{and} \quad \eta_\nu^M = \frac{[\kappa_e / \kappa_j] j_{l}^{(1)}(\kappa_j R)[\kappa_e \kappa_j]}{[\kappa_e / \kappa_j] j_{l}^{(1)}(\kappa_j R)[\kappa_e \kappa_j]} \quad (B.9)
\]

Note that the expressions for \(\vec{V}\) in terms of the Morse and Feshbach vector spherical harmonics may be converted to the corresponding expressions for the \(\vec{Y}_{\ell m} (\Omega)\) using the relations:

\[
j_{l} (\kappa r) \vec{Y}_{\ell m}^e (\Omega) = \mp (-1)^m \left[ \frac{1}{l(l+1)} \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} \bar{M}_{\nu}^{1 \ell m} (\kappa \vec{r})
\]

and

\[
\frac{1}{\kappa} \vec{\nabla} \times \left[j_{l} (\kappa r) \vec{Y}_{\ell m}^e (\Omega) \right] = \mp \left[ \frac{1}{l(l+1)} \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} \bar{N}_{\nu}^{1 \ell m} (\kappa \vec{r})
\]

The expressions for \(M_{\nu}^{3}\) and \(N_{\nu}^{3}\) follow similarly except that \(h_{l}^{(1)}(\kappa r)\) replaces \(j_{l} (\kappa r)\).
and

\[
\eta^M \equiv - \frac{[\mu_i/\mu_o] j_l^{(1)}(\kappa_i R)[\kappa_o Rh_l^{(1)}(\kappa_o R)] - h_l^{(1)}(\kappa_o R)[\kappa_i Rh_l^{(1)}(\kappa_i R)]}{[\mu_i/\mu_o] j_l(\kappa_i R)[\kappa_o Rh_l^{(1)}(\kappa_o R)] - h_l^{(1)}(\kappa_o R)[\kappa_i Rh_l^{(1)}(\kappa_i R)]}
\]  

(B.10)

where \( \kappa_i = \frac{\omega}{c} \sqrt{\varepsilon_i \mu_i} \) and \( \kappa_o = \frac{\omega}{c} \sqrt{\varepsilon_o \mu_o} \) are functions of the dielectric constants inside, \( \varepsilon_i \), and outside, \( \varepsilon_o \), the sphere, and the frequency, \( \omega \). \( R \) is the sphere radius, and \( \mu_i \) and \( \mu_o \) are the respective magnetic permeabilities of the two media. The primes on the bracketed expressions denote differentiation with respect to the argument of the spherical Bessel function contained within it. In terms of the definitions in part A of this appendix, we may write Eq. (B.8) in the more useful form:

\[
\nabla_x (p, p'; \omega) = - \sum_i \sum_{\nu} \left[ D_\nu A^i j_l(r) f_l(r) \right] \vec{A}_\nu(\Omega) \vec{A}_\nu^T(\Omega)
\]  

(B.11)

where the 3x3 matrix \( \vec{A}_i \) is given by

\[
\vec{A}_i = - \frac{i \kappa_i^3}{\varepsilon_i} l (l+1) \begin{bmatrix}
 l(l+1) \eta_i^E & [l(l+1)]^{1/2} \eta_i^E & 0 \\
 [l(l+1)]^{1/2} \eta_i^E & \eta_i^E & 0 \\
 0 & 0 & \eta_i^M
\end{bmatrix}
\]  

(B.12)

The expansion of \( \nabla_x (p, p'; \omega) \) when \( p \) is outside the sphere and \( p' \) is inside the sphere is given by

\[
\nabla_x (p, p'; \omega) = \frac{i \kappa_i^3}{\varepsilon_i} \sum_\nu D_\nu \left[ \xi^M M_\nu^3 (\kappa_i p) M_\nu^{1T} (\kappa_i p') + \xi^E N_\nu^3 (\kappa_o p) N_\nu^{1T} (\kappa_o p') \right]
\]  

(B.13)

where the corresponding Mie coefficients are

\[
\xi^M \equiv \frac{[\mu_i/\mu_o] j_l(\kappa_i R) [\kappa_o Rh_l^{(1)}(\kappa_o R)] - h_l^{(1)}(\kappa_o R) [\kappa_i Rh_l^{(1)}(\kappa_i R)]}{[\mu_i/\mu_o] j_l(\kappa_i R) [\kappa_o Rh_l^{(1)}(\kappa_o R)] - h_l^{(1)}(\kappa_o R) [\kappa_i Rh_l^{(1)}(\kappa_i R)]}
\]  

(B.14)

and

\[
\varepsilon \mu \equiv \frac{\omega}{c} \sqrt{\varepsilon_i \mu_i} \frac{\omega}{c} \sqrt{\varepsilon_o \mu_o}
\]
\[ 
\xi^E \equiv \frac{j_l(\kappa r) [\kappa_r R h^{(1)}(\kappa, R)]' - h^{(1)}_l(\kappa, R) [\kappa_r R j_l(\kappa, R)]'}{[\kappa_r / \kappa_o] j_l(\kappa, R) [\kappa_r R h^{(1)}(\kappa, R)]' - [\kappa_o \mu_r / \kappa_r \mu_o] h^{(1)}_l(\kappa, R) [\kappa_r R j_l(\kappa, R)]'} .
\]  

(B.15)

Note that the Mie coefficients above differ slightly from those in the appendix using the \( \vec{V}_{jlm} \) only because of the slight difference in the way the coefficient in front of the sum in the expression for \( \nabla \cdot \vec{V}(\vec{r}, \vec{r}'; \omega) \) is written in Eq. (B.13).

We can use the expression above to obtain \( \vec{W}^{\text{rad}}_{ij}(\omega) \). For the electric field and magnetic field outside the sphere, we have respectively,

\[ 
\vec{E}(\vec{r}; \omega) = \sum_j \vec{E}_j(\vec{r}; \omega) = \sum_j \nabla (\vec{r}, \vec{r}'; \omega) \cdot \vec{p}_j(\omega)
\]  

(B.16)

and

\[ 
\vec{H}(\vec{r}; \omega) = \frac{c}{i \omega \mu_o} \nabla \times \vec{E}(\vec{r}; \omega) = \sum_j \vec{H}_j(\vec{r}; \omega)
\]  

\[ 
= \sum_j \frac{c}{i \omega \mu_o} \nabla \times \nabla (\vec{r}, \vec{r}'; \omega) \cdot \vec{p}_j(\omega).
\]  

(B.17)

Since

\[ 
\nabla \times \begin{bmatrix} \vec{M}_V^3(\kappa \vec{r}) \\ \vec{N}_V^3(\kappa \vec{r}) \end{bmatrix} = \kappa \begin{bmatrix} \vec{N}_V^3(\kappa \vec{r}) \\ \vec{M}_V^3(\kappa \vec{r}) \end{bmatrix},
\]  

(B.18)

we have

\[ 
\vec{H}_j(\vec{r}; \omega) = \frac{\kappa^3 \kappa_r c}{\varepsilon_r \omega \mu_o} \sum_V D_V \begin{bmatrix} \xi^E V^3(\kappa_r \vec{r}) \vec{M}_V^3(\kappa_r \vec{r}_j) \\ \xi^E V^3(\kappa_r \vec{r}) \vec{N}_V^3(\kappa_r \vec{r}_j) \end{bmatrix}
\]  

\[ 
+ \xi^E V^3(\kappa_r \vec{r}) \vec{M}_V^3(\kappa_r \vec{r}_j) \cdot \vec{p}_j(\omega).
\]  

(B.19)

For \( r \rightarrow \infty \), we have the asymptotic expressions
\[
\begin{align*}
\begin{bmatrix}
\hat{M}_n^\sigma (\kappa_r \vec{r}) \\
\hat{N}_n^\sigma (\kappa_r \vec{r})
\end{bmatrix}
\sim \frac{[l(l+1)]^{1/2} e^{i\kappa_r r}}{\kappa_r r} \begin{bmatrix}
i^{-l(l+1)} \hat{C}_m^\sigma (\Omega) \\
i^{-l} \hat{B}_m^\sigma (\Omega)
\end{bmatrix}.
\end{align*}
\] (B.20)

Using the identity, \( \hat{B}_m^\sigma (\Omega) = \hat{r} \times \hat{C}_m^\sigma (\Omega) \), along with the orthogonality relations above, we may identify the matrix \( \hat{W}_{ij}^{\text{rad}}(\omega) \) as

\[
\hat{W}_{ij}^{\text{rad}}(\omega) = \hat{W}_{ijkl}^{\text{rad}}(\vec{r}, \vec{r}'; \omega),
\]

where

\[
\hat{W}_{ijkl}^{\text{rad}}(\vec{r}, \vec{r}'; \omega) = \frac{1}{2\pi} \frac{c^2}{\omega \kappa_r} \frac{\kappa_r}{|\epsilon_1|^2} \sum_v D_v \begin{bmatrix}
|\xi_v^M|^2 & \hat{M}_v^I (\kappa_r \vec{r}) \\
|\xi_v^F|^2 & \hat{N}_v^I (\kappa_r \vec{r})
\end{bmatrix}^T
\]

\[
+ |\xi_v^F|^2 \begin{bmatrix}
\hat{N}_v^I (\kappa_r \vec{r}') \\
\hat{N}_v^I (\kappa_r \vec{r}')
\end{bmatrix}^T
\]

\] (B.21)

or

\[
\hat{W}_{ijkl}^{\text{rad}}(\vec{r} | \vec{r}'; \omega) = \frac{1}{2\pi} \frac{c^2}{\omega \kappa_r} \frac{\kappa_r}{|\epsilon_1|^2} \sum_v \sum_{i,j=1}^3 D_v \Omega_i^j f_i(r) f_j(r') \hat{A}_v^I (\Omega) \hat{A}_v^I (\Omega')
\]

\] (B.22)

with \( \hat{\Omega}_I \) given by

\[
\hat{\Omega}_I \equiv l(l+1) \begin{bmatrix}
[l(l+1)]^{1/2} |\xi_v^F|^2 & [l(l+1)]^{1/2} |\xi_v^F|^2 & 0 \\
[l(l+1)]^{1/2} |\xi_v^F|^2 & |\xi_v^F|^2 & 0 \\
0 & 0 & |\xi_v^M|^2
\end{bmatrix}.
\] (B.23)

When \( \vec{r} = \vec{r}' \) in (B.8) or (B.22), rotational symmetry implies that

\[
\hat{\nabla}^{\text{rad}}(\vec{r}; \omega) = \nabla^{\text{rad}}(r; \omega) \left( \hat{1} - \hat{r} \hat{r} \right) + \nabla^{\text{rad}}(r; \omega) \hat{r} \hat{r}
\]

\] (B.24)

and

\[
\hat{W}^{\text{rad}}(\vec{r}; \omega) = W^{\text{rad}}(r; \omega) \left( \hat{1} - \hat{r} \hat{r} \right) + W^{\text{rad}}(r; \omega) \hat{r} \hat{r}
\]

\] (B.25)

with
\begin{align}
\nu^{\nu-1}(r; \omega) &= \frac{i \kappa_i^3}{\epsilon_i} \sum_{l=1}^{\infty} (2l + 1) l (l + 1) \eta^{E}_i \left( f^1_i(r) \right)^2, \quad (B.26) \\
\nu^{\nu-1}(r; \omega) &= \frac{i \kappa_i}{2 \epsilon_i} \sum_{l=1}^{\infty} (2l + 1) \left( \eta^M_i \left( f^2_i(r) \right)^2 + \eta^E_i \left( f^3_i(r) \right)^2 \right), \quad (B.27) \\
\widetilde{w}^{\text{ind.} -1}(r; \omega) &= \frac{1}{2 \pi} \frac{c^2}{\omega \kappa_o} \frac{|\kappa_i|^6}{|\epsilon_i|^2} \sum_{l=1}^{\infty} (2l + 1) l (l + 1) |\xi^{E}_i|^2 \left( f^1_i(r) \right)^2, \quad (B.28)
\end{align}

and

\begin{align}
\widetilde{w}^{\text{ind.} -1}(r; \omega) &= \frac{1}{2} \frac{c^2}{\omega \kappa_o} \frac{|\kappa_i|^6}{|\epsilon_i|^2} \sum_{l=1}^{\infty} (2l + 1) \left( |\xi^{M}_i|^2 \left( f^2_i(r) \right)^2 + |\xi^{E}_i|^2 \left( f^3_i(r) \right)^2 \right). \quad (B.29)
\end{align}

\textbf{C) The Function $G^*_\alpha(\vec{r}; \omega)$.}

The quantities that appear in $G^*_\beta(\vec{r}; \omega)$ are given by

\begin{align}
\left[ G^{-1}_0 \right]^{1-1}_{\vec{r}_1 - \vec{r}} &= \left[ \alpha^\to \right]^{-1}_{\omega} - \nabla^{\nu-1}_3 (\vec{r}; \omega) \\
&= \left[ \left[ \alpha^\to \right]^{-1} - \nu^{\nu-1} (r; \omega) \right] \left( \hat{T} - \hat{F} \right) \\
&+ \left[ \left[ \alpha^\to \right]^{-1} - \nabla^{\nu-1} (r; \omega) \right] \hat{F}, \quad (B.30.a)
\end{align}

where we have written

\[ \left[ \alpha^\to \right]^{-1}_{\omega} = \alpha^\to_{\omega} \to. \]

The integrals of $T^{11}_{ij}$ that we require are given in our approximation by

\begin{align}
\int d\vec{r} \nabla^{\nu-1}_{ij} \big|_{\vec{r}_1 = \vec{r}_2} &= \int d\vec{r} \nabla^{\nu-1}_{ij} (\vec{r}; \vec{r}_2; r; \omega) \cdot G^0_{ij} \cdot \nabla^{\nu-1}_{ij} (\vec{r}_1; \vec{r}; \omega). \quad (B.31)
\end{align}

Inserting Eqs. (B.11) and (B.30) and using properties (B.3) and (B.2), one in turn obtains
This expression is most easily resolved into longitudinal and transverse components by considering the case when \((\theta, \phi) = (0, 0)\). This yields

\[
\left[ dp_j T_{1, j}^1 \right]_{r^i, r^j} = - \sum_{l=1}^{\infty} \sum_{a, b, c = 1}^{3} \frac{4\pi D_v}{l(l+1)} \Lambda_j^{ab} \Lambda_j^{bc} f_i^j(r) \tilde{f}_i^j(r) \tilde{A}_v^a(\Omega) \tilde{A}_v^c(\Omega) g_{0, l, j}^{b, b}
\]

(B.32)

where

\[
g_{0, l, j}^{b, b} = \int_0^R ds s^2 \left[ f_i^j(s) \right]^2 \left\{ (1 - \delta_{b, 1}) \left[ (\alpha_j(\omega) - v_{ijc} \downarrow (s; \omega) \right] \right\}^{-1}
\]

\[
+ \delta_{b, 1} \left[ (\alpha_j(\omega) - v_{ijc} \downarrow (s; \omega) \right] \right\}^{-1}
\]

(B.33)

Hence, one can compute the longitudinal and transverse components of \(G_D\) as

\[
g_D^{\downarrow}(r; \omega) = \left[ (\alpha_D(\omega))^{-1} - v_{ijc} \downarrow (r; \omega) \right]^{-1} + \rho_D t_{D, D}(r; \omega) + \rho_A t_{A, D}(r; \omega)
\]

(B.37)

and

\[
g_D^{\uparrow\downarrow}(r; \omega) = \left[ [\alpha_D(\omega)]^{-1} - v_{ijc} \downarrow (r; \omega) \right]^{-1} + \rho_D t_{D, D}(r; \omega) + \rho_A t_{A, D}(r; \omega)
\]

(B.38)

Similarly one has for the components of \(G_A^\downarrow\) :
\( g^\perp_A(r;\omega) = \left[ [\alpha_A(\omega)]^{-1} - v^{sc,\perp}(r;\omega) \right]^{-1} + \rho_D t_A^\perp D(r;\omega) + \rho_A t_A^\perp A(r;\omega) \) \hspace{1cm} (B.39)

and

\[ g^{||}_A(r;\omega) = \left[ [\alpha_A(\omega)]^{-1} - v^{sc,||}(r;\omega) \right]^{-1} + \rho_D t_A^{||} D(r;\omega) + \rho_A t_A^{||} A(r;\omega). \] \hspace{1cm} (B.40)

Note that because of the approximations we have made \( t_A^\perp D(r;\omega) = t_D^\perp D(r;\omega) \) and \( t_A^{|| A}(r;\omega) = t_D^{|| b}(r;\omega) \).

**D) The Function \( G_{ab}(\tilde{r},\tilde{r}';\omega) \).**

Under our approximations, the matrix \( T^{ab}_{ab}(\tilde{r},\tilde{r}';\omega) \) appearing in the integral equation is given by

\[ T^{ab}_{ab}(\tilde{r},\tilde{r}';\omega) \equiv -\tilde{V}^{sc}(\tilde{r},\tilde{r}';\omega). \] \hspace{1cm} (B.41)

Introducing the function \( \tilde{f}_{i,a}(r) \), defined by

\[ \tilde{f}^{l}_{i,a}(r) \equiv f^{l}_{i}(r) \left[ g^{||}_A(r;\omega) \delta_{i,1} + g^\perp_A(r;\omega)(1 - \delta_{i,1}) \right], \] \hspace{1cm} (B.42)

one finds that the integral equation is separable. By writing

\[ G_{ab}(\tilde{r},\tilde{r}';\omega) = \sum_{\nu} \sum_{i,j=1}^3 D_{\nu} \Theta^{l j}_{i} \tilde{f}^{l}_{i,a}(r) \tilde{f}^{l}_{j,b}(r') \bar{A}_{\nu}^a(\Omega) \bar{A}_{\nu}^b(\Omega'), \] \hspace{1cm} (B.43)

and using the orthogonality relations, cf. Eqs. (B.2) and (B.3), in the integral equation we find that

\[ \Theta^{l j}_{i} = -\Lambda^{l j}_{i} - \sum_{k} \frac{4\pi\rho_{l}}{l(l+1)} \Lambda^{k}_{l} \Xi_{i;k} \Theta^{k j}_{l}, \] \hspace{1cm} (B.44)

where
\[ \mathcal{E}_{l,\delta}^k \equiv \int_0^R drr^2 f^k_l(r) \tilde{f}^k_l(r). \] (B.45)
§ References.


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Fig. 1. Initially, a donor molecule absorbs a photon of energy $h\omega$ ($h\nu$) from the medium and is excited to its highest excited state. Two processes may subsequently occur: (1) the donor may reemit the photon (i.e., elastic scattering) or (2) it may decay into a lower excited state from which it can emit a red shifted photon of energy $h\omega$ ($h\nu'$) back into the medium (i.e., inelastic scattering). If we focus our attention on the red shifted photon we see that at this stage three things may happen: (1) the photon can leave the medium, (2) the photon can be absorbed by an acceptor molecule, or (3) the photon may be reabsorbed by a donor which may or may not be the donor which originally emitted it.
Fig. 1.
Fig. 2. Basic elements appearing in the diagrammatic expansion of the propagator matrix. Graph (a) corresponds to the expression $\overrightarrow{G}_{\theta}^{\theta}$, graph (b) corresponds to the expression $-\overrightarrow{G}_{\theta}^{\theta} \cdot T_{ij}^{\theta} \cdot \overrightarrow{G}_{\theta}^{\theta}$, and graph (c) corresponds to the expression $-\overrightarrow{G}_{\theta}^{\theta} \cdot T_{ij}^{\theta} \cdot \overrightarrow{G}_{\theta}^{\theta}$. 
Fig. 2.
Fig. 3. Examples of graphs which may or may not appear in the diagrammatic expansion.

Graph (a) is typical of the class of disconnected diagrams which contribute nothing because $T$ only couples pairs of particles. It corresponds to the matrix product $G_0 \cdot T_{ij} \cdot G_0 \cdot T_{kl} \cdot G_0$ in the $3N \times 3N$ dimensional space. Graph (b) is typical of the class of branching diagrams which also do not contribute. It corresponds to the matrix product $G_0 \cdot T_{ij} \cdot G_0 \cdot T_{kl} \cdot G_0 \cdot T_{jk} \cdot G_0$. Graphs like (c) are not included in the expansion by the definition of the binary collision expansion. It corresponds to the expression $G_0 \cdot T_{ij} \cdot G_0 \cdot T_{ij} \cdot G_0$. Graph (d) gives non-zero contributions to two blocks $G_{ij}$ and $G_{jk}$, namely, $G_0 \cdot T_{ij} \cdot G_0 \cdot T_{ij} \cdot G_0$ and $G_0 \cdot T_{ij} \cdot G_0 \cdot T_{jk} \cdot G_0$. 


Fig. 3.
Fig. 4. Series expansion of $G_{ii}^{\alpha}$ or $G_{\alpha}^{\ddagger}$ for $i \in \alpha$. Expression [1] shows that the terms in the binary collision expansion may be arranged according to the number of particles coupled to particle $i$ where each diagram has an expansion in connected diagrams containing the appropriate number of particles. The line corresponding to particle $i$ has its endpoints marked with an $\times$. The first few terms in the expansions of 2-, 3-, and 4-particle connected diagrams are shown in expressions [2], [3] and [4]. Note that the leading term in the $n$-particle connected series is the $n$-particle diagram consisting of $n-1$ particles connected by a single line to the particle $i$ line, e.g., graphs (a), (b), (c), and (g). The boxed terms, (d), (e), and (f), are representative of the one loop terms.
[1] \[ \ldots = \ldots + \ldots + \ldots + \ldots + \ldots \]

(a)

[2] \[ \ldots = \ldots \]

(b)

[3] \[ \ldots = \ldots + \ldots + \ldots + \ldots + O(T^4) \]

(c) (d) (e) (f)

[4] \[ \ldots = \ldots + O(T^4) \]

(g)

Fig. 4.
Fig. 5. Series expansion of $\tilde{G}_{ij}$ or $G_{\alpha\beta}$ for $i \in \alpha$ and $j \in \beta$. Expression [1] shows that the terms in the binary collision expansion may be arranged according to the number of particles coupled to particles $i$ and $j$. The terms labeled $(a) - (k)$ may be resummed to yield the integral equation. The boxed terms are the first loop corrections.
\[ [1] \quad \text{Diagram 1} = \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \ldots \]

\[ [2] \quad \text{Diagram 2} \equiv \text{Diagram A} \]

\[ [3] \quad \text{Diagram 3} = \text{Diagram B} + \text{Diagram C} + \text{Diagram D} + \text{Diagram E} + \ldots \]

\[ + O(T^4) \]

\[ [4] \quad \text{Diagram 4} = \text{Diagram E} + \text{Diagram F} + \text{Diagram G} + \text{Diagram H} + \text{Diagram I} + \text{Diagram J} + \text{Diagram K} + O(T^4) \]

Fig. 5.
Fig. 6. Leading terms in the expansion of the bilinear quantity $K_{ij}$ for the case $i \neq j$ with $j=1$.
Terms are grouped according to their orders in the density $\rho$ and the binary collision interaction $T$. The terms highlighted by the different kinds of boxes may be summed together using the functions $G_{ij}^{\rho \omega}$.
\( \rho^{0T_1} \) terms:
\[
\begin{array}{c}
\begin{array}{c}
i
\hline
i
\hline
j
\end{array}
\end{array}
\]
\( \rho^{0T_2} \) terms:
\[
\begin{array}{c}
\begin{array}{c}
i
\hline
i
\hline
j
\end{array}
\end{array}
\]
\( \rho^{0T_3} \) terms:
\[
\begin{array}{c}
\begin{array}{c}
i
\hline
i
\hline
j
\end{array}
\end{array}
\]

Fig. 6.
Fig. 7. Leading terms in the expansion of the bilinear quantity $K_{ij}$ for the case $i \neq j$ with $i \neq 1'$ and $j \neq 1'$. Terms are grouped according to their order in $T$. Only the leading order in density is included.
\( \rho^{T^2} \) terms:

\( \rho^{T^1} \) terms:

\( \rho^{T^0} \) terms:

Fig. 7.
Fig. 8. Leading terms in the expansions of the bilinear quantity $K_{ij}$ for the cases $i = j \neq 1$ and $i = j = 1$. These consist of a single term for each case.
\( \rho^0 T^2 \) terms for \( i = j \neq 1' \):

\[
\begin{array}{ccc}
& \scriptstyle i & \\
\scriptstyle i' & \times & \scriptstyle i' \\
& \scriptstyle 1' & \times & \scriptstyle 1' \\
\end{array}
\]

\( \rho^0 T^0 \) terms for \( i = j = 1' \):

\[
\begin{array}{ccc}
& \scriptstyle 1' & \\
\scriptstyle 1' & \times & \scriptstyle 1' \\
\end{array}
\]

Fig. 8.
**Fig. 9.** Plot of $[\text{Tr}(\vec{V} \frac{12}{12} i \vec{V} \frac{12}{12} )]^{1/2}$ as a function of the observer distance from the center of the sphere, $R$, and the cosine of the angle, $\theta$, between the source and observer. $V$ includes both bulk and sphere contributions. The sphere radius is 3.799 microns (µ) and the source distance from the center is 0.379 microns. The resonance frequency in reduced, dimensionless units, $\omega R_{\text{sphere}}/c$, is 60.08857370478906. The polarizabilities are degenerate and assumed to be Lorentzian, $\alpha(\omega) = \alpha_0 / (\omega_0^2 - \omega^2 - i \gamma_0 \omega)$. The parameters used were $\alpha_0 / \omega_0^2 = 6.0 \text{Å}^3$, $\lambda_0 = 2\pi c / \omega_0 = 3730\text{Å}$, and $\gamma_0 / \omega_0 = 0.1$. 


Fig. 10. Plot of $[Tr(V_{12}^{12} t^2 V_{12}^{12})]^{1/2}$ as a function of the observer distance from the center of the sphere, $R$, and the cosine of the angle, $\theta$, between the source and observer. $V$ includes both bulk and sphere contributions. All the parameters are the same as in Fig. 9 except that the source radius is 3.032 microns.
Fig. 11. Plot of \( [\text{Tr}(\hat{V}^{12} \hat{\mathcal{V}}^{12})]^{1/2} \) as a function of the observer distance from the center of the sphere, \( R \), and the cosine of the angle, \( \theta \), between the source and observer. \( V \) includes both bulk and sphere contributions. All the parameters are the same as in Figs. 9 and 10 except that the source radius is 3.79 microns.
\( (g - \gamma) \Lambda_1/[(\Lambda_1^2)^{1/2}] \)
Fig. 12. Plot of \( [\text{Tr}(\hat{T}_{\frac{12}{12}} T_{\frac{12}{12}})]^{1/2} \) as a function of the observer distance from the center of the sphere, \( R \), and the cosine of the angle, \( \theta \), between the source and observer. \( V \) includes both bulk and sphere contributions. All parameters are as in Fig. 9.
Fig. 12.

\[(g^{-\phi}) \frac{\mathcal{Z}}{1}\left[\mathcal{L}_{\mathcal{L}}\right]\]
Fig. 13. Plot of \( \sqrt{\text{Tr}(\hat{T}_{ij}^2 \hat{T}_{kl}^2)} \) as a function of the observer distance from the center of the sphere, \( R \), and the cosine of the angle, \( \theta \), between the source and observer. \( V \) includes both bulk and sphere contributions. All parameters are as in Fig. 10.
Fig. 13.

\[(g^{\lambda})_{z/1}[[\mu_{\perp\perp}]]\]
Fig. 14. Plot of \([T_{\text{ref}} \left\{ \sum_{i=1}^{12} \left( \sum_{j=1}^{i} \rho_{ij} \right) \right\}]^{1/2}\) as a function of the observer distance from the center of the sphere, \(R\), and the cosine of the angle, \(\theta\), between the source and observer. \(V\) includes both bulk and sphere contributions. All parameters are as in Fig. 11.
Fig. 14.

\((g - v) \frac{2}{11} \left[ (L^1 L)^{ij} L^j \right] \)
Fig. 15. Plots of the absolute values of the real and imaginary parts of $t_{\alpha\beta,jm}(r,r')$ and $v_{\alpha\beta,jm}(r,r')$ versus $J$ for all values of $l \in [J-1,J,J+1]$. Both source and observer radii are 0.379 microns and the bulk interaction in $V$ has been dropped. The remaining parameters are as in Figs. 9 and 12. Values smaller than $10^{-23}$ have been cut out of the plots because the decomposition algorithm we used to determine $t_{\alpha\beta,jm}(r,r')$ becomes susceptible to roundoff errors when the smaller modes become sufficiently small relative to the largest mode.
Fig. 15.

$\Re(f_{\alpha\beta}^{\text{ab}},(r,r'))|\left(\text{A}^3\right)$

$|\im(f_{\alpha\beta}^{\text{ab}},(r,r'))|\left(\text{A}^3\right)$

$t_{\alpha\beta}^{\text{ab},\text{IV}}(r,r')$ and $v_{\alpha\beta}^{\text{ab},\text{IV}}(r,r')$ vs. $J$

$t_{\alpha\beta}^{\text{ab},\text{IV}}(r,r') \equiv ''\sigma''$

$v_{\alpha\beta}^{\text{ab},\text{IV}}(r,r') \equiv ''\pi''$
Fig. 16. Plots of the absolute values of the real and imaginary parts of $t_{\alpha\beta, J}^{\alpha\beta}(r, r')$ and $v_{\alpha\beta, J}^{\alpha\beta}(r, r')$ versus $J$ for all values of $l \in [J-1, J, J+1]$. Both source and observer radii are 3.032 microns and the bulk interaction in $V$ has been dropped. The remaining parameters are as in Figs. 10 and 13. Values smaller than $10^{-20}$ have been cut out of the plots because the decomposition algorithm we used to determine $t_{\alpha\beta, J}^{\alpha\beta}(r, r')$ becomes susceptible to roundoff errors when the smaller modes become sufficiently small relative to the largest mode.
Fig. 16.
Fig. 17. Plots of the absolute values of the real and imaginary parts of \( t_{\alpha \beta , Jl} (r, r') \) and \( \nu_{\alpha \beta , Jl} (r, r') \) versus \( J \) for all values of \( l \in [J-1, J, J+1] \). Both source and observer radii are 3.79 microns and the bulk interaction in \( V \) has been dropped. The remaining parameters are as in Figs. 11 and 14. Values smaller than \( 10^{-20} \) have been cut out of the plots because the decomposition algorithm we used to determine \( t_{\alpha \beta , Jl} (r, r') \) becomes susceptible to roundoff errors when the smaller modes become sufficiently small relative to the largest mode.
$t_{\alpha\beta}^{a\beta,III} (r, r')$ and $v_{\alpha\beta}^{a\beta,III} (r, r')$ vs. $J$

Fig. 17.
Fig. 18. Plots of $D_A(\omega)$ versus $\omega$ in reduced frequency units for the case in which the parameters used for the acceptor and donor polarizabilities are non-degenerate. In this case, the frequencies and the damping factors in the polarizability functions are different. The spectrum has been convolved with Gaussian weighting functions, with widths of 0.01 (Fig. 18a) and 0.05 (Fig. 18b) in reduced frequency units, in order to make the computed spectrum easier read on a page of limited size and resolution, and also to demonstrate the effects of instrumental bandwidth. The convolution has no effect on the gross features of the plot, e.g., integrated value, scaling of background values with density, etc. The effect is to replace the sharpest and highest peaks by smaller and wider peaks of equal area. The three panels (a) through (c) correspond to donor densities (equal to the acceptor densities) spaced roughly three orders of magnitude apart. The donor densities displayed are (a) $6.46 \times 10^{-3}\mu M$; (b) $13.9\mu M$; and (c) $3000\mu M$. For densities smaller than $6.46 \times 10^{-3}\mu M$, the spectra do not change aside from the trivial scaling with density. The parameters characterizing the polarizabilities of the molecules were the DC polarizabilities, $\alpha_{0,D}/\omega_{0,D}^2=\alpha_{0,A}/\omega_{0,A}^2=6.0\delta^2$, the frequencies expressed as wavelengths, $\lambda_{0,D}=3530\text{Å}$ and $\lambda_{0,A}=3930\text{Å}$, and the dimensionless damping constants, $\gamma_{0,D}/\omega_{0,D}=0.1056657224$ and $\gamma_{0,A}/\omega_{0,A}=0.09491094148$. The dielectric constants inside and outside the droplet were taken to be 2.1609 and 1.0, respectively. The sphere radius used was 3.79945 microns. Modes from $J=1$ to 89 were included in the calculation. The reduced frequency range displayed corresponds to the 322nm to 442nm wavelength range.
Fig. 18a.
Fig. 18b.
Fig. 19. Plot of $R^{\text{rad}}(\omega)$ versus $\omega$ for the case in which the parameters used for the acceptor and donor polarizabilities are not degenerate. The parameters used are identical to those used in Fig. 18. Also as in Fig. 18, the spectrum has been convolved with Gaussian weighting functions, with widths of 0.01 (Figure 19a) and 0.05 (Figure 19b) in reduced frequency units in order to illustrate the effects of instrumental bandwidth. Again, the three panels (a) through (c) correspond to donor densities (equal to the acceptor densities) spaced roughly three orders of magnitude apart. The donor densities used were (a) $6.46 \times 10^{-3} \mu M$; (b) $13.9 \mu M$; and (c) $3000 \mu M$. For donor densities smaller than $6.46 \times 10^{-3} \mu M$, the radiation spectra do not change.
Fig. 19a.
Fig. 19b.
Fig. 20. Plot of $D_A(\omega)$ versus $\omega$ in the immediate vicinity of a single resonance. Unlike Figs. 18 and 19, this plot is not convolved with a Gaussian weighting function. The figure contains plots for eight densities, logarithmically spaced from $3.00 \times 10^{-6} \mu M$ to $30 \mu M$, including the four densities included in the two previous figures, 18 and 19. For the six lowest densities, the widths of the peaks, numerically estimated by fitting the peaks to a 2 by 2 Pade approximant, are presented. The widths are presented in the reduced frequency units used for the plot. For the lowest three to four densities, the shift of the width is small compared to the intrinsic width of the resonance. For the larger measured shifts in the widths, the increases in the widths appear to be proportional to the density. This would be consistent with the idea that some intrinsic loss, proportional to the density of the added dye molecules, has been added to the medium. The two highest densities are presented as dashed lines. The corresponding peaks have actually broadened and shifted out of the range of the plot. A small "glitch" has developed at the resonance frequency. Whether this "glitch" is a consequence of the theory or of the numerics is an open question.
$D_A (\omega) (\text{Å}^2/\text{s})$

$\omega R_{\text{sphere}} / c$

$\leftarrow 1.14 \times 10^{-6}$

$\leftarrow 1.15 \times 10^{-6}$

$\leftarrow 1.14 \times 10^{-6}$

$\leftarrow 1.14 \times 10^{-6}$

$\leftarrow 1.14 \times 10^{-6}$

$\leftarrow 1.32 \times 10^{-6}$

$\leftarrow 3.51 \times 10^{-6}$

Fig. 20.
Fig. 21. The integral of the function $D_A(\omega)$ plotted in Fig. 18 is plotted as a function of the donor density. Also included in the plot is the equivalent plot for the calculation in which the polarizabilities are degenerate. The non-degenerate case was integrated over the reduced frequency range $\omega R_{sphere} / c = (48.9, 87.0)$ ($\lambda = 274 - 488 nm$) while the degenerate case was integrated over the range $\omega R_{sphere} / c = (54.0, 74.0)$ ($\lambda = 322 - 442 nm$). In the density range the two curves have in common, both functions exhibit similar density profiles, indicating that the overall dependence upon density is not very sensitive to how the donor and acceptor polarizabilities are tuned with respect to each other. The parameters for the degenerate case are the same as in the non-degenerate case used in previous figures, except that $\lambda_{0,A} = \lambda_{0,D} = 3730 \AA$ and $\gamma_{0,A} / \omega_{0,A} = \gamma_{0,D} / \omega_{0,D} = 0.1$. 
\[ \int d\omega D_\omega (\omega) \text{ (arbitrary units)} \]

Fig. 21.

- \( \times \) – Non-degenerate
- \( + \) – Degenerate

\( \rho_D \) (\( \mu \)M)
**Fig. 22.** The integral of the function $R_{\text{rad}}(\omega)$ plotted in Fig. 19 is plotted as a function of the donor density. Also included in the plot is the equivalent plot for the calculation in which the polarizabilities are degenerate. In the density range the two curves have in common, both functions exhibit similar density profiles, indicating that the overall dependence upon density is not very sensitive to how the donor and acceptor polarizabilities are tuned with respect to each other. As in Fig. 21, the non-degenerate case was integrated over the reduced frequency range $\omega R_{\text{sphere}}/c = (48.9, 87.0) \ (\lambda = 274 - 488 \text{nm})$ while the degenerate case was integrated over the range $\omega R_{\text{sphere}}/c = (54.0, 74.0) \ (\lambda = 322 - 442 \text{nm})$. 
\[ \int d\omega R^{\text{rad}}(\omega)/2 \text{ (arbitrary units)} \]

- Non-degenerate
- Degenerate

\[ \rho_D (\mu\text{M}) \]

Fig. 22.
Fig. 23. Ratio of the quantities in Figs. 21 and 22, which plays the role of a quantum yield in our problem, plotted as a function of the donor density. Provided that the function $\Omega_D(\omega)$ is sufficiently broad to include many Mie resonances, then one might expect that the density behavior illustrated here will be largely independent of any details of $\Omega_D(\omega)$ since the overall scale of $\Omega_D(\omega)$ cancels out of the ratio. For the non-degenerate polarizability case, the density dependence starts out as $O(p^{0.98})$ for low density, and gradually switches over to $O(p^{0.12})$ for the last 5 to 6 densities.
\[
2 \int d\omega D_\omega (\omega) / \int d\omega R^\text{rad} (\omega)
\]

- Non-degenerate

+ - Degenerate

\[\rho_D (\mu\text{M})\]

Fig. 23.
Application of a classical model for energy transfer to macroscopic systems.

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ABSTRACT

In a previous paper, we studied a simple classical electrodynamic model for energy transfer processes occurring in micron-sized spherical droplets in which we attempted to incorporate the effects of multiparticle scattering in a systematic fashion by means of a binary collision expansion and diagrammatic resummation techniques. In that paper, we studied the case of steady-state excitation of the donor molecules of the system and were able to compute the observed anomalous density dependence of the transfer. In this paper, we develop the theory for macroscopic systems and find no anomalous behavior. We also attempt to extend the theory to the case of pulsed (or flashed) excitation of a few molecules in the system, and study the propagation of the excitation from donors to acceptors as a function of time in macroscopic systems. Comparisons are made with the work of Haan and Zwanzig [J. Chem. Phys., 68 (1978)] as well as the many works of Loring, Andersen, Fayer and Gochanour on electronic excited state transport in solutions.

MS code no. 1993 PACS numbers:

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§ I. Introduction.

In a previous work,¹ hereinafter referred to as I, we presented a simple classical electrodynamic model for energy transfer processes occurring between dye molecules dissolved within micron-sized spherical droplets. The model described the dye molecules as a collection of classical point dipoles having Lorentzian lineshapes (Drude oscillators) which were coupled by their electrodynamic fields. Classical quantities which measure the amount of energy transfer were defined and computed. The dynamics of the molecules in the system, including the effects of multiparticle scattering, were incorporated by means of a binary collision expansion and the use of diagrammatic resummation techniques. This system was studied in the limit in which the molecules in the system underwent steady-state excitation and it was discovered that in the case of small spheres the theory displayed unusual density dependence, in good agreement with experiment, owing to the different density behaviors associated with spectral regions close to and far from the Mie resonance frequencies of the sphere.

In this paper, we apply the theory to macroscopic systems. We shall repeat the steady-state calculation of the previous paper in the first few sections, where necessary, pointing out the different types of approximations that are specific to the treatment of the bulk. We shall study the theory using a fully radiative dipole interaction as well as using an interaction consisting of only the near-field interaction. The latter shall be referred to as the quasi-static limit. We shall find that so long as the bare medium, i.e., not containing dye molecules, is initially lossy (so that some of the Fourier transforms from the fully radiative calculation are well-defined) the dominant contribution to the transfer comes from very short distances so that to good approximation the interaction can be replaced by the quasi-static limit. Moreover, the unusual density behavior noted in the previous work does not appear since there are no Mie resonances leading to strong interactions that couple large regions of space.
We shall also examine the quasi-static limit of our model in the time domain, for pulsed excitations, in order to discover whether or not the transferred energy is transported diffusively. In this context, we compare our theory with those which proceed directly from a Master equation for the excited-state populations of the molecules using the two-particle quantum mechanical or Förster transition rates. Haan and Zwanzig\(^2\) first analyzed this problem and obtained the first few terms of the density expansion of the Green’s function solution for the Master equation and of the root-mean-square displacement of the excitation from its initial location. This expansion by itself did not reveal diffusive behavior. Therefore, they conjectured that this expansion might be viewed as the short-time limit of function that is ultimately diffusive, and based upon that assumption, postulated a resummation giving diffusive behavior for long times, thus forcing their result into a diffusive form. They were then able to extract a diffusion constant, which scaled with the density of dye molecules as \(\rho^{\frac{4}{3}}\). Later, Gochanour, et. al.\(^3\) re-examined this problem (including its extensions to 1- and 2-D systems, etc.) using more powerful diagrammatic methods. Considering many terms previously omitted in the Haan and Zwanzig treatment, they developed a self-consistent method of approximation in the spirit of Dyson’s equation in quantum mechanics, and were able to show that the transport was non-diffusive at short times and diffusive at long times. They also found that the time interval over which the transition to long time behavior occurred depended upon the density. For low densities, they found that the transport only became diffusive after many decay lifetimes of the molecules in the system whereas for high densities, the transport became diffusive within a single decay lifetime. In the long-time limit, the diffusion constant was again found to scale as \(\rho^{\frac{4}{3}}\).

Our approach will differ in that we shall attempt to extract diffusive behavior, if it can be found in our model, without assuming for this system the Markovian phenomenology that underlies the Master equation approach. Instead, we hope to extract such behavior from the
underlying electrodynamics and a simple model for the dynamics of the individual molecules. We shall only present a naive analysis in the spirit of Haan and Zwanzig’s approach here, and lay the foundation for a more extensive analysis in an appendix and in a section on the long-time asymptotic analysis of the self-propagator, $G^t_b(t)$, in the quasi-static limit.

§ II. Review Of The Model.

In paper I, the details of the model, including the binary collision expansion and the resummations that we employ here, were presented. As most of the theory goes through without change in the bulk limit, here we shall only briefly review the basic model in order to explain our basic approach, and in addition, fix some of the notation. Additional details regarding the binary collision expansion are relegated to appendix A. In this section, we shall also point out the different approximations required for the treatment of the bulk case.

The molecules involved in the transfer process are viewed as collections of classical Drude oscillators which interact by means of their electrodynamic fields. The equations of motion for the dye molecules are written in a Fourier representation as

$$\vec{p}_i(\omega) = \vec{\alpha}_i(\omega) \cdot \left[ \vec{E}_i(\omega) + \vec{Q}_i(\omega) \right], \quad (II.1)$$

where $\vec{\alpha}_i(\omega)$ is the polarizability of the $i$th molecule, $\vec{E}_i(\omega)$ is the electric field experienced by the $i$th molecule due to the presence of other molecules and the dielectric properties of the medium, and $\vec{Q}_i(\omega)$ is a random source function which may be interpreted physically as arising from random initial conditions for each molecule.

In the interest of mathematical simplicity, we shall restrict ourselves to the case in which each molecule is modeled by a single oscillator (however, see I for a discussion of the more general case). The oscillator model that we will employ is that of a damped harmonically-bound charge, or Drude oscillator. The molecular polarizability function in this case takes the Lorentzian form
\[
\alpha_\omega^{-1} \equiv \frac{\alpha_{0,i}^2}{\omega_{0,i}^2 - \omega^2 - i \omega \gamma_{0,i}} = - \frac{\alpha_{0,i}}{\omega - \omega_{0,i}^{\pm} \left(\omega - \omega_{0,i}^{-}\right)},
\]

where the complex frequencies in the last expression are defined as

\[
\omega_{0,i}^{\pm} \equiv \pm \omega_{\gamma,i} - \frac{i \gamma_{0,i}}{2}
\]

and \(\omega_{\gamma,i} \equiv \left[\omega_{0,i}^2 - \left(\gamma_{0,i}/2\right)^2\right]^{1/2}\). \(\omega_{0,i}\) and \(\gamma_{0,i}\) are the bare oscillation frequency and the damping constant of the molecule, respectively. \(\alpha_{0,i}\) denotes the ratio of the square of the effective charge of the oscillator to its effective mass. The parameters \(\alpha_{0,i}\), \(\omega_{0,i}\), and \(\gamma_{0,i}\) depend only upon the type of dye molecule. We shall only consider the simpler case in which the polarizability function is the same for all the dye molecules in the system. Hence, we shall omit the subscripts referring to particle labels, and simply write \(\alpha_{0}, \omega_{0}, \text{ and } \gamma_0\), etc. The damping constant is a sum of contributions from non-radiative decay, \(\gamma_{0}^{NR}\), and from radiative decay, \(\gamma_{0}^{R}\).

The electric field at each molecule is written as a sum of the contributions from the other molecules in the system

\[
\vec{E}_i(\omega) = \sum_{j \neq i} \vec{\nabla}_{ij}(\omega) \cdot \vec{p}_j(\omega)
\]

where the interaction matrix \(\vec{\nabla}_{ij}(\omega) \equiv \vec{\nabla}(\vec{r}_i, \vec{r}_j; \omega)\) may be obtained by solving Maxwell’s equations in the bulk. In our previous paper, the sum Eq. (II.4) included a contribution from \(i = j\). This extra term was necessary in order to incorporate boundary effects arising from the small size of the system. This term is vanishes in the bulk. In small systems, the \(i \neq j\) terms also include additional contributions due to boundary effects that, for the system studied in I, were much larger than the bulk terms which were thus dropped.¹

The random source functions, \(\vec{Q}_i(\omega)\), are simply related to the initial values and first time-derivatives of the molecular dipole moments. They are chosen to mimic the processes by which donor states are populated, including the initial excitation of the molecule by the exter-
nal source as well as the randomization caused by the relaxation of the initial excited donor state to the donor state involved in the transfer process; hence, their stochastic properties depend upon the kind of experiment being performed as well as upon the internal dynamics of the molecules. We shall assume that initial excitation followed by a rapid radiationless transition to the fluorescing states gives our classical dipoles random phases and orientations. Hence, the \( \tilde{Q}_i(\omega) \) will have zero mean. In addition, we assume that the sources for different molecules, or for different Cartesian components of the same molecule are uncorrelated. This allows us to write the frequency-frequency correlation function of the sources as

\[
\langle Q_i^{\mu}(\omega_1)Q_j^{\nu}(\omega_2) \rangle = \frac{1}{3} \Omega_i(\omega_1;\omega_2)\delta^{\mu\nu}\delta_{ij}.
\]  

The dependence of \( \Omega_i(\omega_1;\omega_2) \) upon the external sources enters as follows. Intuitively, in the case of pulsed excitation, each of the \( \tilde{Q}_i(\omega) \) is the Fourier transform of something proportional to \( \delta(t) \), hence \( \tilde{Q}_i(\omega) \) should not depend upon \( \omega \).\footnote{Of course, there would be frequency dependence if the excitation occurs at a time \( t \neq 0 \), since then \( \tilde{Q}_i(\omega) \) picks up a trivial factor of \( e^{i\omega \tau} \).} Therefore, in this case \( \Omega_i(\omega_1;\omega_2) \) does not depend upon either of the two frequencies. In this event, we shall simply omit the frequency dependence from the notation. \( \Omega_i \) then depends only upon the type of molecule and perhaps its location in the system. For example, if the system were illuminated by a narrow beam, then \( \Omega_i \) would be non-zero only if the molecule was in the beam and had an absorption band that overlapped with the frequencies in the beam.

In the case of steady-state illumination of the system, a different form of \( \Omega_i(\omega_1;\omega_2) \) obtains. Since the time correlation functions should then be invariant under time translation, their form therefore must be

\[
\Omega_i(\omega_1;\omega_2) = \Omega_i(\omega_1)\delta(\omega_1 + \omega_2).
\]

In the end, \( \Omega_i(\omega) \) or \( \Omega_i \) will appear in our results only as an overall weighting factor. In our analysis of the steady-state, we shall treat \( \Omega_i(\omega) \) as being independent of frequency. \( \Omega_i(\omega) \)
or $\Omega_i$ may still depend upon the molecules and their locations. We consider systems made up of two types of molecules, termed donors and acceptors. The donors are simply those molecules which have been excited by the external sources, and hence, have non-zero $\Omega_i(\omega_1;\omega_2)$; the acceptors are only excited by their interactions with the donors and other acceptors, and hence, have $\Omega_i(\omega_1;\omega_2)=0$. We shall use the labels D and A to refer to generic donor and acceptor molecules, respectively. In the event that we should need to refer to two generic molecules of the same species, we shall use primes to distinguish them.

We express the solution of Eq. (II.1) in terms of an $N$ particle, $3N \times 3N$ dimensional, Green’s function matrix, $\mathbb{G}(\rho^N; \omega)$, given by

$$\vec{p}_i(\omega) = \sum_j \mathbb{G}_{ij}(\rho^N; \omega) \cdot \vec{Q}_j(\omega).$$  \hspace{1cm} (II.6)

Here $\mathbb{G}_{ij}(\rho^N; \omega)$ denotes the $3 \times 3$ block of $\mathbb{G}(\rho^N; \omega)$ in which particle $j$ is the source of the excitation and particle $i$ is where the excitation is ultimately measured.

All the quantities of interest to us can be expressed as ensemble averages of objects which are bilinear in the dipole moments, $\vec{p}_i(\omega)$. By employing a binary collision expansion of the matrix $\mathbb{G}_{ij}(\rho^N; \omega)$ and some diagrammatic methods, these averages can be expressed in terms of some simple one- and two-particle averaged propagators, $G^s_{\alpha}(\rho'; \omega)$ and $G_{\alpha\beta}(\rho', \rho''; \omega)$, for which approximate algebraic and coupled integral equations, respectively, were presented in paper I and are summarized in appendix A. The functions $G^s_{\alpha}(\rho'; \omega)$ represent the propagation of an excitation which remains on a particle of species $\alpha$ located at $\rho'$ as modulated by the particle’s interaction with the medium and other particles. The function $G_{\alpha\beta}(\rho', \rho''; \omega)$ represents the propagation from a particle of species $\beta$ located at $\rho''$ to a particle of species $\alpha$ located at $\rho'$ as moderated by the medium and other particles in the system. In the bulk, $G^s_{\alpha}(\rho'; \omega)$ does not depend upon $\rho'$ and $G_{\alpha\beta}(\rho', \rho''; \omega)$ only depends upon $\rho'-\rho''$. In order to make this explicit, we shall henceforth write these functions as $G^s_{\alpha}(\omega)$ and $G_{\alpha\beta}(\rho'_{\alpha\beta}; \omega)$ where in the
latter function \( \vec{r}_{\alpha\beta} = \vec{r}_{\alpha} - \vec{r}_{\beta} \). In the bulk, these equations are easily solved in a formal sense since the two-particle propagators can be solved by Fourier transform. In appendix A, we present the expressions for the binary collision expansion in order to define some of the quantities used in the following sections.

§ III. Energy Transfer In The Bulk.

In our previous paper, we showed that the amount of transfer could be measured by a ratio of two classical quantities, the dissipation rate in the acceptors and the total radiation rate to infinity.\(^1\) Expressed in terms of the spatial Fourier transforms of the propagators given above, the steady-state acceptor dissipation rate at lowest order in explicit density dependence is

\[
\frac{<\tilde{W}_A(t)>}{V} = \frac{\rho_{\text{A}} \rho_{\text{D}}}{3(2\pi)^4} \int_{-\infty}^{\infty} d\omega \omega^2 \Gamma_A^{NR}(\omega) \Omega_D(\omega) \left[ dq \omega \Omega^2 dq \Gamma(\omega) \right] \left[ |G_{\text{AD}}(q;\omega)| \cdot |G_{\text{AD}}(q;\omega)| \right]
\]

where in the latter expression, we have eliminated the trace and carried out some of the angular integrations by taking into account the decomposition of the Fourier transform of the two-particle propagator, \( G_{\alpha\beta}(q;\omega) \), into longitudinal and transverse components, \( G_{\alpha\beta}^{\parallel\perp}(q;\omega) \), defined by the equation

\[
G_{\alpha\beta}(q;\omega) = G_{\alpha\beta}^{\parallel}(q;\omega) \hat{q} \hat{q} + G_{\alpha\beta}^{\perp}(q;\omega) (\hat{q} \cdot \hat{q})
\]

and \( \Gamma_A^{NR}(\omega) \) is an oscillator polarizability weighted sum of non-radiative decay constants for a generic acceptor molecule.\(^2\) Since we limit each molecule to a single oscillator, \( \Gamma_A^{NR}(\omega) \) reduces to \( \gamma_0^{NR} \). \( \Omega_D(\omega) \) is the excitation profile for a generic donor molecule. As its role in the theory

\(\downarrow\) In paper I,

\[
\Gamma_A^{NR}(\omega) = \sum_{\nu} \frac{\gamma_0^{NR} | \alpha_{A,\nu}(\omega) |^2}{| \alpha_{A,\nu}(\omega) |^2}
\]
is now fairly trivial, we have treated it as a constant above and shall do so below.

As in the previous paper, the total steady-state radiation rate is written using Poynting’s theorem as

\[
\langle \vec{R}_{A+D \rightarrow \omega}(t) \rangle = \int_{-\infty}^{\infty} d\omega \sum_{i,j} \langle \vec{p}_{ij}(\omega) \cdot \vec{W}_{ij}^{\text{rad}}(\omega) \cdot \vec{p}_{ij}(\omega) \rangle,
\]

where the quantities \( \vec{W}_{ij}^{\text{rad}}(\omega) \) are given by

\[
\vec{W}_{ij}^{\text{rad}}(\omega) = \int \frac{d\Omega}{4\pi} e^{ik\hat{r}_{ij} \cdot \vec{r}} \left( 1 - \hat{r} \hat{r} \right) = \frac{1}{3} \left( j_0(\hat{r}_{ij}) + (\hat{r}_{ij} \cdot \vec{r}) f_2(\hat{r}_{ij}) \right) + \left( \frac{1}{3} - 1 \right) f_2(\hat{r}_{ij}).
\]

The integration over \( \Omega \) denotes an integration over the solid angle, \( \hat{r} \equiv \hat{r}(\Omega) \), and \( k = \omega \sqrt{\epsilon}/c \). If the Förster transfer model is correct, then the dominant contributions to the radiation rates occur in the frequency region in which \( k |\vec{r}_{ij}| \ll 1 \). In this event, we may replace our previous expression by its zero \( k \) limit

\[
\vec{W}_{ij}^{\text{rad}}(\omega) = \frac{2}{3} \hat{r}_{ij}.
\]

The total radiation rate through terms second order in explicit density dependence can then be shown to be
\[
\frac{<\hat{R}_{A+D\rightarrow\omega(t)>}}{V} = \frac{c}{3\pi} \rho_{D0} \int_0^\infty d\omega \frac{|k|^4}{\varepsilon(\mu^* \varepsilon^*)^{1/2}} \Omega_D(\omega) \left\{ \left| g_D^\prime(\omega) \right|^2 + 2 \left| G_{\Delta D}(q ; \omega) \right|^2 \right\}
\]

\[
+ \frac{2\rho_A}{3} \int_0^\infty dq \left\{ \left| G_{\Delta D}(q ; \omega) \right|^2 + 2 \left| G_{\Delta D}(q ; \omega) \right|^2 \right\}
\]

\[
+ \frac{2\rho_D}{3} \int_0^\infty dq \left\{ \left| G_{\Delta D}(q ; \omega) \right|^2 + 2 \left| G_{\Delta D}(q ; \omega) \right|^2 \right\}
\]

\[
+ 2\rho_A \Re\left[ g_{AD}(\omega) g_D^\prime(\omega) \right] + 2\rho_D \Re\left[ g_{DD}(\omega) g_D^\prime(\omega) \right] + \rho_A^2 \left| g_{AD}(\omega) \right|^2
\]

\[
+ 2\rho_A \rho_D \Re\left[ g_{AD}(\omega) g_{DD}(\omega) \right] + \rho_D^2 \left| g_{DD}(\omega) \right|^2 \right\}, \quad (\text{III.6})
\]

where \( g_{\alpha\beta}(\omega) = G_{\alpha\beta}(q = 0; \omega) \equiv G_{\alpha\beta}^{\gamma}(q = 0; \omega) \), \( g_{\alpha}^\prime(\omega) \) is defined by

\[
G_{\alpha}^\prime(\omega) = \left\{ \alpha_{\alpha}^\prime(\omega) + \sum_\gamma \rho_\gamma \int d\vec{r}_\gamma T_{\alpha\gamma}^{\alpha\alpha}(\omega) \right\}^{-1} = g_{\alpha}^\prime(\omega) \quad \rightarrow \quad (\text{III.7})
\]

\( T_{\alpha\gamma}^{\alpha\alpha}(\omega) \) is the diagonal (with respect to particle labels) \( 3 \times 3 \) dimensional block of the binary collision matrix \( \overrightarrow{T}_{\alpha\gamma}(\omega) \) and the sum on \( \gamma \) is over all the component species of dyes in the system. In obtaining the last expression we noted that \( \alpha \) and \( \int d\vec{r}_\gamma T_{\alpha\gamma}^{\alpha\alpha}(\omega) \) are both proportional to \( \overrightarrow{T}_{\alpha\gamma} \). The first three terms in Eq. (III.6) above are the incoherent sum of the radiation that occurs by (1) radiation from an initially excited donor, (2) radiation from an acceptor that is excited by a donor, and (3) radiation from a donor that is excited by another donor. The remaining terms arise from interference effects.

The Fourier transform converts the set of coupled integral equations for \( G_{\alpha\beta}(q, \omega) \) into a set of coupled matrix equations. Here we present their solution when there is but one species of donor and one species of acceptor. The longitudinal and transverse components of the Fourier transformed propagator, \( G_{\alpha\beta}^{\gamma}(q, \omega) \) and \( G_{\alpha\beta}^{\gamma}(q, \omega) \), are then given by the relations
\[ G_{AD}^\nu(q;\omega) = \left[ 1 + \rho_A g_A^\nu(\omega) T_{AA}^{\nu}(q;\omega) \right. \]
\[ \left. - \rho_D g_D^\nu(\omega) T_{AD}^{\nu}(q;\omega) \right] \left[ 1 + \rho_D g_D^\nu(\omega) T_{DD}^{\nu}(q;\omega) \right]^{-1} \rho_A g_A^\nu(\omega) T_{AD}^{\nu}(q;\omega) \right]^{-1} \]
\[ \times \left[ -g_A^\nu(\omega) T_{AD}^{\nu}(q;\omega) \right] \left[ 1 + \rho_D g_D^\nu(\omega) T_{DD}^{\nu}(q;\omega) \right]^{-1} g_D^\nu(\omega) \right] \right), \quad (III.8.a) \]

and

\[ G_{DD}^\nu(q;\omega) = \left[ 1 + \rho_D g_D^\nu(\omega) T_{DD}^{\nu}(q;\omega) \right. \]
\[ \left. - \rho_A g_A^\nu(\omega) T_{AD}^{\nu}(q;\omega) \right] \left[ 1 + \rho_A g_A^\nu(\omega) T_{AA}^{\nu}(q;\omega) \right]^{-1} \rho_D g_D^\nu(\omega) T_{AD}^{\nu}(q;\omega) \right]^{-1} \]
\[ \times \left[ -g_D^\nu(\omega) T_{DD}^{\nu}(q;\omega) g_D^\nu(\omega) + \rho_A g_A^\nu(\omega) T_{DA}^{\nu}(q;\omega) \right] \]
\[ \times \left[ 1 + \rho_A g_A^\nu(\omega) T_{AA}^{\nu}(q;\omega) \right]^{-1} g_A^\nu(\omega) T_{AD}^{\nu}(q;\omega) g_D^\nu(\omega) \right] \right), \quad (III.8.b) \]

etc., where \( \nu = \downarrow | \uparrow \) denotes the transverse and longitudinal components in \( q \)-space of \( G_{\alpha\beta}^{\nu} \).

The longitudinal and transverse components of the \( q \)-space transforms of the off-diagonal (with respect to particle labels) parts of the binary collision operators, \( T_{\alpha\beta}^{\nu}(\mathbf{q};\omega) \), are given by

\[ T_{\alpha\beta}^{\nu \downarrow \uparrow}(q;\omega) = 4\pi \int_0^\infty dr r^2 \left[ T_{\alpha\beta}^{\nu \downarrow \uparrow}(r;\omega) \right. \]
\[ \left. \left( j_0(qr) - \frac{2j_1(qr)}{qr} \right) \right] + T_{\alpha\beta}^{\nu \downarrow \uparrow}(r;\omega) \left[ \frac{2j_1(qr)}{qr} \right] \right] \quad (III.9.a) \]

\[ \text{Note some authors when using the terms longitudinal and transverse use the term in only one space, e.g., \( r \)-space, so that the transform of the longitudinal or transverse part is not necessarily longitudinal or transverse in \( q \)-space. We shall use the terms longitudinal and transverse components in a different sense. We shall only use the terms with respect to variables that the function depends upon. That is, \( G_{\alpha\beta}(\mathbf{r};\omega) \) has longitudinal, \( \hat{r} \hat{r} \), and transverse, \( \hat{r} \hat{r} \), components and \( G_{\alpha\beta}(\mathbf{q};\omega) \) has longitudinal, \( \hat{q} \hat{q} \), and transverse, \( \hat{q} \hat{q} \), components.} \]
\[ T_{\alpha\beta}^{\text{ab}, \perp}(q;\omega) = 4\pi \int_0^\infty dr r^2 \left[ T_{\alpha\beta}^{\text{ab}, \perp}(r;\omega) \left( \frac{j_1(qr)}{qr} \right) + T_{\alpha\beta}^{\text{ab}, \perp}(r;\omega) \left( \frac{j_1(qr) - j_1(qr)}{qr} \right) \right], \quad (\text{III.9.b}) \]

where the longitudinal and transverse components in \( r \)-space, \( T_{\alpha\beta}^{\text{ab}, \nu}(r;\omega) \), are given by

\[ T_{\alpha\beta}^{\text{ab}, \nu}(r;\omega) = -\frac{V^\nu(r;\omega)}{1 - \alpha_\alpha(\omega)\alpha_\beta(\omega)[V^\nu(r;\omega)]^2} \quad (\text{III.10}) \]

and

\[ V^\nu(r;\omega) = \begin{cases} -\frac{2e^{ikr}}{\varepsilon r} \left[ \frac{ik}{r} - \frac{1}{r^2} \right] & \text{for } \nu = || \\
\frac{e^{ikr}}{\varepsilon r} \left[ k^2 + \frac{ik}{r} - \frac{1}{r^2} \right] & \text{for } \nu = \perp. \end{cases} \quad (\text{III.11}) \]

are solutions of Maxwell’s equations. The integrals defining the \( T_{\alpha\beta}^{\text{ab}, \nu}(q;\omega) \) for the fully radiative case above are well defined (for large \( r \)) provided that the dielectric constant (and hence \( k \)) contains an arbitrarily small imaginary part so that the medium is slightly lossy. The Fourier integrals above may then be done numerically.

It is also possible to study the quasi-static limit, in which we let \( c \rightarrow \infty \) in equations (III.11). In this limit, both components, \( V^{||}(r;\omega) \) and \( V^{\perp}(r;\omega) \), of \( \nabla \tilde{\nabla}(q;\omega) \) are proportional to \( r^{-3} \) and one would hope that the resulting theory would be consistent with the standard Förster picture. The integrals defining the self-propagator, \( G_{\alpha}^{\nu}(\omega) \), may in this case be performed analytically and is examined in §VI. The remainder can be obtained asymptotically in certain limits, or must be done numerically. The expressions for the longitudinal and transverse components of the \( r \)-space binary collision operators in the quasi-static limit are simple; i.e.,

\[ T_{\alpha\beta}^{\text{ab}, ||}(r;\omega) = -\frac{2}{\varepsilon} \frac{r^3}{r^6 - 4\alpha_\alpha(\omega)\alpha_\beta(\omega)} \quad (\text{III.12.a}) \]

and
\[ T_{\alpha\beta}^{\omega} (r; \omega) = \frac{1}{\varepsilon} \frac{r^3}{r_0^6 - \frac{\alpha_\omega(\omega)\alpha_\rho(\omega)}{\varepsilon^2}}. \]  

(III.12.b)

The asymptotic limits of the components of the corresponding Fourier-transformed binary collision operators depend on whether the product \( \alpha_\omega(\omega)\alpha_\rho(\omega)q^6 \) is large or small. In the small-\( q \), small-polarizability limit, the quasi-static, Fourier-transformed components behave as:

\[ T_{\alpha\beta}^{\omega^\parallel} (q; \omega) \sim -\frac{4\pi}{3\varepsilon} + \frac{8\pi\log(2)}{9\varepsilon} + \frac{4\pi^2}{\varepsilon 45^{1/2}} \left[ -\frac{\alpha_\omega(\omega)\alpha_\rho(\omega)}{\varepsilon^2} \right]^{1/3} [2-2^{2/3}]q^2 + \cdots \]  

(III.13.a)

and

\[ T_{\alpha\beta}^{\omega^\perp} (q; \omega) \sim -\frac{8\pi}{3\varepsilon} + \frac{8\pi\log(2)}{9\varepsilon} - \frac{4\pi^2}{\varepsilon 45^{1/2}} \left[ -\frac{\alpha_\omega(\omega)\alpha_\rho(\omega)}{\varepsilon^2} \right]^{1/3} [3-2^{2/3} - 1]q^2 + \cdots, \]  

(III.13.b)

whereas in the large-\( q \), large-polarizability limit they can be shown to behave as

\[ T_{\alpha\beta}^{\omega^\parallel} (q; \omega) \sim -\frac{144\pi\varepsilon}{\alpha_\omega(\omega)\alpha_\rho(\omega)q^6}, \]  

(III.14.a)

and

\[ T_{\alpha\beta}^{\omega^\perp} (q; \omega) \sim -\frac{144\pi\varepsilon}{\alpha_\omega(\omega)\alpha_\rho(\omega)q^6}. \]  

(III.14.b)

Therefore, the expressions appearing in Eq. (III.8) should be well behaved in the quasi-static limit.

A comparison of the integrands of Eqs. (III.1) and (III.6) that appear in the fully radiative, bulk calculation with those arising from the quasi-static approximation, as functions of \( q \) with \( \omega \) fixed, shows that to a very good approximation, the bulk results may be regarded as the incoherent sum of two terms: the quasi-static approximation which is very short-ranged (i.e.,

\* Note in Eqs. (III.13) for the small-\( q \), small-polarizability limit, the fractional power is taken as the principal value of the power, i.e. \( \beta^n = |\beta|^n e^{i\arg \beta} \), with the proviso that the argument of the fractional power \([-\beta]^n\) is taken as \([e^{-\pi \text{sign}(\arg \beta)}]^{n}\). The resulting expression is known to be valid for \( |\arg \beta| < 2\pi \).
from roughly 1 to 100 Å) and a longer-ranged part associated with the Lorentzian lineshape of
the propagators $G_{\alpha\beta}(q^2; k)$ in the vicinity of $q = k$. The latter contribution simply arises from
wave-like multiple scattering processes occurring in the system, and is about 2-3 orders of
magnitude smaller than the contribution from the quasi-static contribution. (Note that the op-
posite conclusion was obtained in droplets in the Mie resonance spectral region.)

As an example, Fig. 1 shows the integrand of the $q$ integration leading to the dissipation
rate. The figure exhibits a broad, large feature centered around $q \approx 1 \text{Å}^{-1}$ and a much smaller
feature centered about $q \approx k \approx 10^{-3} \text{Å}^{-1}$. The large feature is found to arise solely from the near-
field, $O(r^{-3})$, part of to the dipole field. The far-field, or $O(e^{ikr} r^{-1})$ contribution is responsible
for the smaller feature near $q \approx k$. In spite of the long range of the far-field interaction, its con-
tribution is small, basically because of the extinction theorem; even for a medium with arbi-
trarily small loss, the region near $k$ acquires an additional loss that may be understood as a re-
normalization of the dielectric constant of the medium, i.e. $\varepsilon \rightarrow \varepsilon + 4\pi \sum_j \rho_j \alpha_j(\omega)$. As the con-
centration is increased, the contribution of the $q \approx k$ region is damped out.

In essence for a CW experiment, one recovers in the classical sense, a picture of non-
radiative energy transfer, in which there is no explicit anomalous density dependence. Our nu-
merical results show the naively expected scaling behavior for the ratio of the rates over the
entire density range studied in paper I. In figures 2 and 3, we have plotted the integrands for
the acceptor dissipation rate and the total radiation rate as functions of frequency for four den-
sities (with fixed mole fraction) for the degenerate polarizability case studied in paper I. The
parameters characterizing the molecules are given in the figure captions. The (optical) frequen-
cy range in the figures is expressed in the same dimensionless units used in paper I by scaling
the frequency with the sphere size used in that calculation. Both figures have one trivial factor
of the donor density factored out. As expected, the remaining parts of acceptor dissipation rate
scale linearly with the (acceptor) density while the remainder of the radiation rate is indepen-
dent of the density. As in our previous work, the classical measure of the amount of transfer is the ratio of the two integrated rates above since the acceptor dissipation rate measures the amount of energy Stokes shifted by the acceptors while the total radiation rate is a measure of the total energy input into the system. Because of the trivial scaling of the spectra in Figs. 2 and 3, this ratio scales linearly with the density.

§ IV. Time Dependence Of The Energy Transfer Process.

We now turn our attention to the search for diffusive behavior in the model. In order to compare with other models, consider the case of an excitation initially located on a single donor molecule situated at the origin. The donor molecule is surrounded by a solvent containing many initially unexcited, randomly distributed, acceptor molecules which can accept the excitation as it proceeds away from the donor. We ask what happens to the excitation in terms of the probability density for the location of the excitation at times $t > 0$, $P(r, t)$, or upon spatial averages computed with it, whichever might be easier to obtain.

Our approach is based upon the behavior of the square of the displacement of the excitation from the donor as a function of time. As is well known, the square of the displacement in a three dimensional diffusion problem obeys the equation

$$<r^2>(t) = 6Dt$$

(IV.1)

where $r$ signifies the displacement, $t$ the time, and $D$ is the diffusion constant. More generally, if $<r^2>(t) \sim At^\eta$, with $\eta > 0$, then the process may be classified as being either sub-diffusive or super-diffusive, depending on whether $\eta < 1$ or $\eta > 1$, respectively. Hence if we can compute a quantity analogous to $<r^2>(t)$, we can (1) determine if it is diffusive and (2) if it is diffusive obtain the diffusion constant.

Our first step is to find a quantity which we may interpret, albeit perhaps in a loose sense, as either a probability density for the excitation or as the density of some conserved
quantity associated with the excitation, and our next step is to analyze, within the context of our classical model, the long-time behavior of the displacement and compare it with the diffusive results presented above.

Clearly, while the individual dipole moments characterize the energy transfer, they oscillate at optical frequencies, have zero mean, and random phase; hence, the local polarization density is not a suitable candidate for characterizing the energy migration. Instead, we use a suitable time-average\(^2\) of the \(p_i^2(t)\); specifically,

\[
P(\vec{r}, t) = N(\{\rho\}, t) \frac{\langle \sum_i p_i^2(t) \delta(\vec{r} - \vec{r}_i) \rangle}{\langle \sum_i p_i^2(t) \rangle}
\]  

(IV.2)

where the sum is over all the molecules in the system, the angle brackets denote the time average in addition to an average over the positions of the particles, and \(N(\{\rho\}, t)\) denotes a normalization factor which depends upon the set of all the number densities (concentrations), \(\{\rho\}\), and the time, \(t\). Note that if we take the standard approach and assume that all the molecules have the same intrinsic damping rate, then we find that our normalization procedure eliminates the intrinsic decay of the oscillators as that part of the decay will cancel between the numerator and the denominator. Of course, there we could define the probability density in terms of other slowly varying mechanical quantities, e.g., using the total energies of the individual excited oscillators, but the different definitions should be equivalent when the the virial theorem is used.

We may write for the left side of Eq. (IV.1)

\(^2\) By a suitable time-average, we mean an average over times long compared to the oscillation frequency of the molecules, but short with respect to the intrinsic decay time of the oscillators.
In the simple case we are studying, in which there is but a single donor molecule and \( N_A \) acceptor molecules, the sum in the numerator may be decomposed into two sets of terms

\[
< \sum_i \hat{p}_i^2(t) \delta(\vec{r} - \vec{r}_i) > = \langle \hat{p}_1^2(t) \delta(\vec{r} - \vec{r}_1) \rangle + N_A \langle \hat{p}_1^2(t) \delta(\vec{r} - \vec{r}_1) \rangle
\]  

(IV.4)

where we have numbered the donor particles and acceptor particles separately beginning at one, using primed numbers to distinguish the donors from the acceptors.†

Inserting our Green’s function expression for the dipole moment into the unnormalized probability density, we have

\[
< \sum_i \hat{p}_i^2(t) \delta(\vec{r} - \vec{r}_i) > = \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} e^{-(\omega_1 + \omega_2)t} \left\{ \langle \vec{Q}_1^T(\omega_1) \cdot \vec{G}_{11}(\omega_1) \cdot \vec{G}_{11}(\omega_2) \cdot \vec{Q}_1(\omega_2) \delta(\vec{r} - \vec{r}_1) \rangle \right. \\
+ \left. N_A \langle \vec{Q}_1^T(\omega_1) \cdot \vec{G}_{11}(\omega_1) \cdot \vec{G}_{11}(\omega_2) \cdot \vec{Q}_1(\omega_2) \delta(\vec{r} - \vec{r}_1) \rangle \right\}.
\]  

(IV.5)

By employing the averaged propagators, \( G_{\alpha}(\omega) \) and \( G_{\alpha\beta}(\vec{r};\omega) \), and the expansion method of the previous paper, we have through second order in explicit density dependence (i.e., not including that contained within the propagators) the following expression for the numerator of Eq. (IV.2)

---

† In this section, there is a single donor. However, in order to keep our notation consistent with that in our previous paper, we shall employ the following convention for labeling particles throughout this paper. Acceptor molecules are numbered from 1 to \( N_A \) and donor molecules are numbered from 1 ′ to \( N_D \).
\[
\left\langle \sum_{\ell} \delta_{\ell} \left( \delta(\vec{r} - \vec{r}_\ell) \right) \right\rangle - \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} e^{-(\omega_1 + \omega_2)\Omega_{D}(\omega_1, \omega_2)} \left\{ \delta(\vec{r}) \left[ Tr \left[ G_{D}^T(\omega_1) \cdot G_{D}^T(\omega_2) \right] \right. \right.
\]
\[
+ \rho_{A} \int d\vec{r} \left[ G_{AD}^T(\omega_1) \cdot G_{AD}(\omega_2) \right] \left. \right|_{\vec{r}_A = \vec{r}_D}^{\vec{r}_D = 0}
\]
\[
+ \rho_{A} \int d\vec{r} \left[ - G_{AD}(\omega_1) \cdot T_{DA}^{DD}(\omega_1) \cdot G_{D}^T(\omega_1) + G_{AA}(\omega_1) \cdot [G_{A}^{-1}(\omega_1)]^T \cdot G_{A}^{-1}(\omega_1) \right]_{\vec{r}_A = \vec{r}_D}^{\vec{r}_D = 0}
\]
\[
+ \rho_{A} \int d\vec{r} \left[ - G_{A}^{-1}(\omega_2) \cdot T_{AA}^{DA}(\omega_2) \cdot G_{AD}(\omega_2) + G_{AD}(\omega_2) \cdot T_{DD}^{DA}(\omega_2) \cdot G_{D}^T(\omega_2) \right]_{\vec{r}_A = \vec{r}_D}^{\vec{r}_D = 0}
\]
\[
+ G_{AA}(\omega_2) \cdot [G_{A}^{-1}(\omega_2)]^T \cdot G_{A}^{-1}(\omega_2) \right]_{\vec{r}_D = 0} + O(\rho_{A}^{3}) + \right. \right\} . \quad (IV.6)
\]

We note that the terms proportional to \( \delta(\vec{r}) \) contribute only to the density expansion of the denominator in Eq. (IV.3), i.e. only to the normalization, while the other terms contribute to both the numerator and the denominator. In particular, the simplest approximation for \( \left\langle r^2(t) \right\rangle \) in which we keep only the leading order terms in density from the numerator and denominator involves a ratio of contributions from the first and third terms in Eq. (IV.6) only. We denote this ratio by \( \left\langle r^2\rangle_{0}(t) \right\rangle \). We have

\[
\left\langle r^2\rangle_{0}(t) \right\rangle \approx \frac{\rho_{A} \int d\vec{r}_{A} \cdot Tr \left[ G_{AD}^T(\vec{r}_A) \cdot G_{AD}(\vec{r}_A) \right]}{Tr \left[ G_{D}^T(t) \cdot G_{D}(t) \right]} . \quad (IV.7)
\]


An analysis based upon the use of Eq. (IV.7) is examined in appendix E as a suggestion for further work. This analysis is not examined here because of the difficulties involved in obtaining a usable approximate form for \( T(q; \omega) \). Instead, in the next section we examine a naive expansion for Eq. (IV.3).

§ V. Results Of A Naive Density Expansion For The Probability Density And Displacement.

The simplest, albeit naive, approach to obtaining \( \langle r^2 \rangle(t) \) is to undo some of the resumptions performed in the previous paper in order to obtain our density-dependent propagators. We do this by expanding all the propagators appearing in Eq. (IV.6) in the acceptor density, keeping only the lowest order terms. Formally, we may write

\[
G^{(s)}_a(\omega) - G^{(s)(0)}_a(\omega) + \rho_\lambda G^{(s)(1)}_a(\omega) + \rho_\lambda^2 G^{(s)(2)}_a(\omega) + \rho_\lambda^3 G^{(s)(3)}_a(\omega) + \cdots \tag{V.1}
\]

and

\[
G^{(s)}_{ab}(\vec{r}; \omega) - G^{(s)(0)}_{ab}(\vec{r}; \omega) + \rho_\lambda G^{(s)(1)}_{ab}(\vec{r}; \omega) + \rho_\lambda^2 G^{(s)(2)}_{ab}(\vec{r}; \omega) + \cdots . \tag{V.2}
\]

By inserting these expressions into the expansions, we obtain for the numerator of Eq. (IV.3) the following expansion in which we keep only the two leading order terms in density

\[
\int d\vec{r} \int d^2r \rho_\lambda \left[ \operatorname{Tr} \left( G^{(s)(0)}_{AB}(\omega_1) \cdot G^{(s)(0)}_{AB}(\omega_2) \right) \right]_{\rho_\lambda = 0} + \rho_\lambda \int d\vec{r} \int d^2r \rho_\lambda \left[ \operatorname{Tr} \left( G^{(s)(1)}_{AB}(\omega_1) \cdot G^{(s)(0)}_{AB}(\omega_2) + G^{(s)(0)}_{AB}(\omega_1) \cdot G^{(s)(1)}_{AB}(\omega_2) \right) \right]_{\rho_\lambda = 0}
\]
\begin{equation}
\int d^2 r \sum_i \langle \hat{p}_i^2 \rangle \delta(\vec{r} - \vec{r}_i) = 33.9452889 \Omega_D \rho_A \left( \frac{\alpha_0}{\omega_\gamma} \right)^2 \left( \frac{t \alpha_0}{\epsilon \omega_\gamma} \right)^{5/3} e^{-\gamma t} \times \left[ 1 - 0.65092 \frac{\rho_A \alpha_0}{\epsilon \omega_\gamma} + O \left( \frac{1}{\omega_\gamma} \right) \right]. \tag{V.4}
\end{equation}

Similarly, for the first few terms in the expansion of the denominator, we have

\begin{equation}
\int d^2 r \sum_i \hat{p}_i^2 \delta(\vec{r} - \vec{r}_i) = - \int \frac{d \omega_1}{2\pi} \frac{d \omega_2}{2\pi} e^{-(\omega_1 + \omega_2)^t} \Omega_D(\omega_1, \omega_2) \left[ Tr \left[ G_D^{(0)T}(\omega_1) \cdot G_D^{(0)}(\omega_2) \right] 
+ \rho_A Tr \left[ G_D^{(0)T}(\omega_1) \cdot G_D^{(1)}(\omega_2) + G_D^{(1)T}(\omega_1) \cdot G_D^{(0)}(\omega_2) \right] \right]
\end{equation}
\[ + \rho_A \int d^3 \mathbf{r} A \langle \mathbf{G}_D^{(0)}(\omega_1) \cdot T_{D}^{DP}(\omega_1) \cdot \mathbf{G}_D^{(0)}(\omega_1) \rangle^T \]

\[ + \rho_A \int d^3 \mathbf{r} A \langle \mathbf{G}_D^{(0)}(\omega_2) \cdot T_{D}^{DP}(\omega_2) \cdot \mathbf{G}_D^{(0)}(\omega_2) \rangle \]

\[
\frac{1}{T} \mathbb{E} \left[ \mathbf{G}_D^{(0)}(\omega) \cdot \mathbf{G}_D^{(0)}(\omega) \right]_\lambda = O(\rho_A^2),
\]

where we have only kept the first two orders in density as in the numerator. In the degenerate polarizability case, the integrals appearing above in Eq. (V.5) may all be performed analytically. One finds that all the \(O(\rho_A)\) terms cancel. After the time average, one obtains

\[
\int d^3 \mathbf{r} \sum_i \mathbf{p}_i^2 \delta(\mathbf{r} - \mathbf{r}_i) > -\frac{3}{2} \Omega_D \left( \frac{\alpha_0}{\omega_\gamma} \right)^2 e^{-\gamma t} + O(\rho_A^2).
\]

Since the last four terms in the above expression for the denominator all cancel, and as we are in the regime \(\omega_\gamma \gg 1\), Eq. (V.4) takes the form

\[
<r^2(t)> = 22.63028 \left( \frac{\alpha_0}{\epsilon \omega_\gamma} \right)^{5/3} \rho_A t^{5/3} \left( 1 - 0.650919 \rho_A \frac{\alpha_0}{\epsilon \omega_\gamma} \right) t.
\]

where \(\epsilon\) is the dielectric constant. If the small density limit we are studying can be taken as implying that \((\rho_A t \alpha_0)/(\epsilon \omega_\gamma) \ll 1\), then in the spirit of Haan and Zwanzig, we can make a conjecture as to the resummation of the bracketed quantity which appears in Eq. (V.7). That is

\[
\left[ 1 - Bt \right] \sim \left[ 1 + \frac{2}{3} Bt \right]^{-2/3}.
\]

Combining this conjecture with our results, one finds that in the large \(t\) limit one obtains a diffusive limit in which the diffusion constant is \(39.4820 \left( \frac{\alpha_0}{\epsilon \omega_\gamma} \right)^{1/3} \rho_A^{1/3}\). This result is at odds with the results of Haan and Zwanzig\(^2\) and with the results of Gochanour, et. al.\(^3(a)\) who both predict a diffusive limit with a diffusion constant proportional to \(\rho_A^{1/3}\).
VI. Analysis Of The Approximate $G_D^r(t)$.

The analysis of the approximate $G_D^r(t)$ and to a lesser extent the analysis of the approximate $G_{AD}(r^2,t)$ is simplified in the limit in which the polarizability functions of the donors and acceptors are the same and in which the quasi-static interaction is used. In appendix E, we examine the possibility of evaluating $<r^2>_t(t)$ in the degenerate polarizability limit without having to undo the resummations used to obtain the results of the previous section. We do this by looking at the leading order approximation $<r^2>_0(t)$ to $<r^2>_t(t)$. For now, however, we focus on the behavior of the propagator $G_D^r(t)$ as it is interesting in and of itself. In this treatment, the donor density can be taken to be zero, hence we have

$$G_D^r(t) = \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega t} G_D^r(\omega) = \frac{e^\gamma}{\omega} \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{\alpha^{-1}(\omega) + \rho_{\Lambda} d\kappa T^{DD}_{AD}(\omega)}.$$  (VI.1)

The integral appearing in the denominator can be written as

$$\int d^3r_A T^{DD}_{AD}(\omega) = \frac{4\pi}{3} \int d\rho_{\Lambda} \mathbf{r}_{\Lambda}^2 \left[ T^{DD}_{AD}^{\perp}(\omega) + 2 T^{DD}_{AD}^{\parallel}(\omega) \right],$$  (VI.2)

where we have introduced a small $r$ cutoff, $\Lambda$ in order to mimic the effect of the pair correlation function, $g(r)$, which, if included in the theory presented in paper I, would have acted to cut the integration off at distances of the order of the diameter of the molecules. By using the quasi-static interaction, this may be written after transformation of the integration variable and some elementary contour integration tricks as

* The terms in the cutoff integral may be expressed in terms of the integrals $\int du [u^2-\beta^2]^{-1}$, with $\text{Re}(x)>0$ and $\text{Im}(x)=0$, which may be shown to be given by a contour integral around a path $C$ which starts just above the point $u=x$, hugs the positive real axis from above out toward infinity, follows a counter-clockwise circular arc around the origin, returns hugging the positive real axis from below back to just below the point $u=x$, and then loops back to the starting point in a clockwise circular arc around $u=x$. The integral is given by

$$\int_x^\infty du \frac{1}{u^2-\beta^2} = -\frac{1}{2\pi i} \int_C du \frac{\log(x-u)}{u^2-\beta^2} = -\frac{1}{2\pi} \left[ \log(x-\beta) - \log(x+\beta) \right]$$

where the branch cut in the logarithm occurs when the argument is both real and negative.
\[
\int d^3k T^{DD}_{\alpha\beta}(\omega) = -\frac{4\pi}{9\varepsilon} \left\{ \left[ \log(\Lambda^3 + \frac{\alpha}{\varepsilon}) - \log(\Lambda^3 - \frac{\alpha}{\varepsilon}) \right] + \left[ \log(\Lambda^3 + \frac{2\alpha}{\varepsilon}) - \log(\Lambda^3 - \frac{2\alpha}{\varepsilon}) \right] \right\}
\]

\[
= -\frac{4\pi}{9\varepsilon} f(\omega),
\]

(VI.3)

where for each bracketed pair of logarithms one must be careful to use the same branch of the logarithm.

By using a Lorentzian model for the polarizability function, and taking the interaction to be just near-field contribution, we find that \( G^0_0(t) \) may be written as

\[
G^0_0(t) = -\frac{\alpha_0}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \frac{(\omega - \omega_0^+)(\omega - \omega_0^-)}{(\omega - \omega_0^+)(\omega - \omega_0^-) + \Gamma f(\omega)},
\]

(VI.4)

where \( \Gamma = (4\pi\rho\alpha_0)/(9\varepsilon) \). The function \( f(\omega) \) defined above can be rewritten as

\[
f(\omega) = \log \left[ \frac{(\omega - \omega_{01,-,\Lambda})(\omega - \omega_{1,-,\Lambda})}{(\omega - \omega_{01,+})(\omega - \omega_{1,+})} \right] - \log \left[ \frac{(\omega - \omega_{01,+})(\omega - \omega_{1,-,\Lambda})}{(\omega - \omega_{01,-})(\omega - \omega_{1,+})} \right]
\]

\[
+ \log \left[ \frac{(\omega - \omega_{2,-,\Lambda})(\omega - \omega_{2,-,\Lambda})}{(\omega - \omega_{2,+})(\omega - \omega_{2,+})} \right] - \log \left[ \frac{(\omega - \omega_{2,+})(\omega - \omega_{2,-,\Lambda})}{(\omega - \omega_{2,-})(\omega - \omega_{2,+})} \right],
\]

(VI.5)

where we have additionally defined the parameters \( \omega_{j,\Lambda}^{\pm} \) by

\[
\omega_{j,\Lambda}^{\pm} = -\frac{i\gamma_0}{2} \pm \omega_{j,\Lambda}.
\]

(VI.6)

with \( \omega_{j,\Lambda} = \left[ \omega_j^2 + j\Delta \right]^{1/2} \) and \( \Delta = \alpha_0/(\varepsilon\Lambda^3) \).

In order to analyze (VI.4), we must fully specify the set of branch cuts which make \( f(\omega) \) single-valued. In each of the logarithms in appearing in the expression for \( f(\omega) \), we require only two branch lines connecting the pairs of branch points on either side of the imaginary axis, i.e., \( \omega_0^+ \) is connected with \( \omega_{j,\Lambda}^+ \) and \( \omega_0^- \) is connected with \( \omega_{j,\Lambda}^- \), and this choice is depicted in Fig. 4. We also note that in the \( \Lambda \rightarrow 0 \) limit, the branch lines extend along the entire line \( \text{Im}(\omega) = -i\gamma_0/2 \) and along the entire imaginary axis. (As \( \Lambda \rightarrow 0 \), the innermost parts of the
branch cuts merge at the imaginary axis and then proceed vertically to \( \pm i \infty \).

By combining \( f(\omega) \) with the remainder of the denominator, we must search for poles in addition to the singularities associated with the branches. In looking for the roots of the denominator

\[
g(\omega) \equiv (\omega - \omega_{h}^{+}) (\omega - \omega_{h}^{-}) + f(\omega) = 0,
\]

there are some obvious places in which to look. We note that when \( \text{Im}(\omega) = -i \gamma_{0}/2 \) and either \( |\text{Re}(\omega)| > \omega_{2,A} \) or \( |\text{Re}(\omega)| < \omega_{2,A} \), the logarithms are all purely real and the products of the factors outside of the logarithm are also real. Hence, we first look for roots of the form \( \omega = s - i \gamma_{0}/2 \) where \( \text{Im}(s) = 0 \). By defining \( z = s^{2} - \omega_{r}^{2} \), the equation for the poles, Eq. (VI.7) may be written as

\[
z + \Gamma \log \left( \frac{|z - \Delta|}{|z + 2\Delta|} \right) \log \left( \frac{|z - 2\Delta|}{|z + \Delta|} \right) = 0,
\]

where the only solutions of interest to us are those corresponding to points off the branch lines, i.e., \( |z| > 2\Delta \) and \( z > -\omega_{r}^{2} \). Fig. 5 shows that depending upon the value of \( \Gamma \), and hence the density, there is at least 1 and as many as 2 solutions of this form for \( z \). For sufficiently small \( \Gamma \), one finds two solutions for \( z \), and hence, four poles of the form \( \pm (\omega_{r}^{2} + z)^{1/2} - i \gamma_{0}/2 \). Moreover, it is easy to show that as \( \Gamma \to 0^{+} \), the two solutions have the form

\[
z = 2 \Delta \pm 12 \Delta e^{-2\Delta/\Gamma}
\]

(giving rise to four poles exponentially close to the ends of the branch cuts. (Note: \( \Gamma/\Delta = \eta/3 \) where \( \eta \) is the hard sphere packing fraction.) These poles are indicated in Fig. 4 using boxed points. For large \( \Gamma \), there is no longer a solution with \( z < 0 \) of this form. This is because the two solutions with \( z < 0 \) have merged at the imaginary frequency axis when \( \Gamma \) reached the critical value \( \Gamma' \) given by
\[ \Gamma^* \equiv \frac{\omega^2}{\log \frac{\omega_{1,\Lambda} \omega_{2,\Lambda}}{\omega_{0,\Lambda} \omega_{2,\Lambda}}} \] 

\[(VI.10)\]

As we shall see in a moment, when \( \Gamma \) exceeded \( \Gamma^* \) these poles did not disappear, rather they simply changed form. Asymptotic analysis of the remaining solution for \( z \) shows that as \( \Gamma \to +\infty \), \( z \) behaves as 
\[ z \sim (6\Delta\Gamma)^{1/2}. \]

We now seek complex roots of the form \( \omega = -\frac{i\gamma_0}{2} + is \) in which the parameter \( s \) is purely real. In this limit, the various parts of Eq. (VI.7) are again purely real and \( s \) is determined from

\[ y = \Gamma \log \left[ \frac{(y + \Delta)(y + 2\Delta)}{(y - \Delta)(y - 2\Delta)} \right], \]

\[(VI.11)\]

where \( y = \omega^2 + s^2 \), and we require solutions with \( y > \omega^2 \). Analysis shows that this equation yields 2 solutions for \( s \) of opposite sign (i.e. one solution for \( y \)) when \( \Gamma > \Gamma^* \). The poles in this limit are shown in Fig. 4 using points labeled by + signs. It is initially somewhat disconcerting to discover that as \( \Gamma \to \Gamma^* \) one solution has become underdamped. However, when typical molecular parameters are used it follows that the acceptor density at which this transition occurs is never reached in practice.‡

Having tried solutions for which the logarithm and the other factors in the denominator are purely real, we now look for roots in which the logarithm and other factors in Eq. (VI.7) are purely imaginary. Possible solutions are \( \omega = \pm (\omega^2 + is)^{1/2} - i\frac{\gamma_0}{2} \). In the + case, Eq. (VI.7) may be rewritten as

‡ The value of the acceptor density defined by \( \Gamma^* \) is inversely proportional to \( \alpha_g/\omega_i^2 \) which is of the order magnitude of the molecular volume of the acceptor. The constant of proportionality is roughly two, so this density is comparable to or larger than the density of the pure acceptor (no solvent).
\( is + 2i \Gamma[\pi \text{sign}(s) - \arctan(s/\Delta) - \arctan(s/(2\Delta))] = 0. \) \hspace{1cm} (VI.12)

Examining this equation graphically reveals that no solution of this type exists. Finally, numerical methods show no other roots. Since the densities of interest seem to fall into the regime \( \Gamma \ll \Gamma^* \), we shall focus exclusively on the \( \Gamma \to 0^+ \) asymptotic expansions from now on.

We now deform the integration contour so that they surround the branch cuts and poles. Let us first consider the contributions from the poles. The residues of the poles are inversely proportional to the derivative of \( g(\omega) \) evaluated at the poles. Carrying out the differentiation, one obtains

\[
g'(\omega) = 2\omega + i\gamma_0 + \Gamma \left\{ \frac{1}{\omega - \omega_{1,\Lambda}^+} + \frac{1}{\omega - \omega_{1,\Lambda}^-} - \frac{1}{\omega - \omega_{-1,\Lambda}^-} - \frac{1}{\omega - \omega_{-1,\Lambda}^+} \right. \\
+ \left. \frac{1}{\omega - \omega_{2,\Lambda}^+} + \frac{1}{\omega - \omega_{2,\Lambda}^-} - \frac{1}{\omega - \omega_{-2,\Lambda}^-} - \frac{1}{\omega - \omega_{-2,\Lambda}^+} \right\}. \hspace{1cm} (VI.13)
\]

In the physically interesting, low density limit, use of the asymptotic expansions given in Eq. (VI.9) shows that \( g'(\omega_{\text{pole}}) \sim O(\Gamma e^{2\Delta/\Gamma}) \), where \( \Gamma \to 0^+ \). Hence, the contributions of the poles are exponentially small in this regime.

By taking account of the discontinuity across the branch cuts that stem from the logarithms, and by shifting the integration variable, we rewrite the integration so that \( G_B(t) \) is again given by an integration along the real frequency axis

\[
G_B(t) = 2\alpha e^{-\kappa t/2} \left\{ \int_{\omega_{1,\Lambda}^+}^{\omega_{1,\Lambda}^-} d\omega \frac{\Gamma \sin(\omega t)}{\omega - \omega_{1,\Lambda}^+} + \int_{\omega_{1,\Lambda}^+}^{\omega_{1,\Lambda}^-} d\omega \frac{\Gamma \sin(\omega t)}{\omega - \omega_{1,\Lambda}^-} \right. \\
+ \left. \int_{\omega_{-1,\Lambda}^+}^{\omega_{-1,\Lambda}^-} d\omega \frac{2\Gamma \sin(\omega t)}{\omega - \omega_{-1,\Lambda}^+ + \Gamma H(\omega)} + \int_{\omega_{-1,\Lambda}^+}^{\omega_{-1,\Lambda}^-} d\omega \frac{\Gamma \sin(\omega t)}{\omega - \omega_{-1,\Lambda}^- + \Gamma H(\omega)} \right\}. \hspace{1cm} (VI.14)
\]
where \( H(\omega) \) is given by

\[
H(\omega) = \log \left[ \prod_{j=1}^{2} \frac{\left| \omega - \omega_{j,\Lambda} \right| \left| \omega + \omega_{j,\Lambda} \right|}{\left| \omega - \omega_{j,\Lambda} \right| \left| \omega + \omega_{j,\Lambda} \right|} \right].
\]

If the integrands appearing in Eq. (VI.14), aside from a factor of \( 2\alpha_{0} e^{-\gamma t/2} \sin(\omega t) \), is plotted as a function of \( \Gamma \), then as \( \Gamma \to 0 \) the dominant feature of the spectrum is a very narrow peak near \( \omega = \omega_{p} \). In addition, there are two broad, minor lobes in the regions from \( \omega_{-2,\Lambda} \) to \( \omega_{-1,\Lambda} \) and from \( \omega_{1,\Lambda} \) to \( \omega_{2,\Lambda} \). As \( \Gamma \) is increased, the lobes grow at the expense of the central peak which broadens and shrinks. This is illustrated in Fig. 6. The form of this spectrum is to a certain extent analogous to that which occurs for Davydov splitting in molecular crystals. The spectrum differs from that which might be observed in a molecular crystal since in solution there is always a continuous distribution of molecular positions, and hence, a broad distribution of splittings rather than a set of sharp splittings results. The trend observed in Fig. 6, that is the broadening of the central peak and the growth of the lobes, is to be expected since as the density is increased, the number of molecules that have their spectra split increases.

The details of the long-time asymptotic analysis of the three integrals in the latter equation are presented in appendix D, as they are somewhat lengthy, and we shall only quote the results here

\[
G_{D}(t) = 2\alpha_{0}^{-1} e^{-\gamma t/2} \left( \frac{\sin(\omega_{0} t)}{2\omega_{0}} e^{-\gamma t/2} \right)
\]

\[
+ \frac{1}{\Gamma t} \left[ \cos(\omega_{-2,\Lambda} t) - \cos(\omega_{-1,\Lambda} t) \right] \frac{\pi \sin(\omega_{-2,\Lambda} t) + 2\gamma_{E} \cos(\omega_{-2,\Lambda} t)}{\log(6\Delta t/\omega_{-2,\Lambda})} \right]^{2} - \frac{\pi \sin(\omega_{-2,\Lambda} t) + 2\gamma_{E} \cos(\omega_{-2,\Lambda} t)}{\log(6\Delta t/\omega_{-2,\Lambda})} \right]^{3}
\]

\[
+ \frac{3\pi \sin(\omega_{-1,\Lambda} t) + 2\gamma_{E} \cos(\omega_{-1,\Lambda} t)}{\log(3\Delta t/\omega_{-1,\Lambda})} \right]^{2} - \frac{3\pi \sin(\omega_{-1,\Lambda} t) + 2\gamma_{E} \cos(\omega_{-1,\Lambda} t)}{\log(3\Delta t/\omega_{-1,\Lambda})} \right]^{3}
\]
where $\gamma_E \approx 0.577215 \cdots$ is Euler’s constant. The first term is the contribution of the central peak in the frequency spectrum. Numerical treatment of the integrals shows that this expansion works well up to moderate densities. Note that if $(\Gamma t/\omega_0) \ll 1$, then the important contributions are from the first term, while for $(\Gamma t/\omega_0) \gg 1$, the logarithmic terms win out.

We show in appendix E that the integrals which contribute to $G_{\text{AD}}(q,t)$ exhibit similar behavior when we employ the large-$q$ asymptotic expansion for $T(q;\omega)$. That is, there is an exponentially damped sinusoidal contribution from $\omega \sim \omega_q$ and logarithmically decreasing terms. The problem in analyzing this expression is that the slow fall off of the logarithms implies that several terms of the asymptotic series must me kept, making it very difficult to decide which terms can be thrown away. One also finds that the $q$-dependence of the sinusoidal term is very weak.

§ VII. Conclusions.

We have examined our classical model in the steady-state limit and found that, as expected, there is no anomalous density behavior and the dominant contributions come from molecules located within the typical range for Förster transfer in the bulk, namely the 50–100Å region.

We have also compared a naive approximation to our theory, in which we have expanded out the density dependence of our propagators, with the standard phenomenological models in
the pulsed-excitation limit and found that if the theory has a diffusive limit, then a different scaling for the diffusion constant than that predicted by the standard models is predicted.

We have also examined the one of the propagators, the self-propagator for the donor, which appears in the denominator of our zeroth order expression for the square of the excitation’s displacement from the donor, without re-expanding the density dependence and discovered that on a time scale that depends upon the density its behavior changes over from simple, damped, oscillation to complicated oscillatory and logarithmic behavior. In appendix E, the formalism for a treatment of the problem without re-expanding the propagators is presented. There we see that if we employ some of the asymptotic expansions for the binary collision operators, then we can obtain an expression for the two-particle propagator similar to that for the self-propagator. Unfortunately, the resulting expressions are so convoluted that it is difficult to see where any sort of useful limit might be extracted.

§ VIII. Acknowledgment.

A portion of this work was supported by the National Sciences and Engineering Research Council of Canada, by Le Fonds pour la Formation de Chercheurs et l’Aide à la Recherche du Québec and by the National Science Foundation. One of us, A.C.P., also wishes to thank the Chemistry Department of McGill University for their hospitality.
Appendix A. Density Expansion Of The Propagators.

As is well known, a naive density expansion for the quantities of interest to us may be obtained by employing the binary collision expansion of the $3N \times 3N$ propagator matrix $\hat{\mathcal{G}} (\hat{\mathcal{R}}^N : \omega)^5$

$$\hat{\mathcal{G}} (\hat{\mathcal{R}}^N : \omega) = \hat{\mathcal{G}}_0 - \hat{\mathcal{G}}_0 \cdot \sum_{\alpha} \hat{T}_{\alpha} \cdot \hat{\mathcal{G}}_0 + \hat{\mathcal{G}}_0 \cdot \sum_{\alpha} \hat{T}_{\alpha} \cdot \hat{\mathcal{G}}_0 \cdot \sum_{\beta \neq \alpha} \hat{T}_{\beta} \cdot \hat{\mathcal{G}}_0 - \cdots , \quad (A.1)$$

where the binary collision matrices defined by

$$\hat{T}_{\alpha} = - \hat{\nabla}_{\alpha} + \hat{\nabla}_{\alpha} \cdot \hat{\mathcal{G}}_0 \cdot \hat{T}_{\alpha} = - \hat{\nabla}_{\alpha} + \hat{T}_{\alpha} \cdot \hat{\mathcal{G}}_0 \cdot \hat{\nabla}_{\alpha}$$

(A.2)

describe the full interaction of the pairs of particles $\alpha \equiv (i, j)$ and $\hat{\mathcal{G}}_0 = \hat{\nabla}_0^{-1}$. Within each term, a given summation is over all possible pairings of particles in the system except for the pair of particles being summed over in the summation, if any, which appears immediately to its left.

We note the following:

(i) $\hat{\mathcal{G}}_0$ is a block diagonal (in particle labels) matrix made up of the polarizability functions for all the molecules;

(ii) by construction, the only non-zero blocks of the matrices $\hat{T}_{\alpha}$ are those in which only the particles from the pair $\alpha \equiv (i, j)$ are involved (i.e., only $\hat{T}_{\alpha}^{ii}, \hat{T}_{\alpha}^{ij}, \hat{T}_{\alpha}^{ji},$ and $\hat{T}_{\alpha}^{jj}$); and

(iii) in macroscopically large systems, in the limit $r_{ij} \to \infty$, if we use the full radiative expression for the fields we have $\hat{T}_{\alpha}^{ij} \sim - \hat{\nabla}_{\alpha}^{ij} \sim O(r_{ij}^{-1})$ and $\hat{T}_{\alpha}^{ii} \sim O(r_{ij}^{-2})$ and if we use the quasi-static\(^7\) or Förster limit for the interaction we have $\hat{T}_{\alpha}^{ij} \sim O(r_{ij}^{-3})$ and $\hat{T}_{\alpha}^{ii} \sim O(r_{ij}^{-6})$.

As a consequence of (i) and (ii) many of the terms in the formal expansion above, Eq. (A.1), vanish. They were identified in the diagrammatic expansion in paper I and we shall not repeat that analysis here.

\(^{7}\) In the quasi-static limit the electric field is $V = \frac{3\epsilon \mathcal{P}}{8\pi r^3}$. 

\___\____
An approximate expression for the one particle or self-propagator may be obtained by dropping the loop contributions which are the contributions in which particles interact more than once. The resulting series for the loopless self-propagator, $G_\beta(\omega)$, is a geometric series, and is easily resummed to give

$$G_\beta(\omega) = \left[ \alpha_\beta^{-1}(\omega) + \sum_\gamma \rho_\gamma \int d^2 \gamma T^{\beta\gamma}_0(\omega) \right]^{-1}$$  \hspace{1cm} (A.3)$$

where the sum on $\gamma$ is over all the component species of dyes in the system.

The series for the loopless two-particle propagators, $G_{\alpha\beta}(\vec{r}; \omega)$ are slightly more complicated because they are interrelated. Instead of an algebraic equation, one finds that they are related by a set of coupled integral equations

$$G_{\alpha\beta}(\vec{r}; \omega) = - G_\alpha(\omega) \cdot T^{\alpha\beta}_{\alpha\beta}(\vec{r}; \omega) \cdot G_\beta(\omega)$$

$$- \sum_\gamma \rho_\gamma \int d^2 r G_\alpha^*(\omega) \cdot T^{\alpha\gamma}_{\alpha\gamma}(\vec{r} - \vec{r}'; \omega) \cdot G_{\gamma\beta}(\vec{r}'; \omega)$$  \hspace{1cm} (A.4)$$

in which $\alpha$, $\beta$ and $\gamma$ label the various component species.

The analysis of the two body propagator, $G_{\alpha\beta}(\vec{r}; \omega)$, in the bulk is simplified owing to translational invariance; in this case, the self-propagators are independent of position and the two body propagators depend only upon differences of particle positions, we can formally solve the integral equations by Fourier transform, i.e.

$$G_{\alpha\beta}(\vec{q}; \omega) = - G_\alpha^*(\omega) \cdot T^{\alpha\beta}_{\alpha\beta}(\vec{q}; \omega) \cdot G_\beta(\omega) - \sum_\gamma \rho_\gamma G_\alpha^*(\omega) \cdot T^{\alpha\gamma}_{\alpha\gamma}(\vec{q}) \cdot G_{\gamma\beta}(\vec{q}; \omega)$$  \hspace{1cm} (A.5)$$

In the special case in which we are interested, this equation simplifies to

$$G_{AD}(\vec{q}; \omega) = - G_A^*(\omega) \cdot T^{AD}_{AD}(\vec{q}; \omega) \cdot G_B(\omega) - \rho_A G_A^*(\omega) \cdot T^{AA}_{AA}(\vec{q}) \cdot G_{AD}(\vec{q}; \omega)$$  \hspace{1cm} (A.6)$$

since $\rho_D = 0$. 
After decomposing $G_{AD}(q; \omega)$ into its longitudinal, $\hat{q} q$, and transverse, $\perp \hat{q} q$, components, we have

$$G_{AD}^\sigma(q; \omega) = \frac{G^\lambda_A(\omega)T_{AD}^{\lambda\lambda}(q; \omega)G^\perp_B(\omega)}{1 + \rho_A G^\lambda_A(\omega)T_{AA}^{\lambda\lambda}(q; \omega)}$$

$$\sigma = \{ |, \perp \}.$$  \hspace{1cm} (A.7)

Note that even in the quasi-static limit, no closed form expressions for $T_{AD}^{\lambda\lambda}(q; \omega)$ or $T_{AA}^{\lambda\lambda}(q; \omega)$ in terms of simple functions exist. The small-$q$ and large-$q$ limits of these functions are relatively easy to work out and show that the inverse spatial Fourier transforms of $G_{AD}^\sigma(q; \omega)$ also exist.

§ Appendix B. Functions Appearing In The Naive Density Expansion.

The functions that are integrated over spatial coordinates in the expansions of the numerator of Eq. (IV.3), i.e., Eq. (V.3), are described in greater detail below. We shall provide general expressions that are then evaluated in the degenerate polarizability limit.

The zeroth order in density contribution to the single particle propagator is given by

$$G_D^{(0)}(t) = \int_{-\infty}^{\infty} \frac{d \omega}{2\pi} e^{-i\omega t} G_D^{(0)}(\omega) = \int_{-\infty}^{\infty} \frac{d \omega}{2\pi} e^{-i\omega t} \alpha_D(\omega)$$

$$= \frac{\alpha_0}{\omega_0} e^{-\gamma t/2} \sin(\omega_0 t).$$  \hspace{1cm} (B.1)

The first order in density contribution to the single particle propagator is found by expanding Eq. (A.3). One obtains

$$G_D^{(1)}(t) = -\int_{-\infty}^{\infty} \frac{d \omega}{2\pi} \int d^3 \rho_A G_D^{(0)}(\omega) T_{DD}^{\rho\gamma}(\omega) G_D^{(0)}(\omega) e^{-i\omega t} = -\int_{-\infty}^{\infty} \frac{d \omega}{2\pi} \int d^3 \rho_A G_D^{(0)}(\omega) T_{DD}^{\rho\gamma}(\omega) e^{-i\omega t}.$$  \hspace{1cm} (B.2)

The binary collision matrix $T$ is given by
\[ T_{AD}^{DD} = - V_{AD}^{DA} \cdot G_0^{AA} \cdot V_{AD}^{AD} \cdot \left[ 1 - G_0^{DD} \cdot V_{AD}^{DA} \cdot G_0^{AA} \cdot V_{AD}^{AD} \right]^{-1}. \]  \hspace{1cm} (B.5)

By resolving \( V \) into its longitudinal and transverse components, and expressing \( G_0^{\beta \alpha} \) in terms of the polarizabilities, one obtains for each component the following relation

\[ T_{AD}^{DD,\sigma} = - \frac{\alpha_\sigma[V^\sigma]^2}{1 - \alpha_\sigma \alpha_\sigma [V^\sigma]^2}, \]  \hspace{1cm} (B.6)

where we have adopted the following notation for the decomposition of \( V \) and \( T \) into their longitudinal and transverse components:

\[ V(\vec{r}; \omega) \equiv \sum_{\sigma = \uparrow \downarrow } V^\sigma(\omega) \vec{B}^\sigma \equiv V^{\parallel}(\omega)\vec{r} + V^{\perp}(\omega)(1 - \vec{r} \hat{r}) . \]  \hspace{1cm} (B.7)

In the expressions that follow, we shall use the Greek superscripts and subscripts as a shorthand for the functional dependence on position variables, as well as to designate both the longitudinal and transverse components; i.e., we shall use \( V^\sigma \) as a shorthand for \( V^\sigma(r_A) \) and \( \vec{B}^\sigma \) denotes \( \vec{B}^\sigma(r_A) \). Similarly, we shall use the subscript or superscript \( \nu \) when the function depends on the position variable \( r_A \), or the corresponding unit vector. The subscript or superscript \( \mu \) indicates dependence upon the position variable \( r_A \), or the corresponding unit vector.

This allows us to write the first order density correction to the self-propagator as

\[ G^{(1)}_{1}(t) = \sum_{\sigma = \uparrow \downarrow } \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int d\vec{r}_A \frac{\alpha_\sigma[V^\sigma]^2}{\alpha_\sigma^{-1} \alpha_\sigma [V^\sigma]^2} \vec{B}^\sigma e^{-i\omega t} . \]  \hspace{1cm} (B.8)

When one employs the Lorentzian model for the polarizability functions of the acceptors and the donors, the equation for the poles in the above equation is a 6th order equation in \( \omega \) which factorizes into a product of a 2nd order equation and a 4th order equation. In the degenerate polarizability case, the 4th order equation factorizes into two 2nd order equations which are easily solved. In this event, the first order correction Eq. (B.8) can be written as
\[ G_{D}^{(1)}(t) = -\sum_{\sigma = \pm} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \int d^{3}r_{A} \frac{\alpha_{0}^{3} [\Sigma] e^{-i\omega t}}{(\omega - \omega_{0}^{+})(\omega - \omega_{0}^{-})(\omega - \omega_{0}^{+})(\omega - \omega_{0}^{-})(\omega - \omega_{0}^{+})(\omega - \omega_{0}^{-})}, \tag{B.9} \]

which is easily evaluated using methods of contour integration. The factors in the denominator, \( \omega_{0}^{\pm} \) and \( \omega_{0}^{\pm} \), denote the pairs of solutions of the equations \( \alpha^{-1}(\omega) + V^{\sigma} = 0 \) and \( \alpha^{-1}(\omega) - V^{\sigma} = 0 \), respectively. The result of the integration is

\[ G_{D}^{(1)}(t) = \alpha_{0} e^{-\gamma_{d}/2} \sum_{\sigma = \pm} \frac{1}{2\pi} \int d^{3}r_{A} B^{\sigma} \]

\[ \times \left[ -\frac{\sin(\omega_{d} t)}{\omega_{d}} + \frac{\sin(t [\omega_{0}^{\pm} + \alpha_{0} V^{\sigma}]^{1/2})}{2 [\omega_{0}^{\pm} + \alpha_{0} V^{\sigma}]^{1/2}} + \frac{\sin(t [\omega_{0}^{\pm} - \alpha_{0} V^{\sigma}]^{1/2})}{2 [\omega_{0}^{\pm} - \alpha_{0} V^{\sigma}]^{1/2}} \right]. \tag{B.10} \]

For the two body propagator we have at zeroth order in density,

\[ G_{AD}^{(0)}(\omega) \equiv -G_{A}^{(0)}(\omega) \cdot T_{AD}^{AD}(\omega) \cdot G_{D}^{(0)}(\omega) = \sum_{\sigma = \pm} \frac{1}{\alpha_{0}^{3} [\Sigma] e^{-i\omega t}}. \]

In the degenerate Lorentzian polarizability case

\[ G_{AD}^{(0)}(r, t) \equiv -\frac{\alpha_{0}^{3} [\Sigma] e^{-i\omega t}}{2 \omega_{d}^{2}} \sum_{\sigma = \pm} \left[ \frac{\sin(t [\omega_{0}^{\pm} + \alpha_{0} V^{\sigma}]^{1/2})}{[\omega_{0}^{\pm} + \alpha_{0} V^{\sigma}]^{1/2}} - \frac{\sin(t [\omega_{0}^{\pm} - \alpha_{0} V^{\sigma}]^{1/2})}{[\omega_{0}^{\pm} - \alpha_{0} V^{\sigma}]^{1/2}} \right] B^{\sigma}. \tag{B.11} \]

Its first density correction is

\[ G_{AD}^{(1)}(\omega) = \int d^{3}r_{A} \left[ G_{A}^{(0)}(\omega) \cdot T_{AD}^{AD}(\omega) \cdot G_{D}^{(0)}(\omega) \cdot T_{DA}^{DD}(\omega) \cdot G_{D}^{(0)}(\omega) \right] \]

\[ + G_{A}^{(0)}(\omega) \cdot T_{AA}^{AD}(\omega) \cdot G_{A}^{(0)}(\omega) \cdot T_{AD}^{AD}(\omega) \cdot G_{D}^{(0)}(\omega) \]

\[ + G_{A}^{(0)}(\omega) \cdot T_{AA}^{AD}(\omega) \cdot G_{A}^{(0)}(\omega) \cdot T_{A}^{AD}(\omega) \cdot G_{D}^{(0)}(\omega) \]

\[ + G_{A}^{(0)}(\omega) \cdot T_{AA}^{AD}(\omega) \cdot G_{A}^{(0)}(\omega) \cdot T_{A}^{AD}(\omega) \cdot G_{D}^{(0)}(\omega) \]  \tag{B.12} \]

and by inverting the frequency transform, it follows that
\[ G^{(1)}_{AB} (\vec{r}, t) = \frac{\alpha_0}{2} e^{-\gamma t' \gamma / 2} \left\{ \sum_{\mu, \nu = \pm 1} \frac{1}{2} \int d^3 \vec{B} \cdot \vec{B} \, \nu \right\} \frac{V^\mu V^\nu}{(V^\mu + V^\nu)(V^\mu - V^\nu)} \]

\[ \times \sum_{\pm} \left[ \frac{\sin(t [\omega_0^2 \pm \alpha_0 V^\mu]) \omega_0^2}{\omega_0^2 \pm \alpha_0 V^\mu} - \frac{\sin(t [\omega_0^2 \pm \alpha_0 V^\nu]) \omega_0^2}{\omega_0^2 \pm \alpha_0 V^\nu} \right] \]

\[ + \frac{8\pi}{9e} \sum_{\sigma} \frac{1}{2} \sum_{j = 1} \vec{B}_j \cdot \vec{B}_\sigma \]

\[ \times \left[ \frac{1}{V^\sigma} \left\{ \frac{\sin(t [\omega_0^2 + \alpha_0 V^\sigma]) \omega_0^2}{\omega_0^2 + \alpha_0 V^\sigma} - \frac{\sin(t [\omega_0^2 - \alpha_0 V^\sigma]) \omega_0^2}{\omega_0^2 - \alpha_0 V^\sigma} \right\} \right] \log \left| \frac{\frac{j}{\epsilon \Lambda^3} - V^\sigma}{\frac{j}{\epsilon \Lambda^3} + V^\sigma} \right| \]

\[ - 4\alpha_0^2 V^\sigma \left\{ \frac{\omega_0^2 [\omega_0^2 - \alpha_0 V^\sigma]}{\omega_0^2 - (\omega_0^2 - \alpha_0 V^\sigma)} \right\} \int_\omega d\omega \frac{\sin(\omega \tau)}{\omega^2 - \omega^2} \right\}. \] (B.13)

where \( P \) denotes the principal value of the integral. The other quantities in Eqs. (V.3) are also straightforward to obtain. They are

\[ \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i \omega t} G^{(0)}_D (\omega) \cdot T^{DD}_{DA} (\omega) \cdot G^{(0)}_D (\omega) = - \alpha_0 e^{-\gamma t' / 2} \sum_{\sigma = \pm 1} \frac{1}{2} \vec{B}_j \cdot \vec{B}_\sigma \]

\[ \times \left[ \frac{\sin(t [\omega_0^2 + \alpha_0 V^\sigma]) \omega_0^2}{2[\omega_0^2 + \alpha_0 V^\sigma]} + \frac{\sin(t [\omega_0^2 - \alpha_0 V^\sigma]) \omega_0^2}{2[\omega_0^2 - \alpha_0 V^\sigma]} \right] \] (B.14)

\[ \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i \omega t} G^{(0)}_A (\omega) \cdot T^{AA}_{AA} (\omega) \cdot G^{(0)}_A (\omega) = \]

\[ = \frac{\alpha_0}{2} e^{-\gamma t' / 2} \sum_{\sigma, \mu = \pm 1} \frac{1}{2} \vec{B}_\mu \cdot \vec{B}_\sigma \frac{V^\mu}{(V^\mu - V^\sigma)(V^\mu + V^\sigma)} \]

\[ \times \sum_{j = -1}^1 \left[ \frac{V^\sigma \sin(t [\omega_0^2 + j \alpha_0 V^\mu]) \omega_0^2}{[\omega_0^2 + j \alpha_0 V^\mu]} - \frac{V^\mu \sin(t [\omega_0^2 + j \alpha_0 V^\sigma]) \omega_0^2}{[\omega_0^2 + j \alpha_0 V^\sigma]} \right] \]. (B.15)
\[ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} G_{A\lambda}^{(0)}(\omega) \cdot T_{DA}^{DP}(\omega) \cdot G_{D\lambda}^{*(0)}(\omega) = \frac{\alpha_0}{2} e^{-i\gamma t/2} \sum_{\sigma, \nu=1}^{j} \frac{V^\nu \hat{B}^\sigma \cdot \hat{B}^\nu}{(V^\nu - V^\sigma)(V^\nu + V^\sigma)} \]

\[ \times \sum_{j=-1}^{1} \left[ \frac{V^\nu \sin(t[\omega_0^2 + j \alpha_0 V^\nu]^{1/2})}{[\omega_0^2 + j \alpha_0 V^\nu]^{1/2}} - \frac{V^\nu \sin(t[\omega_0^2 + j \alpha_0 V^\sigma]^{1/2})}{[\omega_0^2 + j \alpha_0 V^\sigma]^{1/2}} \right], \quad (B.16) \]

and

\[ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} G_{A\lambda}^{(0)}(\omega) \cdot \left[ G_{A\lambda}^{*(0)}(\omega) \right]^{-1} \cdot G_{A\lambda}^{(0)}(\omega) = \]

\[ = \frac{\alpha_0}{2} e^{-i\gamma t/2} \sum_{\mu, \nu=1}^{j} \frac{V^\mu V^\nu \hat{B}^\mu \cdot \hat{B}^\nu}{(V^\mu - V^\nu)(V^\mu + V^\nu)} \]

\[ \times \sum_{j=-1}^{1} \left[ \sin(t[\omega_0^2 + j \alpha_0 V^\mu]^{1/2}) \right] - \frac{\sin(t[\omega_0^2 + j \alpha_0 V^\nu]^{1/2})}{[\omega_0^2 + j \alpha_0 V^\nu]^{1/2}}, \quad \text{ (B.17)} \]

§ Appendix C. Evaluation Of Terms In The Naive Density Expansion In The Degenerate Polarizability Case.

We identify the terms in Eq. (V.3) as follows

\[ \int d^3r \rho \rho^2 \sum \delta(\vec{r} - \vec{r}_1) > - \rho_A n_1 + \rho_A^2 \left( n_{2a} + n_{2b} + n_{3aa} + n_{3ab} + n_{3ac} + n_{3ba} + n_{3bc} + n_{3bb} \right) \]

\[ + n_{3bc} + n_{3ca} + n_{3cb} + n_{3cc}, \quad \text{(C.1)} \]

where we have labeled the individual terms in the expansion in the obvious fashion. The following six equations summarize the results obtained after performing a time average in order to remove the oscillations at optical frequencies.

\[ n_1 \sim (1 + 2^{2/3}) \frac{2\pi^2}{\Gamma(8/3)} \left( \frac{\alpha_0}{\omega_\gamma} \right)^2 \left( \frac{t \alpha_0}{\epsilon \omega_\gamma} \right)^{5/3} e^{-\gamma t} = 33.94542889 \left( \frac{\alpha_0}{\omega_\gamma} \right)^2 \left( \frac{t \alpha_0}{\epsilon \omega_\gamma} \right)^{5/3} e^{-\gamma t}, \quad \text{(C.2)} \]
\[ n_{2a} - n_{2b} = -\frac{8\pi^4}{9\Gamma(8/3)} \frac{(2^{2/3} + 1)(2^{5/3} - 1)}{2^{8/3}} \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}, \] \\
\[ = -50.99995889 \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}, \quad \text{(C.3)} \]

\[ n_{3aa} - n_{3bb} = \frac{\pi^4}{9} \frac{(1 + 2^{2/3})}{\Gamma(8/3)} \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t} \] \\
\[ = 18.61258737 \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}, \quad \text{(C.4)} \]

\[ n_{3ab} - n_{3ba} = \frac{(34.6296 \cdots)}{2^{11/3}} \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t} = 2.72691 \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}, \quad \text{(C.5)} \]

\[ n_{3cc} = \frac{2\pi^4}{9} \frac{(1 + 2^{2/3})}{\Gamma(8/3)} \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t} = 37.22517474 \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}, \quad \text{(C.6)} \]

and

\[ n_{3ae} - n_{3ca} - n_{3ce} - n_{3eb} = \frac{(-81.8233 \cdots)}{2^{11/3}} \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t} \] \\
\[ = -6.44318 \left\{ \frac{\alpha_0}{\omega_\gamma} \right\}^2 \left\{ \frac{t\alpha_0}{\epsilon\omega_\gamma} \right\} e^{-\gamma_\gamma t}. \quad \text{(C.7)} \]

For the terms which appear in the denominator we have

\[ \int d\mathbf{r} < \sum_i \hat{p}_i^2 \delta(\mathbf{r} - \mathbf{r}_0) > = d_1 + \rho_A(d_{2a} + d_{2b} + d_3 + d_4), \quad \text{(C.8)} \]

where we have again labeled the individual terms in the obvious fashion and only kept the first two orders in density as in the numerator.
\[ d_1 = 3 \left( \frac{\alpha_0}{\omega_f} \right)^2 e^{-\gamma_f} \sin^2(\omega_f t) - \frac{3}{2} \left( \frac{\alpha_0}{\omega_f} \right)^2 e^{-\gamma_f}, \]  
(C.9)

\[ d_{2a} \sim d_{2b} \sim -\frac{2\pi^2}{3\epsilon} \left( \frac{\alpha_0}{\omega_f} \right)^3 e^{-\gamma_f}, \]  
(C.10)

and

\[ d_3 \sim d_4 \sim -\frac{2\pi^2}{3\epsilon} \left( \frac{\alpha_0}{\omega_f} \right)^3 e^{-\gamma_f}. \]  
(C.11)

\textbf{§ Appendix D. Details Of The Asymptotic Analysis Of } \mathcal{G}_D(t)\textbf{.}

The three remaining integrals in the expression, Eq. (VI.14), for the propagator \( \mathcal{G}_D(t) \) may be studied asymptotically by considering the integral \( I_m(\alpha, \beta, \Gamma) \), defined by

\[ I_m(\alpha, \beta, \Gamma) \equiv \int_{\alpha}^{\beta} \frac{m \Gamma e^{i \omega t}}{[\omega^2 - c^2 + \Gamma h(\omega)]^2 + m^2 \pi^2 \Gamma^2}, \]  
(D.1)

for the following 3 sets of values for the parameters \( \alpha, \beta, \) and \( m \)

\[ (\alpha, \beta, m) = \begin{cases} (a, b, 1) \\ (b, d, 2) \\ (d, f, 1). \end{cases} \]  
(D.2)

The function \( h(\omega) \) is defined by

\[ h(\omega) \equiv \log \left| \frac{\omega^2 - d^2}{\omega^2 - a^2} \right| \left| \frac{\omega^2 - f^2}{\omega^2 - b^2} \right|, \]  
(D.3)

where the parameters, \( a \) through \( f \), all of which are real and positive, obey the relations

\[ a < b < c < d < f, \]

with \( a^2 \equiv c^2 - 2\Delta, \) \( b^2 \equiv c^2 - \Delta, \) \( d^2 \equiv c^2 + \Delta, \) and \( f^2 \equiv c^2 + 2\Delta. \)

Our approach to the integrals is to deform the integrals into the upper half-plane using Cauchy's theorem so as to obtain integrals that we can analyze as \( t \to \infty \) by the method of
The steepest descent paths are easily seen to be the two parameterized curves \( \alpha + iu \) and \( \beta + iu \) where \( u \geq 0 \). Employing Cauchy's theorem, we can deform the integration onto these curves and a curve at infinity. In performing this analysis, we must of course note what singularities, if any, appear in the denominators of the integrands when these expressions are continued onto the complex plane. In the three regions defined in Eq. (D.2) we may rewrite \( h(\omega) \) in a form such that \( h(\omega) \) may be analytically continued onto the entire complex plane except for branch cuts along the entire real axis outside of the interval \((\alpha, \beta)\). We write

\[
h(\omega) = \log(d - \omega) + \log(d + \omega) + \log(f - \omega) + \log(f + \omega) - \log(b - \omega) - \log(b + \omega)
\]

- \( \log(\omega - a) - \log(\omega + a) \),

(D.4.a)

\[
h(\omega) = \log(d - \omega) + \log(d + \omega) + \log(f - \omega) + \log(f + \omega) - \log(\omega - b) - \log(\omega + b)
\]

- \( \log(\omega - a) - \log(\omega + a) \),

(D.4.b)

and

\[
h(\omega) = \log(\omega - d) + \log(\omega + d) + \log(f - \omega) + \log(f + \omega) - \log(\omega - b) - \log(\omega + b)
\]

- \( \log(\omega - a) - \log(\omega + a) \),

(D.4.c)

where the branch cuts for all logarithms are along the negative real axis.

We look for the roots of the denominator

\[
[\omega^2 - c^2 + \Gamma h(\omega)]^2 + m^2\pi^2\Gamma^2 = 0
\]

(D.5)

in the complex \( \omega \) plane. The solutions of Eq. (D.5) for each of the three functions \( h(\omega) \) may be written in the form \( \omega = (c^2 + iu)^{1/2} \), where the principal value of the square root is taken and \( u > 0 \). In this case the real parts of the logarithms all cancel and \((\omega - c)(\omega + c)\) is purely imaginary. The implicit equations for \( u \) corresponding to each of the cases above are
\( u = 2\Gamma[ \arctan(u/\Delta) + \arctan(u/(2\Delta))] \), \hspace{1cm} \text{(D.6.a)}

\( u - 2\pi\Gamma = 2\Gamma[ \arctan(u/\Delta) + \arctan(u/(2\Delta))] \), \hspace{1cm} \text{(D.6.b)}

and where the equation in the third case is the same as that for the first. The first and third equations only have positive solutions for \( u \) when \( 3\Gamma > \Delta \), while the second equation has a positive solution which falls in the range \( (2\pi\Gamma, 4\pi\Gamma) \) for all values of \( \Gamma \). We note that \( \Re((e^2 + iu)^{3/2}) \geq c \) so that in two of the cases, \((\alpha, \beta) = (b, d)\) and \((\alpha, \beta) = (d, f)\), the root may move into or out of the region defined by \( \alpha < \Re(\omega) < \beta \) and \( \Im(\omega) > 0 \) as \( \Gamma \) varies. In fact, for small \( \Gamma \), the root is in \( b < \Re(\omega) < d \) and for larger \( \Gamma \) the root moves into \( d < \Re(\omega) < f \). Since the analysis of the integrals is dominated by the region near the endpoints of the integration, we shall find it convenient below to deform the integration contours so that the roots do not cross them as \( \Gamma \) is varied.

**A) The Integral \( I_1(a, b, \Gamma) \).**

Let us consider this integral when in which \((\alpha, \beta) = (a, b)\) and \( m = 1 \). Examination of the denominator of the integrand for \( I_1(a, b, \Gamma) \) shows that the poles are outside of the region bounded by the lines \((a, b), (a, a+i \infty), (a+i \infty, b+i \infty),\) and \((b+i \infty, b)\). Hence, for \( t > 0 \), we have by Cauchy’s theorem

\[
I_1(a, b, \Gamma) = \int_a^a + i \infty d\omega \frac{\Gamma e^{i\omega}}{\left[\omega^2 - c^2 + \Gamma h(\omega)\right]^2 + \Gamma^2 \pi^2}
- \int_b^b + i \infty d\omega \frac{\Gamma e^{i\omega}}{\left[\omega^2 - c^2 + \Gamma h(\omega)\right]^2 + \Gamma^2 \pi^2}.
\]

We analyze these integrals in the dual limit of large \( t \) and small \( \Gamma \). We change the integration variable in the first of these integrals to \( \omega = a + i\omega \). The behavior of the integral is for the most part dominated by the behavior of the exponential function, \( e^{-\omega t} \), appearing in the
numerator of the integrand. Since $t$ is large the dominant contribution to the integral comes from the region in which $u$ is small. This allows us to expand the factors in the denominator about $u = 0$ so that

$$
\int_{\alpha}^{\alpha + i\infty} d\omega \left\{ \ldots \right\} \sim \frac{i e^{int}}{\Gamma} \int_{0}^{\epsilon t} du \frac{e^{-int}}{\left[ \log \left( \frac{6\Delta}{a} e^{-2\Delta/T} \right) - \log(u) - i\frac{\pi}{2} + O(u) \right]^{2} + \pi^{2}}.
$$

\hspace{1cm} \text{(D.8)}

In order to understand the effect of the parameter $\Gamma$ being small, we make the change of variable $u \to u/t$ and obtain

$$
\int_{\alpha}^{\alpha + i\infty} d\omega \left\{ \ldots \right\} \sim \frac{i e^{int}}{\Gamma t} \int_{0}^{\epsilon t} du \frac{e^{-u}}{\left[ \log \left( \frac{6\Delta}{a} e^{-2\Delta/T} \right) - \log(u) - i\frac{\pi}{2} + O(u/t) \right]^{2} + \pi^{2}}.
$$

\hspace{1cm} \text{(D.9)}

Clearly, further approximations depend upon the magnitude of the dimensionless factor $(6\Delta e^{-2\Delta/T} / a)$ that appears in the denominator. Inserting the typical ranges of the values for these parameters as we employed in our previous paper, we find that $(6\Delta e^{-2\Delta/T} / a) \ll 1$. In order to carry out the analysis, we break the integral from $0$ to $\epsilon t$ into two pieces, one from $0$ to $(6\Delta e^{-2\Delta/T} / a)^{1/2}$ and the other from $(6\Delta e^{-2\Delta/T} / a)^{1/2}$ to $\epsilon t$. A bound for the contribution of the first integral is easily obtained as

$$
\left| \int_{0}^{(6\Delta e^{-2\Delta/T} / a)^{1/2}} du \left\{ \ldots \right\} \right| \leq \frac{\left[ 6\Delta t e^{-2\Delta/T} \right]^{1/2}}{\left[ \frac{6\Delta t}{a} e^{-2\Delta/T} \right]} \frac{4}{3\pi^{2}}.
$$

\hspace{1cm} \text{(D.10)}

In the second integral, the dominant contributions come from the regions where the factor $\log(6\Delta e^{-2\Delta/T} / a)$ is the largest. Hence, we obtain
\[
\int_{\frac{6\Delta t}{a} e^{-2\Delta/\Gamma}}^{e^{\frac{6\Delta t}{a} - e^{-2\Delta/\Gamma}}} du \left( \cdots \right) \sim \frac{1}{\log \left( \frac{6\Delta t}{a} e^{-2\Delta/\Gamma} \right)} \left( \frac{\frac{6\Delta t}{a} e^{-2\Delta/\Gamma}}{\frac{6\Delta t}{a} - e^{-2\Delta/\Gamma}} \right) \int_{\frac{6\Delta t}{a} e^{-2\Delta/\Gamma}}^{e^{\frac{6\Delta t}{a} - e^{-2\Delta/\Gamma}}} du e^{-u} \\
\times \left[ 1 + \frac{2\log(u) + i\pi}{\log \left( \frac{6\Delta t}{a} e^{-2\Delta/\Gamma} \right)} + \cdots \right]. \tag{D.11}
\]

We are now free to extend the lower and upper limits of the remaining integration to 0 and \( \infty \), respectively. Since the contribution of the first part of the integral is small compared to the second part, we have

\[
\int_{0}^{\frac{b}{\beta} + i\infty} du \left( \cdots \right) \sim \frac{ie^{iat t}}{\Gamma t \left( \log \left( \frac{6\Delta t}{a} e^{-2\Delta/\Gamma} \right) \right)^2} \left[ 1 + \frac{i\pi - 2\gamma_E}{\log \left( \frac{6\Delta t}{a} e^{-2\Delta/\Gamma} \right)} + \cdots \right]. \tag{D.12}
\]

where \( \gamma_E = 0.577215 \cdots \) is Euler’s constant.

A similar analysis of the second integral shows that

\[
\int_{\frac{b}{\beta}}^{\frac{b}{\beta} + i\infty} du \left( \cdots \right) \sim \frac{ie^{ibt}}{\Gamma t \left( \log \left( \frac{3\Delta t}{b} e^{-\Delta/\Gamma} \right) \right)^2} \left[ 1 - \frac{i\pi + 2\gamma_E}{\log \left( \frac{3\Delta t}{b} e^{-\Delta/\Gamma} \right)} + \cdots \right]. \tag{D.13}
\]

B) The Integral \( I_2(b, d, \Gamma) \).

We now turn our attention to the integral in which \((\alpha, \beta) = (b, d)\) and \( m = 2 \). As we saw earlier, if we deform the integration onto the contours defined by the lines \((b, b + i\infty), (b + i\infty, d + i\infty), (d + i\infty, d)\), then the region enclosed the above 3 contours and the line \((b, d)\) contains a pole only if \( \Gamma \) is sufficiently small. Since the pole is of the form \((c^2 + iu^*)^{\frac{1}{2}}\), we can choose a slightly different form for the contours so that the pole is always enclosed. This second choice of contours includes the line \((b, b + i\infty)\), the curve defined by \((d^2 + iu)^{\frac{1}{2}}\) where the parameter \( u \) ranges from 0 to \( \infty \), and a curve at infinity joining \( b + i\infty \) and \((d^2 + i\infty)^{\frac{1}{2}}\).
integral along \((b, b + i\infty)\) is a steepest descent integral and may be handled in a fashion identical to those in the previous section of this appendix. The path along \((d^2 + iu)^{1/2}\) is not a steepest descent path, but its asymptotic behavior in the large limit is again determined by its behavior near \(u > 0\) where it is tangent to the steepest descent path. Moreover, this behavior is the same as along the steepest descent path. The reason is that the integrand is analytic in the small neighborhood enclosed by the two paths near the point \(\omega = d\). Hence, we may apply the method of the previous section to the evaluation of this integral as well. We therefore obtain

\[
I_2(b, d, \Gamma) \sim -\frac{2ie^{ibt}}{\Gamma t} \left[ \log \left( \frac{3\Delta t}{b} e^{-\Delta t/\Gamma} \right) \right]^2 \left[ 1 + \frac{i\pi - 2\gamma}{\log \left( \frac{3\Delta t}{b} e^{-\Delta t/\Gamma} \right)} + \cdots \right]
\]

\[
-\frac{2ie^{idt}}{\Gamma t} \left[ \log \left( \frac{3\Delta t}{d} e^{-\Delta t/\Gamma} \right) \right]^2 \left[ 1 - \frac{i\pi + 2\gamma}{\log \left( \frac{3\Delta t}{d} e^{-\Delta t/\Gamma} \right)} + \cdots \right]
\]

\[
+ \frac{e^{ict - n\gamma t/c}}{2c}.
\]

(D.14)

The difference between the asymptotic expansions arising from the two different integration paths is a term that is sub-dominant.

C) The Integral \(I_1(d, f, \Gamma)\).

We now turn our attention to the integral in which \((\alpha, \beta) = (d, f)\) and \(m = 1\). As in the previous case, if we use the steepest descent paths, \((d, d + i\infty)\) and \((f, f + i\infty)\) then we have to be careful about poles entering and leaving the region as the \(\Gamma\) is increased from zero. Since the poles are again of the form \((e^{2} + iu^*)^{1/2}\) with \(u^*\) real and positive, we can exclude the pole from the enclosed region by using the following paths parameterized by \(u\), a positive real parameter, \((d^2 + iu)^{1/2}\) and \((f^2 + iu)^{1/2}\). As in the previous subsection, both paths are not steepest
descent paths. Also as before the asymptotic expansions are determined by the behaviors of the integrands in the neighborhood of \( u = 0 \), and these expansions are the same as those of the integrals along the steepest descent paths. Again we note that if we included the pole contribution by using the steepest descent paths, then we would find that the pole contribution is sub-dominant. Carrying out the analysis as before we obtain

\[
I_1(d, f, \Gamma) \sim -\frac{ie^{idt}}{\Gamma t} \left[ \log \left( \frac{3\Delta t}{d} e^{-\Delta^2/\Gamma} \right) \right]^2 \left[ 1 + \frac{i\pi - 2\gamma_E}{\log \left( \frac{3\Delta t}{d} e^{-\Delta^2/\Gamma} \right)} + \cdots \right]
\]

\[
-\frac{ie^{if\pi}}{\Gamma t} \left[ \log \left( \frac{6\Delta t}{f} e^{-2\Delta^2/\Gamma} \right) \right]^2 \left[ 1 - \frac{i\pi + 2\gamma_E}{\log \left( \frac{6\Delta t}{f} e^{-2\Delta^2/\Gamma} \right)} + \cdots \right]. \quad (D.15)
\]

**D) Expression For \( G_b(t) \).**

Collecting the results of the previous 3 sections we take the imaginary part of the sum of the 3 parts of the integral to obtain
\[ \text{Im}(I_1(a, b, \Gamma)) + \text{Im}(I_2(b, d, \Gamma)) + \text{Im}(I_3(d, f, \Gamma)) \sim \frac{\sin(ct)}{2c} \left( -\frac{\pi}{\Gamma} \right) e^{\frac{\pi}{\Gamma}} \]

\[ + \frac{1}{\Gamma t} \left\{ \frac{\cos(at)}{\left( \log \left( \frac{6\Delta t}{a} e^{-2\Delta / \Gamma} \right) \right)^2} - \frac{\pi \sin(at) + 2\gamma_E \cos(at)}{\left( \log \left( \frac{6\Delta t}{a} e^{-2\Delta / \Gamma} \right) \right)^3} \right\} \]

\[ + \frac{\cos(bt)}{\left( \log \left( \frac{3\Delta t}{b} e^{-\Delta / \Gamma} \right) \right)^2} - \frac{3\pi \sin(bt) + 2\gamma_E \cos(bt)}{\left( \log \left( \frac{3\Delta t}{b} e^{-\Delta / \Gamma} \right) \right)^3} \]

\[ - \frac{\cos(dt)}{\left( \log \left( \frac{3\Delta t}{d} e^{-\Delta / \Gamma} \right) \right)^2} + \frac{-3\pi \sin(dt) + 2\gamma_E \cos(dt)}{\left( \log \left( \frac{3\Delta t}{d} e^{-\Delta / \Gamma} \right) \right)^3} \]

\[ - \frac{\cos(ft)}{\left( \log \left( \frac{6\Delta t}{f} e^{-2\Delta / \Gamma} \right) \right)^2} + \frac{-\pi \sin(ft) + 2\gamma_E \cos(ft)}{\left( \log \left( \frac{6\Delta t}{f} e^{-2\Delta / \Gamma} \right) \right)^3} \]. (D.16)
§ Appendix E. Suggestions For Future Work.

We can also consider the density expansion of Eq. (IV.2) directly by Fourier transforming it in space. We write the numerator of Eq. (IV.2) and its Fourier transform as

\[ F(\vec{r}, t) \equiv \langle \sum_i \tilde{\rho}_i^2(t) \delta(\vec{r} - \vec{r}_i) \rangle \quad \text{(E.1)} \]

and

\[ F(\vec{k}, t) \equiv \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} F(\vec{r}, t) = \langle \sum_i \tilde{\rho}_i^2(t) e^{-i\vec{k}\cdot\vec{r}_i} \rangle, \quad \text{(E.2)} \]

respectively.

If we expand out the explicit density dependence, i.e. that not contained in the propagators, we have for the formal asymptotic expansion of the numerator

\[ F(\vec{k}, t) \sim F_0(\vec{k}, t) + \rho_A F_1(\vec{k}, t) + \cdots. \quad \text{(E.3)} \]

By carrying out this expansion, and taking advantage of the fact that Eq. (IV.6) shows that

\[ F_0(\vec{k}, t) = F_0(\vec{k} = 0, t) = \langle Tr[\mathbf{G}_D^T(t) \cdot \mathbf{G}_D(t)] \rangle, \quad \text{(E.4)} \]

we have

\[ P(\vec{k}, t) - 1 + \rho_A \frac{F_1(\vec{k}, t) - F_1(\vec{k} = 0, t)}{F_0(\vec{k} = 0, t)} + \cdots. \quad \text{(E.5)} \]

From Eq. (IV.6), we find that the numerator of the second term is

\[ F_1(\vec{k}, t) - F_1(\vec{k} = 0, t) = \langle d\vec{r} (e^{-i\vec{k}\cdot\vec{r}} - 1) Tr \left[ \mathbf{G}_{AD}^T(\vec{r}, t) \cdot \mathbf{G}_{AD}(\vec{r}, t) \right] \rangle > \quad \text{(E.6)} \]

\[ = \left\langle \frac{d\vec{q}}{(2\pi)^3} Tr \left[ \mathbf{G}_{AD}^T(\vec{k} - \vec{q}, t) \cdot \mathbf{G}_{AD}(\vec{q}, t) - \mathbf{G}_{AD}^T(-\vec{q}, t) \cdot \mathbf{G}_{AD}(\vec{q}, t) \right] \right\rangle, \quad \text{(E.7)} \]

where many terms from Eq. (IV.6) have canceled out between numerator and denominator.
Note that we have left the angle brackets to denote the fact that we still have to do the time average in order to handle the optical frequency behavior. If we Taylor expand everything about $\vec{k} = 0$ it follows that

$$\rho_A \frac{F_1(\vec{k}, t) - F_1(\vec{k} = 0, t)}{F_0(\vec{k} = 0, t)} = \frac{k^2}{6} \rho_A \langle d\vec{p}^2 Tr \left[ G^T_{AD}(\vec{p}, t) \cdot G_{AD}(\vec{p}, t) \right] > . \tag{E.8}$$

The last ratio in the above equation is the lowest order in density approximation to $\langle r^2 \rangle(t)$ appearing in Eq. (IV.3). Eq. (E.5) can be exponentiated to obtain

$$P(\vec{k}, t) \sim e^{-\frac{k^2 \langle r^2 \rangle(t)}{6}}. \tag{E.9}$$

The equation above is to be expected from a cumulant expansion. If $\langle r^2 \rangle(t) = 6Dt$ we obtain the standard expression $P(\vec{k}, t) = e^{-Dk^2 t}$ so that $D$ is extracted from $\langle r^2 \rangle(t)$ if it is $O(t)$ at long times. Eq. (IV.6) provides us with another means of obtaining the probability density, since we only need the second derivative of $F_1(\vec{k}, t) - F_1(\vec{k} = 0, t)$, and it is not necessary to transform back into $r$-space. In the degenerate polarizability limit, we have

$$\left. \frac{\partial^2}{\partial \vec{k}^2} \left[ F_1(\vec{k}, t) - F_1(\vec{k} = 0, t) \right] \right|_{\vec{k} = 0} =$$

$$= \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{q}}{(2\pi)^3} e^{-i(\omega_1 + \omega_2)t} \langle Tr \left[ G^T_{AD}(-\vec{q}, \omega_1) \frac{\partial^2}{\partial \vec{q}^2} G_{AD}(\vec{q}, \omega_2) \right] > . \tag{E.10}$$
Eq. (E.11) can be rewritten as

\[
e^{-\frac{1}{2\pi^2} \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} e^{-i(\omega_1+\omega_2)t} \int_0^\infty dq}\]

\[
\left< \frac{q^2 \partial T^{\parallel}(q;\omega_1)}{\partial q} \frac{\partial T^{\parallel}(q;\omega_2)}{\partial q} \right>_{[G^s(\omega_1)]^{-1} + \rho_A T^{\parallel}(q;\omega_1)} \left[ [G^s(\omega_2)]^{-1} + \rho_A T^{\parallel}(q;\omega_2) \right]^2
\]

\[
\left< \frac{2q^2 \partial T^{\perp}(q;\omega_1)}{\partial q} \frac{\partial T^{\perp}(q;\omega_2)}{\partial q} \right>_{[G^s(\omega_1)]^{-1} + \rho_A T^{\perp}(q;\omega_1)} \left[ [G^s(\omega_2)]^{-1} + \rho_A T^{\perp}(q;\omega_2) \right]^2
\]

+ 4 \left[ \frac{T^{\perp}(q;\omega_1) - T^{\parallel}(q;\omega_1)}{[G^s(\omega_1)]^{-1} + \rho_A T^{\parallel}(q;\omega_1)} \left[ [G^s(\omega_2)]^{-1} + \rho_A T^{\perp}(q;\omega_2) \right] \right]

\times \left[ \frac{T^{\perp}(q;\omega_2) - T^{\parallel}(q;\omega_2)}{[G^s(\omega_2)]^{-1} + \rho_A T^{\perp}(q;\omega_2)} \left[ [G^s(\omega_2)]^{-1} + \rho_A T^{\perp}(q;\omega_2) \right] \right]
\]

where we have taken \( \rho_D \) to be zero and dropped the particle labels from the \( T(q;\omega) \) since all the \( T_{a_0}^{a_0}(q;\omega) \) are the same in this case. Note that the expression above still requires a time average to remove the oscillations at optical frequencies.

Defining \( \chi^0(q,t) \) by

\[
\chi^0(q,t) = \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[G^s(\omega)]^{-1} + \rho_A T^0(q;\omega)}.
\]

(E.12)

Eq. (E.11) can be rewritten as

\[
\frac{\partial^2}{\partial k^2} \left[ F_1(k,t) - F_1(k=0,t) \right]_{\vec{k}=0} =
\]

\[
= \frac{1}{2\pi^2} \rho_A^2 \int_0^\infty dq \left< \frac{q^2 \partial T^{\parallel}(q;\omega)}{\partial q} \right]^2 + 2q^2 \left< \frac{\partial T^{\perp}(q;\omega)}{\partial q} \right]^2 + 4\left( \chi^0(q,t) - \chi^0(q,t) \right)^2 >.
\]

(E.13)
Hence, all that remains is to develop an approximation to $\chi^0(q,t)$.

One approximation we might be interested in trying is to use the high-$q$, large-polarizability limit of $T(q:ω)$ presented in Eq. (III.14). Of course, we must then impose a small-$q$ cutoff. Since each component of $T(q:ω)$ then takes the form $\xi\alpha^{-2}q^{-6}$, in order to compute Eq. (E.11), it is easy to show that we only require differences and derivatives with respect to $q^{-6}$ of the integral

$$\chi(\xi, q, t) = \int_{-\infty}^{\infty} dω \frac{1}{2\pi} e^{-iωt} \frac{1}{[G^+(ω)]^{-1} + ρ_A α^{-2}q^{-6}}$$

$$= \int_{-\infty}^{\infty} dω \frac{1}{2\pi} e^{-iωt} \frac{1}{α^{-1} - \frac{4π}{9ε} ρ_A f(ω) + ρ_A α^{-2}q^{-6}}.$$

(E.14)

In fact, from Eq. (III.14), we can write for the high-$q$ limit, $T^{||} = \xi\alpha^{-2}q^{-6}$ and $T^{\perp} = -\xi\alpha^{-2}q^{-6}$. So that Eqs. (E.11) and (E.13) can be written as

$$\frac{\partial^2}{\partial k^2} \left[ F_{j}(\vec{k}, t) - F_{j}(\vec{k} = 0, t) \right] \bigg|_{\vec{k} = 0} =$$

$$= -\frac{1}{2π^2} \rho_A \int_{q_0}^{\infty} dq \left< [q \frac{∂^{2}\chi(\xi, q, t)}{∂q^2}]^2 + 2[q \frac{∂^{2}\chi(\xi, q, t)}{∂q^2}]^2 \right>$$

where the cutoff $q_0$ has been introduced to keep the approximation of $T(q:ω)$ valid. Note that the angle brackets remain to remind us that we need to time average, or equivalently beat together the appropriate terms, discarding the high frequency terms.

An *ad hoc* approximation would be to simply discard the logarithmic contributions in the denominator above. However, this approach has severe problems. It is easily seen that if $f(ω)$ is set to zero, then $\chi(ξ, q, t)$ takes the form
\[
\chi(\xi, q, t) = \int_{-\infty}^{\infty} \frac{d \omega}{2\pi} e^{-i \omega t} \left[ \frac{1}{\alpha^{-1}} - \frac{1}{\alpha^{-1} + \frac{q^6}{\rho_{\Lambda} \xi}} \right].
\] (E.16)

The first term is independent of \( q \) and the second has poles at

\[
\pm \sqrt{\omega_0^2 + \frac{\alpha_0 q^6}{\rho_{\Lambda} \xi}} - \frac{i \gamma_0}{2}.
\]

and hence, behaves singularly as \( \rho_{\Lambda} \to 0 \). The reason for this singular behavior is that these poles correspond to combinations of \( \omega \) and \( q \) which violate the conditions under which our approximation of \( T(q; \omega) \) by \( \xi \alpha^{-2} q^{-6} \) is valid. Clearly, this pole is an artifact of our approximation and should be disregarded, but then the remaining part of \( \chi(\xi, q, t) \) has no \( q \)-dependence. Hence, it is not permissible to simply disregard the contribution of the logarithms.

As \( \Gamma \to 0^+ \), the correct asymptotic analysis of Eq. (E.14) parallels that of \( G_6(t) \). Eq. (VI.7) for the denominator is replaced by

\[
g(\omega) \equiv (\omega - \omega_0^2)(\omega - \omega_0^6) + \Gamma f(\omega) - \zeta \Gamma(\omega - \omega_0^2)^2(\omega - \omega_0^6)^2 = 0
\] (E.17)

where \( \zeta = 9\xi/\left(4\pi \alpha_0^2\right) \).

The set of roots that gave us all the problems above, i.e.,

\[
\pm \sqrt{\omega_0^2 + \frac{\alpha_0 q^6}{\rho_{\Lambda} \xi}} - \frac{i \gamma_0}{2},
\]

are still asymptotic solutions of \( g(\omega) \) above. However, the approximation of \( T(q; \omega) \) by \( \xi \alpha^{-2} q^{-6} \) is not valid in this limit, so one can argue that we should ignore the contribution of the residues of these poles entirely.

If we now follow the procedure leading to Eq. (VI.9), and look for solutions of the form \( \pm (\omega_0^2 + \epsilon)^{1/2} - i \gamma_0/2 \), we find that Eq. (VI.9) is replaced by
which again gives rise to four poles exponentially close to the ends of the branch cuts of $f(\omega)$. As before, there are no solutions of the form $\omega = \pm (\omega_0^2 + i\gamma)^{1/2} - i\gamma/2$.

The contributions of the poles are determined by the reciprocal of

$$g'(\omega) = (2\omega + i\gamma_0)[1 - 2\zeta q^{-6}\Gamma(\omega - \omega_0^+)(\omega - \omega_0^-)]$$

$$+ \Gamma \left\{ \frac{1}{\omega - \omega_{1,\Lambda}^+} + \frac{1}{\omega - \omega_{1,\Lambda}^-} - \frac{1}{\omega - \omega_{-1,\Lambda}^+} - \frac{1}{\omega - \omega_{-1,\Lambda}^-} \right\}$$

evaluated at the poles. Again, as the poles are exponentially close to the endpoints of the branch cuts, the contributions of the poles are exponentially small in the $\Gamma \to 0^+$ limit. Hence, we obtain an expression very similar to our previous expression for $G_D^+(t)$

$$\chi(\xi, q, t) = 2\alpha e^{-\xi^2/2} \left\{ \int_{\omega_{1,\Lambda}}^{\omega_{-1,\Lambda}} d\omega \frac{\Gamma \sin(\omega t)}{\left[ \omega^2 - \omega_0^2 + \Gamma H(\omega) - \zeta q^{-6}\Gamma(\omega^2 - \omega_0^2) \right]^2 + \pi^2 \Gamma^2} \right\}$$

$$+ \int_{\omega_{1,\Lambda}}^{\omega_{-1,\Lambda}} d\omega \frac{2\Gamma \sin(\omega t)}{\left[ \omega^2 - \omega_0^2 + \Gamma H(\omega) - \zeta q^{-6}\Gamma(\omega^2 - \omega_0^2) \right]^2 + 2^2 \pi^2 \Gamma^2}$$

$$+ \int_{\omega_{1,\Lambda}}^{\omega_{-1,\Lambda}} d\omega \frac{\Gamma \sin(\omega t)}{\left[ \omega^2 - \omega_0^2 + \Gamma H(\omega) - \zeta q^{-6}\Gamma(\omega^2 - \omega_0^2) \right]^2 + \pi^2 \Gamma^2} \right\}.$$  (E.20)

The analysis of the above integrals for long times parallels that for the self-propagator. The logarithmic terms are simply obtained from those for the self-propagator in (VI.16) by making the following substitutions:
\[
\frac{6\Delta t}{\omega_{-2,\Lambda}} e^{-2\Delta / \Gamma} \rightarrow \frac{6\Delta t}{\omega_{-2,\Lambda}} e^{-2\Delta / \Gamma - 4\zeta q^{-6}\Delta^2}, \quad (E.21)
\]

\[
\frac{3\Delta t}{\omega_{-1,\Lambda}} e^{-\Delta / \Gamma} \rightarrow \frac{3\Delta t}{\omega_{-1,\Lambda}} e^{-\Delta / \Gamma - \zeta q^{-6}\Delta^2}, \quad (E.22)
\]

\[
\frac{3\Delta t}{\omega_{1,\Lambda}} e^{-\Delta / \Gamma} \rightarrow \frac{3\Delta t}{\omega_{1,\Lambda}} e^{-\Delta / \Gamma + \zeta q^{-6}\Delta^2}, \quad (E.23)
\]

and

\[
\frac{6\Delta t}{\omega_{2,\Lambda}} e^{-2\Delta / \Gamma} \rightarrow \frac{6\Delta t}{\omega_{2,\Lambda}} e^{-2\Delta / \Gamma + 4\zeta q^{-6}\Delta^2}. \quad (E.24)
\]

The sinusoidal term from Eq. (VI.16) is replaced by

\[
\text{Im} \left\{ \frac{e^{i\omega_p}}{2\omega_p (1 - 3\Gamma / \Delta - 4\pi i \zeta q^{-6}\Gamma^2)} \right\}, \quad (E.25)
\]

where

\[
\omega_p \sim \omega_q + \frac{i \pi \Gamma}{\omega_q} + \frac{\Gamma^2}{2\omega_q} \left\{ \frac{6\pi i}{\Delta} + \frac{\pi^2}{\omega_q^2} \right\} + \frac{\Gamma^3}{2\omega_q} \left\{ -4\zeta q^{-6}\pi^2 + \frac{18\pi i}{\Delta^2} + \frac{6\pi^2}{\Delta \omega_q^2} - \frac{i \pi^3}{\omega_q^4} \right\} + \cdots. \quad (E.26)
\]

Note that \(\omega_p\) depends very weakly upon \(\zeta q^{-6}\), and thence, very weakly upon \(q\). Inserting the above we have
\[
\chi(\xi, q, t) \sim 2 \omega_0 e^{-\gamma d/2} \left| \text{Im} \left[ \frac{e^{i \omega q}}{2 \omega_p (1 - 3 \Gamma / \Delta - 4 \pi i \xi q^{-6} \Delta^2)} \right] \right|
\]

\[
+ \frac{1}{\Gamma} \left[ \frac{\cos(\omega_{2, \Lambda} t)}{\log \left( \frac{6 \Delta t}{\omega_{2, \Lambda}} e^{-2 \xi \Gamma - 4 \xi q^{-6} \Delta^2} \right)} \right]^2 - \frac{\pi \sin(\omega_{2, \Lambda} t) + 2 \gamma \cos(\omega_{2, \Lambda} t)}{\log \left( \frac{6 \Delta t}{\omega_{2, \Lambda}} e^{-2 \xi \Gamma - 4 \xi q^{-6} \Delta^2} \right)} \right]^{3/2}
\]

\[
\frac{\cos(\omega_{1, \Lambda} t)}{\log \left( \frac{3 \Delta t}{\omega_{1, \Lambda}} e^{-\xi \Gamma - \xi q^{-6} \Delta^2} \right)} + \frac{3 \pi \sin(\omega_{1, \Lambda} t) + 2 \gamma \cos(\omega_{1, \Lambda} t)}{\log \left( \frac{3 \Delta t}{\omega_{1, \Lambda}} e^{-\xi \Gamma - \xi q^{-6} \Delta^2} \right)} \right] \right]^{3/2}
\]

\[
- \frac{\cos(\omega_{2, \Lambda} t)}{\log \left( \frac{6 \Delta t}{\omega_{2, \Lambda}} e^{-2 \xi \Gamma + 4 \xi q^{-6} \Delta^2} \right)} + \frac{-\pi \sin(\omega_{2, \Lambda} t) + 2 \gamma \cos(\omega_{2, \Lambda} t)}{\log \left( \frac{6 \Delta t}{\omega_{2, \Lambda}} e^{-2 \xi \Gamma + 4 \xi q^{-6} \Delta^2} \right)} \right] \right]^{3/2}
\]

(E.27)

If we employ only the first term of the expression above, the analysis of the terms in Eq. (E.15) is comparatively simple. The integrand in the last term of Eq. (E.15) becomes

\[
\langle [\chi(\xi, q, t) - \chi(-\xi, q, t)]^2 \rangle \sim - \left[ \frac{\alpha_0}{\omega_f} \right]^2 \left[ \frac{e^{-\gamma d/(2 \pi \Gamma / q)} \sin^2 \left( 2 \xi \pi \Gamma^3 t / (q \Delta \omega_f) \right)}{1 - 3 \Gamma / \Delta} \right]^2
\]

(E.28)

so that depending upon the magnitude of \( \Phi = 2 \xi \pi \Gamma^3 t / (q \Delta \omega_f) \) this term’s contribution to \( \langle r^2 \rangle \) via Eq. (E.15) will scale as \( \rho^{5/2} \) (small \( \Phi \)) or as \( \rho^{-1/2} t^{1/6} \) (large \( \Phi \)). Employing typical values for the molecular parameters, cutoff, and the time scale of interest, one typically finds that for most values of density the former, or small-\( \Phi \), limit obtains. If there is an intermediate range where this term is \( O(t) \), then the expected scaling of \( \langle r^2 \rangle \) is \( \rho^2 t \). The terms involving \( q \partial \chi(\xi, q, t) / \partial q \) provide simple powers of \( \rho \) and \( t \) since the oscillatory factors beat to zero and as a consequence the density and time dependence arises from whatever factors of \( \rho \) and \( t \) are brought out by the differentiation rather than any scaling of integrals.
One can also consider these expressions in the small-\(q\) limit. The question of a diffusive limit can be answered by examining the frequency shifts induced by the density dependent terms in \([G^r(\omega)]^{-1} + \rho T^\sigma(q; \omega)\). (Recall that our time-averaging procedure will eliminate the high frequency oscillations and extract the envelope arising from the small frequency shifts.) Writing the small-\(q\) limit of \(T^\sigma(q; \omega)\) as \(A^\sigma + B^\sigma(-\alpha^2(\omega))^{1/3}q^2\), where \(A^\sigma\) and \(B^\sigma\) are defined by Eq. (III.13), we must solve the dispersion relation

\[
[G^r(\omega)]^{-1} + \rho T^\sigma(q; \omega) \equiv \alpha^{-1}(\omega) - \frac{4\pi}{9e} \rho f(\omega) + \rho A^\sigma + \rho B^\sigma(-\alpha^2(\omega))^{1/3}q^2 = 0.
\]

In solving for \(\alpha^{-1}(\omega)\) perturbatively, one must balance the first term against the last term. Therefore, one finds 5 solutions of the form

\[
\alpha^{-1}(\omega) - (B^\sigma \rho q^3)^{3/5} e^{2k\pi i/5}
\]

for \(k = -2, \cdots, 2\). Hence, for the Lorentzian polarizability function that we have employed throughout the paper, we obtain 10 poles which differ from the original 2 poles by complex frequency shifts that scale as \(\rho^{3/5} q^{6/5}\). Hence, if there is true diffusion in the model, it must come from higher order corrections not yet considered.
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Fig. 1. Plot of the function $q^2 \{ |G_{AB}|^2 + 2 |G_{AD}|^2 \}$ which appears in the integrand of the acceptor dissipation rate in the bulk case for $k = \omega/e/\epsilon = 2.08931 \times 10^{-3} \text{Å}^{-1}$. The solid line is the result of a calculation using the full dipole field while the dashed line is the result of a calculation using only the dipole near-field interaction. The acceptor and donor polarizabilities are degenerate with Lorentzian parameters $\alpha_\omega/\omega_0^2 = 6.0 \text{Å}^3$, $\lambda_\omega = 3730 \text{Å}$, and $\gamma_\omega/\omega_0 = 0.1$. The acceptor and donor densities were both $30 \mu M$, and the dielectric constant of the medium was $\epsilon = 2.1609$. 
\[ q^2 \{ |G_{AD}(q)|^2 + 2 |G_{AD}^\perp(q)|^2 \} (\text{Å}^{10}) \]

\[ q (\text{Å}^{-1}) \]

Fig. 1.
Fig. 2. Plot of the integrand for the acceptor dissipation rate. The figure contains plots for 4 densities, logarithmically spaced from 30μM to 3.0×10^4μM, of the integrand of the acceptor dissipation rate (except for a trivial factor of the donor density which has been divided out) appearing in Eq. (III.1). As in paper I, we denote the integrand with a factor of donor density divided out by $D_A(\omega)$. The factor of $\Omega_D(\omega)$ has been set to unity. The densities increase by a factor of ten with each line proceeding from the bottom of the figure to the top. The acceptors and donors have degenerate polarizability functions. The parameters characterizing the polarizabilities were $\alpha_0/\omega_0 = 6.0\text{Å}^3$, $\lambda_0 = (2\pi c)/\omega_0 = 3730\text{Å}$, and $\gamma_0/\omega_0 = 0.1$. 
Chapter 2.

Fig. 2.
Fig. 3. Plot of the integrand for the total radiation rate. The figure contains plots, for the same 4 densities as appear in figure 2, of the integrand of the total radiation rate appearing in Eq. (III.6). One factor of the donor density has been divided out and the $\Omega_0(\omega)$ factor has been set to unity. As in paper I, the integrand of Eq. (III.6) with one factor of donor density factored out is denoted by $R_{\text{rad}}(\omega)$. Note that this function is virtually independent of density.
Fig. 3.
Fig. 4. Singularities of $G_B(\omega)$ in the quasi-static limit. The branch cuts and integration contours needed for the inversion of the Fourier transform are indicated along with the locations of the poles for $\Gamma < \Gamma^*$ (□ points) and $\Gamma > \Gamma^*$ (+ points).
Singularities of $G^s_D(\omega)$

Fig. 4.
Fig. 5. Graphical solution of the dispersion relation for $G_R(t)$. The solution of Eq. (VI.8) is presented graphically for $\Gamma = 0.5$. The figure indicates 2 solutions. Solutions with $\epsilon < -\omega_0^2$ which occur when $\Gamma \geq \Gamma^*$ are not allowed.
Fig. 5.

\[ y_1(z) = -\frac{z}{\Gamma}, \text{ for } \Gamma = 0.5 \]

\[ y_2(z) = \log\left(\frac{|z-\Delta||z-2\Delta|}{|z+\Delta||z+2\Delta|}\right) \]
Fig. 6. The spectral weight multiplying $2\alpha_0 e^{-\gamma t^2/2} \sin(\omega t)$,

$$
\tilde{G}_D^s(\omega) = \left[ \frac{\Gamma\Theta(\omega - \omega_{-2,\Lambda})\Theta(\omega_{-1,\Lambda} - \omega)}{[\omega^2 - \omega_\gamma^2 + \Gamma H(\omega)]^2 + \pi^2 \Gamma^2} \right.
$$

$$
\left. + \frac{2\Gamma\Theta(\omega - \omega_{-1,\Lambda})\Theta(\omega_{1,\Lambda} - \omega)}{[\omega^2 - \omega_\gamma^2 + \Gamma H(\omega)]^2 + 2\pi^2 \Gamma^2} + \frac{\Gamma\Theta(\omega - \omega_{1,\Lambda})\Theta(\omega_{2,\Lambda} - \omega)}{[\omega^2 - \omega_\gamma^2 + \Gamma H(\omega)]^2 + \pi^2 \Gamma^2} \right],
$$

in Eq. (VI.14) for the propagator $G_D(t)$ is plotted for 10 $\Gamma$’s logarithmically spaced from $\Gamma = 10^{-4}$ to $\Gamma = 1$. In the figure, $\Delta/\omega_\gamma^2 = 0.1$. The frequency range extends from $\sqrt{\omega_\gamma^2 - 2\Delta}$ to $\sqrt{\omega_\gamma^2 + 2\Delta}$. The sharpest central peaks correspond to the lowest densities.
Fig. 6.
Fluorescence quenching in molecules near rough metal surfaces.

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(Received: March 25, 1985)
(accepted: August 7, 1985)

ABSTRACT

A classical electrodynamic near field calculation for the interaction of a Drude oscillator molecular dipole with a rough metal surface is presented. Effects of electromagnetic coupling between surface bumps (assumed to be prolate hemispheroids) and the bulk metal are included. Fluorescence lifetimes are found to be two to four orders of magnitude smaller than those predicted for a flat plane in calculations on silver, and for sufficiently short distances, an avoided crossing splitting is predicted.

PACS numbers: 68.90+g, 78.30.Er, and 33.50.-j.
§ I. Introduction.

Recent experiments have demonstrated the validity of classical electrodynamic explanations of many aspects of the behavior of molecular systems near metal surfaces of various morphologies.\textsuperscript{1-3} Electrodynamic models have been invoked to describe surface enhanced Raman spectroscopy (SERS),\textsuperscript{4-7,9-12} fluorescence quenching near metal surfaces,\textsuperscript{12-15} and photochemical processes near metal surfaces.\textsuperscript{16}

In an electromagnetic model, the metal affects a molecular dipole by modifying its local electromagnetic field. The observed effects are attributed to the interaction of the dipole with its image in the metal, enhancement of the local field caused by the shape of the metal, and interaction with plasmon resonances.\textsuperscript{5-7} The latter two are particularly important near a roughened metal surface. A thorough study of how all these interactions are coupled requires the solution of Maxwell’s equations for the dipole—metal system. However, since only a few systems are exactly solvable, it has generally been necessary to make approximations.

So far, all models of fluorescence which include a molecular dipole near a metal plane with surface roughness have neglected the electromagnetic coupling of the metal protrusions with the plane. Other workers have examined the response of the combined bump—plane system to an external field,\textsuperscript{9,10} but apparently none have examined the bump—plane system’s interaction with a dipole. In this paper, we present a model for the near field behavior of the fluorescence lifetime of a molecular dipole which includes the effects of coupling of the fields inside the plane and a prolate hemispheroidal bump. In Sec. II, we present the model. In Sec. III, we compare the frequency dependence of our result with that predicted by the model used by Gersten and Nitzan\textsuperscript{6} to treat SERS (in which the plane is approximated by a perfect conductor), and with that predicted by the model of Prock, Chance, and Silbey\textsuperscript{13} which neglects the presence of surface roughness entirely. While many of the qualitative features of the simpler Gersten and Nitzan model are observed, we observe additional resonances due to the coupling
of even parity modes by the planar surface. We also examine the distance dependence of the
inverse lifetime and compare with that calculated by Prock, Chance, and Silbey. Our results
indicate a decrease in the dipole lifetime of three to four orders of magnitude over their result.
Finally, at short distances, we observe avoided crossings.

§ II. Theory: A Drude Oscillator Near A Prolate Hemispheroid.

In this section, we present a model for a dipole near a metal surface with a single prolate
hemispheroidal protrusion. Henceforth, we restrict our attention to dipoles oriented perpendic-
ular to the plane and located along the symmetry axis of the protrusion. The hemispheroid has
height $a$ and width $b$ and the dipole is located at a height $d$ above the bump (cf. Fig. 1). The
problem is treated in prolate spheroidal coordinates defined by

$$
x = f (\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \cos \phi,
$$

(2.1a)

$$
y = f (\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \sin \phi,
$$

(2.1b)

and

$$
z = f \xi \eta,
$$

(2.1c)

where $f = (a^2 - b^2)^{1/2}$. We also introduce $\xi_0 \equiv \frac{a}{f}$, and $\xi_1 \equiv \frac{a + d}{f}$.

The molecular dipole is modeled as a harmonically bound charge. We envision the di-
pole as having been created by an impulse at $t=0$, and we assume that its subsequent time
evolution satisfies

$$
\ddot{\mathbf{\mu}} + \gamma_0 \dot{\mathbf{\mu}} + \omega_0^2 \mathbf{\mu} = -\frac{e^2}{m} \mathbf{E}_r \quad (t > 0),
$$

(2.2)

where $\mathbf{E}_r$ is the reflected field at the dipole position due to the presence of the metal interface,
$m$ is the effective mass of the dipole, and $\gamma_0$ and $\omega_0$ are, respectively, the damping constant and
the oscillation frequency of the dipole in the absence of the metal.

For sufficiently small fields, the frequency shift and lifetime of the molecule may be calculated perturbatively and are given by

\[ \Delta \omega \equiv \omega_{\text{eff}} - \omega_0 - \frac{\gamma_0^2}{8\omega_0} - \frac{e^2}{2m\omega_0} \text{Re} \left[ T_r(\omega_0) \right] \]  

(2.3a)

and

\[ \gamma_{\text{eff}} \equiv \gamma_0 + \frac{e^2}{m\omega_0} \text{Im} \left[ T_r(\omega_0) \right], \]  

(2.3b)

where \( T_r(\omega) \equiv E_r(\omega)/\mu(\omega) \) is the reflected field due to a unit dipole.

By introducing the quantum yield \( q \equiv \frac{2e^2\omega_0\gamma^2_0(\epsilon^+)^{1/2}}{3m\gamma_0(\epsilon^+)^{3/2}} \), and normalizing the lifetime to the free dipole lifetime, Eq. (2.3b) can be rewritten as

\[ \gamma^* \equiv \frac{\gamma_{\text{eff}}}{\gamma_0} = 1 + \frac{3}{2} q \frac{c^3}{\omega_0^3(\epsilon^+)^{1/2}} \text{Im} \left[ T_r(\omega_0) \right]. \]  

(2.4)

where \( \epsilon^+ \) is the dielectric constant of the medium containing the dipole (cf. Fig. 1).

Thus, in the perturbative limit, the problem of determining the fluorescence lifetime of a dipole reduces to the determination of the reflected field at the dipole position. In general, this is a complicated function of the geometry, but it has been found using different levels of approximation for several special cases.\(^5\text{--}^7,\text{~}11,\text{~}13\text{--}15\)

In surface enhanced Raman scattering, the reflected fields have been treated in the near field approximation.\(^5\text{--}^7\) Gersten and Nitzan have examined the case of a dipole parallel to the symmetry axis of an isolated prolate spheroid,\(^7\) and the case of a dipole near a prolate hemispheroid on a perfectly conducting plane.\(^6\) Their result for the reflected field of a prolate hemispheroid on a perfectly conducting plane is

\[ E_r = \frac{\mu(\omega)}{4\epsilon^+ R^3} + \frac{2(1-K)\mu(\omega)}{\epsilon^+ f^3} \sum_{n \text{ odd}} \frac{(2n+1)|Q_n(\tilde{\xi})|^2P_n(\tilde{\xi})P_n(\tilde{\xi})}{P_n(\tilde{\xi})Q_n(\tilde{\xi}) - KP_n(\tilde{\xi})Q_n(\tilde{\xi})}. \]  

(2.5)
where $K$ is the ratio of the dielectric constant in the bump to that in the region containing the dipole.

In this work, we also make the near field approximation; however, rather than choosing the plane to be a perfect conductor we treat it as a metal with the same dielectric properties as the hemispheroid. Thus, we incorporate effects of the electromagnetic coupling between the hemispheroid and the plane. Berreman, Ruppin, and Das and Gersten have examined the problem of the interaction of the plane—bump system with an external field.

The resulting boundary value problem is complicated by the necessity of matching the potentials and displacement fields in each region across the metal surface. Following Das and Gersten, we break the system into three regions: (a) above the plane and the bump, (b) inside the bump and its mirror image in the plane, and (c) below the plane and the mirror image of the bump (cf. Fig. 1). The potentials in the three regions are denoted as $\Phi^+$, $\Phi^0$ and $\Phi^-$, respectively. We then write the potential in regions (a) and (c) such that the boundary conditions on the plane are trivially satisfied. Afterwards, all that remains is to match the potentials to region (b). In effect, the boundary value problem is transformed from one posed on the plane and the protrusion to one posed only on the boundary of region (b). The potentials are written as

$$\Phi^+ = \frac{\mu(\omega)}{\varepsilon f^2} \left[ \frac{2}{1 + K} \sum_{n \text{ even}} (2n + 1) P_n(\eta) g_n(\xi, \xi_1) \right]$$

$$+ \frac{\mu(\omega)}{\varepsilon f^2} \left[ \frac{2K}{1 + K} \sum_{n \text{ odd}} (2n + 1) P_n(\eta) g_n(\xi, \xi_1) \right]$$

$$+ 2 \sum_{n = 0}^{\infty} (2n + 1) P_n(\eta) Q_n(\xi) A_n ,$$  \hspace{1cm} (2.6a)

$$\Phi^0 = \sum_{m = 0}^{\infty} C_m P_m(\eta) P_m(\xi) / P_m(\xi_0) ,$$  \hspace{1cm} (2.6b)
and

\[
\Phi' = \frac{\mu(\omega)}{\varepsilon f^2} \left[ \frac{2}{1+K} \sum_{n=0}^{\infty} (2n+1) P_n(\eta) g_n(\xi, \xi_1) \right] \\
+ 2 \sum_{n \text{ even}} (2n+1) P_n(\eta) Q_n(\xi) A_n + \frac{2}{\mu} \sum_{n \text{ odd}} (2n+1) P_n(\eta) Q_n(\xi) A_n, \tag{2.6c}
\]

where

\[ g_n(\xi, \xi_1) = \theta(\xi - \xi_1) Q_n(\xi) P_n(\xi_1) + \theta(\xi_1 - \xi) Q_n(\xi_1) P_n(\xi). \]

\[ P_n \text{ and } Q_n \text{ are Legendre functions of the first and second kind, respectively, and } \theta \text{ is the Heaviside step function.} \]

By employing the usual boundary conditions [i.e., continuity of \( \Phi \) and \( \varepsilon \partial \Phi / \partial \xi \)], and using the orthogonality of the Legendre polynomials, we derive a matrix equation for the expansion coefficients; i.e.,

\[
\sum_{n \text{ odd}} (2n+1) <m \mid n> F_n + \frac{F_m}{K-1} \left[ (K+1) \frac{P_m(\xi_0)}{P_m(\xi_0)} - 2K \frac{Q_m(\xi_0)}{Q_m(\xi_0)} \right] = -\frac{2}{1+K} \frac{P_m(\xi_0) Q_m(\xi_1)}{Q_m(\xi_1)} + \frac{2}{1+K} \frac{P_m(\xi_1) Q_m(\xi_0)}{Q_m(\xi_0)} \quad (m \text{ even, } \neq 0) \tag{2.7a}
\]

and

\[
\sum_{n \text{ even, } \neq 0} (2n+1) <m \mid n> F_n + \frac{1}{1-K} F_m \left[ (K+1) \frac{P_m(\xi_0)}{P_m(\xi_0)} - \frac{2 Q_m(\xi_0)}{Q_m(\xi_0)} \right] = -\frac{2}{1+K} \frac{P_m(\xi_0) Q_m(\xi_1)}{Q_m(\xi_1)} + \frac{2}{1+K} \frac{P_m(\xi_1) Q_m(\xi_0)}{Q_m(\xi_0)} \quad (m \text{ odd}), \tag{2.7b}
\]

where the \( A_n \) are given in terms of the \( F_n \) by

\[
A_n = \frac{\mu(\omega)}{\varepsilon f^2} \left[ \frac{F_n}{1-K} - \frac{1}{1+K} \frac{P_n(\xi_0) Q_n(\xi_1)}{Q_n(\xi_0)} \right] \quad (n \text{ even }, \neq 0), \tag{2.8a}
\]
$A_0 = F_0 = 0$, \hspace{1cm} (2.8b)

$$A_n = \frac{\mu(\omega)}{\varepsilon f^2} \left[ \frac{K}{K-1} \frac{F_n}{Q_n(\xi_0)} - \frac{K}{1+K} \frac{P_n(\xi_0)Q_n'(\xi_1)}{Q_n(\xi_0)} \right] \quad (n \text{ odd}), \hspace{1cm} (2.8c)$$

the $C_m$ by

$$C_m = (2m+1) \left\{ \frac{\mu(\omega)}{\varepsilon f^2} P_m(\xi_0)Q_m'(\xi_1) + \left[ 1 + \frac{1}{K} \right] A_mQ_m(\xi_0) \right\} \quad (m \text{ odd}), \hspace{1cm} (2.8d)$$

$$\equiv \frac{(2m+1)}{K} \frac{P_m(\xi_0)}{P_m(\xi_0)} \left[ \frac{\mu(\omega)}{\varepsilon f^2} P_m(\xi_0)Q_m'(\xi_1) + (1+K)Q_m(\xi_0)A_m \right] \quad (m \text{ even} \neq 0), \hspace{1cm} (2.8e)$$

$$\equiv \frac{\mu(\omega)}{\varepsilon f^2} \left\{ \frac{2}{1+K} Q_0(\xi_1) + \frac{K-1}{K+1} \sum_{n \text{ odd}} (2n+1)P_n(\xi_0)Q_n(\xi_1)<0|n> \right\}$$

$$+ \left[ 1 - \frac{1}{K} \right] \sum_{n \text{ odd}} (2n+1)A_nQ_n(\xi_0)<0|n>, \quad (m = 0), \hspace{1cm} (2.8f)$$

and where

$$<m|n> \equiv \int_0^1 dx \ P_m(x)P_n(x).$$

The reflected field at the dipole position is given by

$$E_r = \frac{\mu(\omega)}{\varepsilon} \left[ \frac{K-1}{K+1} \right] \frac{1}{4f^2\frac{2\tau_{plasmon}}{\gamma^n}} - \frac{2}{f} \sum_{n=0}^{\infty} (2n+1)Q_n(\xi_1)A_n. \hspace{1cm} (2.9)$$

§ III. Frequency And Distance Dependences.

In the near field approximation, a Drude approximation for the dielectric function of the metal implies that only the reduced plasmon lifetime, $\omega_{plasmon}/\tau_{plasmon}$, appears in the calculation. By using the data given in Ref. 18, we find the reduced plasmon lifetime to be equal to 179 for silver ($\omega_{plasmon} = 5.79 \times 10^{15} \text{sec}^{-1}$ and $\tau_{plasmon} = 3.1 \times 10^{-14} \text{sec}$). In addition, we assume the dielectric constant in the + region to be unity. The matrix equation given above was solved by
truncating the sums in Eqs. (2.7). However, since the surface plasmon resonances are rather narrow and since $<m|n>$ decays slowly as $(m-n)$ increases, slow convergence was obtained for all but the lowest frequency resonance. For the results which follow, 63 terms in the expansion were kept.

Figures 2 through 5 display the real and imaginary parts of the reflected field due to a unit dipole at various distances above the plane in units of the bump height. Figure 2 shows a plot of the real part of the fields as a function of the oscillation frequency for the case shown in Fig. 3. Because of the simple relationship between the lifetime and the imaginary part of the reflected field, we first examine the differences between the reflected fields that we calculate and the fields that are calculated with the approximation previously employed by Gersten and Nitzan; i.e., by approximating the plane by a perfect conductor.

Our results for the higher order resonances agree with those of Gersten and Nitzan in the limit where the dipole is very close to a "flat" hemispherical bump (cf. Fig. 3, $R=1.10$). In this limit, the bump behaves like a flat plane, and hence, both results agree closely even though the actual metal plane is replaced by a perfect conductor in the Gersten and Nitzan calculation. Nonetheless, examination of the lower order resonances reveals the presence of additional modes which are not contained in the approximate model, (the perfect conductor calculation contains only odd order Legendre polynomials), as well as, some discrepancies in the magnitudes of the fields (see below). Furthermore, the lowest frequency resonance, the one with the largest dipole character, is lowered in energy.

In the limit of needle-like bumps (cf. Fig. 4), the imaginary parts of our fields at short distances are in close agreement with those calculated with the approximations of Gersten and Nitzan indicating that the predominant effect at short distances are the intense fields in the vicinity of the points. Absent from the Gersten and Nitzan picture is of course a peak corresponding to the planar surface plasmon resonance at $\omega/\omega_{\text{plasmon}} = (1 + \varepsilon^+)^{-1/2} = 2^{-1/2}$ (for
\(\varepsilon^+ = 1\). This is clearly seen in Fig. 4; at the shortest distance the fields are completely dominated by the presence of the bump while at the larger distances the planar surface plasmon contribution becomes more and more important.

From Figs. 3 and 5, we see that the biggest differences between our predictions and those of Gersten and Nitzan would predict occur for hemispherical bumps when the dipole—bump distance is greater than or equal to half the bump height. At this point, the fields we calculate are roughly half those predicted by Gersten and Nitzan, the positions of the resonances are greatly shifted, and more resonances are observed (the perfect mirror selection rule of only odd orders is broken). The former is physically reasonable since we no longer have a perfect mirror reflecting all of the fields back to the dipole. As the fields are on the order of half of those predicted by Gersten and Nitzan, their predicted enhancements for SERS would differ from ours by as much as a factor of 1/16 due to the smaller amplification of the fields seen by both the dipole and the detector, and the fluorescence lifetime we would predict would be about twice their prediction.

Figure 6 shows the dependence of the inverse lifetime on the frequency of the free dipole oscillation as calculated perturbatively for a dipole sitting at fixed distances above the plane. The curves are plotted for aspect ratios of \(b/a = 0.1\) and 1.0 as well as for a flat plane. As a function of frequency, the inverse lifetimes are in general two to four orders of magnitude greater than those predicted for a plane by Prock, Chance, and Silbey. As is expected from Eq. (2.4), there is a resonance in the decay rate at each of the reflected field resonances (cf. Figs. 3—5).

As a crude check the validity of the perturbative result in the resonance region, we computed spectra by squaring the calculated dipole moment and fitted it to a single Lorentzian in order to obtain the effective lifetime. Figure 7 shows the lifetimes calculated both perturbatively [cf. Eq. (2.3b)] and by fitting the calculated spectra as a function of the free dipole oscillation.
tion frequency for fixed free dipole lifetime and distance in units of the bump height. Our calculation of the lifetimes by both methods give an enhancement at short distances which is, in general two to four orders of magnitude larger than that predicted by the planar geometry. The figure shows that one can use a perturbative treatment in the resonance region so long as the particular resonance involved is not particularly strong. In general, we find that the perturbative result is generally good (i.e., to ~ 30%), even in the resonance regions. Note however, that this result is misleading; as we now show, many of the resonances in the region plotted are split (this is especially true near very prolate bumps).

At short distances, the reflected field per unit dipole becomes large, and consequently the interaction between the dipole and the surface is strong. In this case, the validity of the expressions given above for the lifetime and the frequency shift comes into question. However since, the spectrum of the reflected field is approximately Lorentzian, we can easily derive approximate expressions for the lifetime and the frequency shift

\[ \Delta \equiv \omega - \omega_0 - \frac{1}{2} \left[ \delta - \frac{i}{2} (\gamma_0 + \gamma_s) \right] \]

\[ \pm \frac{1}{2} \left[ \Lambda / \omega_0^2 + \delta^2 - \frac{1}{4} (\gamma_0 - \gamma_s)^2 - i \delta (\gamma_0 + \gamma_s) \right]^{1/2}, \quad (3.1) \]

with \(|\Delta| \ll \omega_0\) and \(|\delta| \ll \omega_0\), where \(\delta = \omega_s - \omega_0\), and where the reflected field per unit dipole [cf. Eqs. (2.3)] has been approximated by

\[ T_s(\omega) = \frac{m}{e^2} \frac{\Lambda}{(\omega_s^2 - \omega^2 - i \omega \gamma_s)}. \quad (3.2) \]

The constants \(\Lambda\), \(\omega_s\), and \(\gamma_s\) are chosen to fit the reflected field in the frequency range of interest. Note that the parameter \(\Lambda\) characterizes the magnitude of the reflected field (per unit dipole) and consequently the strength of the dipole—surface interaction.

Note that for sufficiently large coupling (as will be the case close enough to the surface),
Eq. (3.1) predicts that the resonance is split. This is an example of the well-known avoided crossing splitting. In this case the spectrum is no longer a simple Lorentzian. Moreover, since the free dipole inverse lifetime, $\gamma_0$, is generally much smaller than the inverse lifetime of the surface plasmon resonance, $\gamma_s$, Eq. (3.1) predicts that the effective dipole lifetime approaches a value which is roughly twice the surface plasmon lifetime. The splitting is expected to occur when the dipole is located close to the surface. The effect is shown in Figs. 8—10 where we present 3D plots of the logarithm of the square of the dipole moment versus frequency and free oscillation frequency for fixed distances and quantum yields. In Fig. 8, each slice parallel to the $\Delta$ axis corresponds to a spectrum of a single molecule. Notice that as the molecular resonance frequency is brought into resonance with that of the surface (i.e., $\delta \rightarrow 0$) the induced splitting is increased. Similarly, in Figs. 9 and 10, each slice of the surface parallel to the $\omega$ axis is a frequency spectrum corresponding to a dipole with an oscillation frequency, $\omega_0$, in the absence of the metal. Notice the appearance of an avoided crossing splitting each time $\omega_0$ is near a surface reflected field resonance (cf. Figs. 9 and 4). In addition, as the surface—molecule coupling is reduced by moving the molecule further from the surface the splitting disappears (cf. Fig. 10); this is expected from Eq. (3.1).

In an experiment, what is observed at the detector is not the just dipole moment of the molecular dipole but rather the total power radiated by the combined dipole—metal system. We take this to be given by the classical dipole radiation formula with the dipole moment given by the total effective dipole moment of the system; i.e., of the molecule plus its images in the metal. The total effective dipole moment is thus the molecular dipole moment multiplied by a frequency dependent factor, $\Omega(\omega)$, which may be extracted from the potential in the $+\ $region. We find

$$
\Omega(\omega) = \frac{2K}{1+K} + 2 \left[ \frac{K F_1}{(K-1)Q_1(\xi_0)} - \frac{K \xi_0 Q_1(\xi_1)}{(1+K)Q_1(\xi_0)} \right].
$$

(3.3)
The observed power spectrum is obtained by multiplying the square of the molecular dipole moment by an effective cross section for radiation, assumed proportional to $|\Omega(\omega)|^2$. The dipole cross section for a hemispherical bump is plotted in figure 11. Note that the total dipole strength of the resonances can be much less than the total strength (cf. Fig. 3). Multiplying in the cross section alters the form of the spectrum primarily at short distances. In Fig. 12, we show spectra with and without the effective dipole cross section in an avoided crossing region. The surface is able to amplify the dipole intensity for frequencies near the resonance frequencies of the bump [see e.g., Fig. 12(c)].

Let us now turn our attention to the distance dependence of the various models. For the case of a planar interface, the reflected field for a perpendicular dipole was shown to be

$$E_R = -\frac{k^3 \mu}{\varepsilon^*} \int_0^\infty du \frac{R^1}{L^*} \frac{u^3}{e^{-2L^*d}},$$

(3.4)

where

$$k^2 \equiv \frac{\omega^2}{c^2} \varepsilon^*, \quad R^1 = \frac{\varepsilon^* L^- - \varepsilon^- L^+}{\varepsilon^* L^- + \varepsilon^- L^+}, \quad D \equiv kd,$$

and

$$L^* \equiv -i \left[ \frac{\varepsilon^*}{\varepsilon^* - u^2} \right]^{1/2}.$$  

At short dipole to plane distances the field has a leading order $d^{-3}$ dependence given by the near field approximation. For the planar case, one finds that the next few radiative corrections, which are proportional to $d^{-2}$ and $d^{-1}$, also contribute significantly to the lifetime; for planar surfaces, we are in general far from the surface plasmon resonance and as a consequence the imaginary part of the leading order term in the reflected field is small. Here, we expect the leading order term to suffice because the distribution of resonances throughout the frequency range implies that we will be near a resonance. Ruppin\textsuperscript{15} has treated the case of a
dipole near a metal sphere exactly. He found that perpendicular dipoles were less strongly quenched than they were by a planar surface when $0.1 < kd < 1.4$ and also did not observe the long distance interference effects characteristic of a planar surface.

Figure 13 shows the distance dependence of the normalized lifetime for a dipole near a hemispherical bump in comparison with that of a dipole near a plane. Plotted in the figure are the normalized lifetimes calculated as a function of the distance from the plane for the molecular dipole in the presence of a 100 Å bump, and for the molecular dipole near a plane using Eq. (3.4), the near field approximation and the near field plus the radiative corrections. One observes two to four order of magnitude enhancement at short distances.

§ IV. Conclusions.

The various electromagnetic models neglect different aspects of the problem. Prock, Chance and Silbey neglect the effect of surface roughness while Gersten and Nitzan neglect the coupling between the metal plane and the hemispheroid. In addition, both Gersten and Nitzan and we have carried out near field calculations which are only valid close to the hemispheroid (where the fields are in any case most intense). We expect that far from the surface the Prock, Chance, and Silbey approximation should hold, while as the dipole moves closer to a bump on the surface, the near field result should be valid.

One point which we have not addressed is the effect of distributions of bumps on a surface. Several authors have examined this problem in relation to SERS. Laor and Schatz examined random distributions of bumps on a surface and found that the observed enhancements were smaller and noted the possibility of collective resonances. On the other hand, Wang and Chu performed a similar calculation for a 2-dimensional array of spheroids on a surface and found that the single bump model worked fairly well.
The signal observed at the detector will be made up of contributions of molecules on planar domains plus those from molecules near bumps. As the frequency spectrum for the dipole near a bump is much broader than for a dipole near a plane, one might expect this effect to be difficult to observe in an experiment in the frequency domain. In a time domain experiment, the decay of the dipoles near a plane would be expected to appear as an initial transient decay.

We have also not examined the question of the observability of the avoided crossing splitting. Since there will inevitably be some distribution in aspect ratios and distances of the dipole from the bump and the plane, one would expect to see a distribution of lifetimes and splittings. This will obscure the avoided crossing splitting. However, the effect might be still observed on suitably prepared surfaces such as those described in Ref. 3.

The model can be readily extended to higher order multipoles for which the axial symmetry is maintained. Finally, we have not considered any quantum effects. In particular, model calculations\textsuperscript{22} for hydrogen near a metal surface show a distance dependence of the polarizability which cannot be explained within the classical Drude picture. We plan to extend these calculations to the spheroidal bump geometry, but nonetheless expect that the main new result of this work, namely, the avoided crossing, will still occur.

§ Acknowledgements.

We would like to thank Steve Arnold for useful discussions. A portion of this work was supported by the National Science Foundation under project number CHE83-02423. One of us, (A.C.P.) was supported by a NSF Minority Graduate Fellowship.
§ References.


22 M. Bawendi and D. Ronis (unpublished).
Fig. 1. Geometry of the problem. $a$ is the major axis, $b$ the minor axis, and the dipole is located at a height $d$ above the protrusion. The prolate spheroidal coordinates are defined by a scale factor, $f$, given by $f \equiv [a^2 - b^2]^{1/2}$, and the relations $\xi_0 \equiv a/f$ and $\xi_1 \equiv (a+d)/f$. 
Fig. 1.
Fig. 2. The real part of the reflected field of a unit dipole above a hemispherical bump of unit radius as a function of its oscillation frequency. The metal optical constants are those for silver as described in the text. The panels labeled (a), (b), and (c) correspond to distances in units of the bump height of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively.
Chapter 3.

Fig. 2.

\[ \text{Re}(E_r) \]

\[ \text{Re}(10^{-3}E_r) \]

\[ \text{Re}(10^{-1}E_r) \]

\[ \text{Re}(E_r) \]

\( \omega/\omega_{\text{plasmon}} \)
Fig. 3. The imaginary part of the reflected field of a unit dipole above a hemispherical bump of unit radius as a function of its oscillation frequency. The solid line is our result and the dotted one is that obtained using the approximations of Gersten and Nitzan. The panels labeled (a), (b), and (c) correspond to distances, in units of the bump height, of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively. The dotted, Gersten-Nitzan, data in panels (b) and (c) are scaled by a factor of 1/2 in addition to the scaling indicated by the labels.
\[ \text{Im} \left( \frac{10^{-4} E_r}{\omega} \right) \]

\[ \times 10 \]

\[ \frac{\omega}{\omega_{\text{plasmon}}} \]

\[ \text{Fig. 3.} \]
**Fig. 4.** The imaginary part of the reflected field of a unit dipole above a prolate hemispheroidal bump of aspect ratio $b/a = 0.1$. The Gersten--Nitzan approximation is the dotted line. The panels labeled (a), (b), and (c) correspond to distances in units of the bump height of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively.
Chapter 3.

Fig. 4.
**Fig. 5.** The imaginary part of the reflected field of a unit dipole above a prolate hemispheroidal bump of aspect ratio \( b/a = 0.4 \). The result of Gersten—Nitzan approximation, multiplied by a factor of 1/2, is the dotted line. The panels labeled (a), (b), and (c) correspond to distances in units of the bump height of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively.
Fig. 5.
Fig. 6. The logarithm of the normalized inverse lifetime for a 100 Å bump is plotted as a function of the dipole oscillation frequency in the absence of the metal using the perturbative result. The plot assumes a quantum yield of 1.0. The panels labeled (a), (b), and (c) correspond to distances in units of the bump height of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively. The solid, dotted and dash-dot lines correspond to aspect ratios, $b/a$, of 0.1, 1.0 (hemisphere), and $\infty$ (plane), respectively.
Fig. 6.
Fig. 7. The perturbative and fitted normalized inverse lifetimes are plotted as a function of free dipole oscillation frequency for a dipole of unit quantum yield 10 Å above a 100 Å bump with $b/a = 0.1$. 
Fig. 7.
Fig. 8. A 3D plot of the logarithm of the square of the magnitude of the dipole moment versus oscillation frequency on one axis and the free dipole oscillation frequency on the other. This figure is calculated for a dipole 10 Å above a 100 Å prolate hemispheroidal bump with $b/a = 0.1$. The frequency range is centered about the lowest plasmon resonance, $\omega_p = 0.2640 \omega_{\text{plasmon}}$ with a window $0.075 \omega_{\text{plasmon}}$ wide. $\Delta$ and $\delta$ are defined in the text ($\delta = \Delta = 0$ lies in the middle of the plot), and the quantum yield is taken to be unity. Note that the jagged appearance of the peak maxima is an artifact of the number of points used in the plotting program.
Fig. 8.
Fig. 9. A 3D plot of the logarithm of the square of the magnitude of the dipole moment versus oscillation frequency on one axis and the free dipole oscillation frequency on the other. This figure is calculated for a dipole 10 Å above a 100 Å prolate hemispheroidal bump with $b/a = 0.1$. The frequency range is centered about the plasmon frequency at $\omega_p = 0.3519 \omega_{plasmon}$ with a window of $0.21 \omega_{plasmon}$ wide. Note that three avoided crossings appear. The quantum yield is taken to be unity.
**Fig. 10.** The same as Fig. 9 except that the dipole is now placed 55 Å above a 100 Å prolate hemispheroidal bump with $b/a = 0.1$. 
Fig. 11. The dipole cross section is plotted as a function of oscillation frequency for a hemispherical bump. The panels labeled (a), (b), and (c) correspond to distances in units of the bump height of 1.1, 1.55, and 2.0 above the planar portion of the surface, respectively.
Fig. 11.
Fig. 12. Some plots of the logarithm of the square of the magnitude of the dipole moment with (dashed lines) and without (solid lines) the effective dipole moment cross section multiplied in for a dipole located 10Å above a 100Å bump with $b/a = 0.1$ (cf. Fig. 9). The three panels correspond to choices of the free dipole resonance frequency of $\omega_0/\omega_{\text{plasmon}} = 0.376$ (a), 0.351 (b), and 0.322 (c). The frequency range plotted contains three plasmon resonances (cf. Fig. 4), and in particular, there is one at $\omega/\omega_{\text{plasmon}} = 0.352$. Note that while a dipole may not be exactly resonant with a particular plasmon resonance, the observed dipole moment is nonetheless enhanced near the surface resonance because of the large dipole moment induced in the hemispheroid.
Fig. 12.
Fig. 13. The logarithm of the normalized lifetime is plotted versus $kd$ and compared with that predicted for a plane. Plotted are: (1) [———] the normalized lifetime as calculated for a hemispherical 100 Å bump using our model; (2) [— -- ] the normalized lifetime as calculated using the integral expression of Ref. 13; (3) [.....] the normalized lifetime calculated from the near field approximation; and (4) [— ⋅ ⋅ ⋅ ] the normalized lifetime calculated using the near field approximation including the first radiative correction. Note that $kd$ does not extend to zero in the figure.
Fig. 13.

$$\log_{10}\left(\frac{\tau}{\tau_0}\right)$$

versus

$$kd$$
Concluding Remarks And Recommendations For Further Work.
Concluding Remarks And Recommendations For Further Work.

In this section, I would like to make some concluding remarks indicating where further work is either needed or possible. Most of these depend upon advances in computer technology, however, a few are of a more formal nature.

Let me address those opportunities which have arisen or will arise simply because of recent or future advances in computer speed and hardware precision.

It is interesting to note that in the course of time during which the work described in this thesis the speed of computer hardware that was available to us has increased by a factor of the order of 50. This has enormous consequences vis-a-vis what can be studied. During the period in which much of the work in chapter 1 was done, the typical amount of CPU time necessary to generate a spectrum such as those which appear in the figures of chapter 1 with sufficient resolution to obtain reliable integrated spectra was of the order of 8 to 12 months. The advent of the Intel i486 chip for PC’s and the first generation of Sun SPARC machines brought this time down into the 2 to 4 month range. And now the most recent introduction of Pentium-based PC’s and the next generation of SPARC workstations have brought this time down into the 2 to 4 week range. This speed increase will allow several improvements. First, it will enable a much more thorough exploration of the parameter space (of frequencies, damping constants, etc.) in order to search for anomalous density behavior. Previous hardware only allowed a comparatively small handful of cases to be studied. Second, more direct methods of integration for the spectrum are possible now that more points are easily computed. In chapter 1 for example we presented two sets of spectra. One was computed early in this research, and as a result in order to complete the final integration in a reasonable amount of time it was necessary to develop customized integration algorithms in order to insure that the contributions of the very narrow, but very tall peaks were correctly incorporated with a minimum number of points. This approach was complicated in that an algorithm that might be good enough to
compute an integrated spectrum might not be good enough for evaluating a convolution. As it becomes easier to compute more points, these integrations can be handled by more standard algorithms. In the second set of spectra presented in chapter 1, we were able to employ an adaptive trapezoid algorithm which enabled us to do spectra and convolutions with a reasonable degree of confidence in the results. Third, it allows more complicated approximations for the propagators to be studied. For example, if raw CPU speeds or advances in multiple processor computing which allow an increase by perhaps another factor of 10 to 100 in computing speed become easily available, it might be possible to incorporate the mode decomposition of \( T \) presented in Figs. 15 - 17 of chapter 1 directly into the calculation in place of the approximation of \( T \) by \( -V \).

Another computing advance that will have implications for this work will be an advance in hardware precision. As we have noted above, the computation in chapter 1 involved integrating a large number of very narrow peaks. We noted in chapter 1 that some of the features were narrow enough that we were approaching the limits of machine precision. When we examined the spectra in detail there were some features that we attributed to being the result of rounding and truncation errors. Soon computers are expected to be moving from their current 32-bit architecture to a 64-bit architecture. Hopefully we will also see a corresponding improvement in floating point precision from double precision (8 bytes or 15 digits) to quad precision (16 bytes or about 25 digits). Some 32 bit machines (e.g. VAXes) have compilers that already allow quad precision calculations, but are much too slow to use in these calculations.

Now let me comment about some items of a more formal nature regarding the energy transfer processes. My comments fall into two classes: (1) possible refinements and/or extensions of the classical model we employ in chapters 1 and 2; and (2) the possibility of switching to a quantum mechanical treatment.
Regarding extensions of the classical model, there are a few possibilities that might be investigated beyond what was discussed in appendix E of chapter 2. First of all in the calculations presented in chapters 1 and 2 the polarizability functions of the acceptors and donors were deterministic functions of frequency. One possible extension is to make these polarizability functions random functions, say with zero mean and non-zero correlations only between polarizabilities of the same molecule. This change has two effects. First it moves some of the randomization effects from the random source functions to the molecules themselves. Second it will change the nature of the series expansions for the propagators, requiring different resum-mations.

Switching to a quantum mechanical, or more correctly, a quantum field theoretical description, provides a number of advantages. Before describing them let me first be clear as to what sort of quantum mechanical model I am envisioning. Many others have already done quantum mechanical calculations by inserting orientation averaged transition rates obtained by Fermi’s Golden Rule into master equations. It would be interesting to pursue a calculation analogous to the classical treatment we have performed here. First, the definitions of the quantities to be computed for rates, and populations are no longer fraught with the ambiguities in the classical model. Second, it is easier to incorporate a simple model for the internal dynamics of the donors, and acceptors. Third, we can directly look for coherent processes that might not be found using the simple quantum approach described above. Finally, since a quantum field theoretical treatment will be an expansion in powers of two small parameters, the density and Planck’s constant, the nature of the propagators obtained may change.