

Resonant Enhancement and Dissipation in Nonequilibrium van der Waals Forces

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Dispersion forces between molecules that are in relative motion, coupled to baths at different temperatures, or in excited states, are calculated using a Green function Liouville space expansion that extends the celebrated McLachlan response theory to the nonlinear regime. Our dynamical theory is applicable to systems that may be in any initial nonequilibrium state and that are subject to an arbitrary time-dependent coupling. In contrast to equilibrium forces which are attractive, nonequilibrium forces may be attractive or repulsive, exhibit chemically specific resonances, are far stronger, and may be nonconservative (with either positive or negative dissipation).

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Fluctuation-induced long-range forces are universal and have been well studied for systems in thermodynamic equilibrium [1,2]. However, many interesting systems are not in equilibrium when they interact. Cells run on interactions between molecules that have been chemically excited, e.g., by conversion of ATP. Optically excited molecules interact during photosynthesis [3], photochemical reactions [4], excitonic processes in molecular aggregates [3], and experiments using fluorescence resonance energy transfer (FRET) [5,6]. Closely spaced micromechanical components may exist at different temperatures or under optical illumination. Furthermore, the coupling between systems is rarely constant in time. Molecules in a gas undergo fleeting encounters, while the coupling between molecules in a liquid may oscillate at bond vibrational frequencies. Theoretical and experimental attention to nonequilibrium van der Waals-Casimir forces has focused on systems where the specific material properties are either irrelevant (e.g., dynamic Casimir forces [7,8]) or very simple (e.g., few-level gaseous atoms [9–11]).

McLachlan derived an expression for the equilibrium two-body van der Waals force that is applicable to systems with complex internal dynamics: it expresses the interaction free energy in terms of generalized *single-system* linear response functions [Eq. (10) below], which may be determined through experiment, simulation, or at various levels of theory [12,13]. The McLachlan formula is valid at any temperature and includes classical (Keesom force, induction force), and quantum (dispersion force) contributions within one framework. We have generalized the McLachlan formalism to include: time-dependent coupling associated with relative motion; nonequilibrium initial conditions corresponding to different temperatures or athermal distributions; and higher order corrections related to nonlinear single-molecule response functions. The equilibrium force appears as a special case in our

theory. Our calculations are based on a novel field theory Green function approach to superoperators in Liouville space. We first summarize the formalism, and then calculate the force for some model systems.

Consider the Hamiltonian of two interacting molecules, a and b :

$$H = H_a(q_a, p_a) + H_b(q_b, p_b) - J(z(t))B, \quad (1)$$

where q_j and p_j are an internal coordinate and momentum, respectively, of molecule j ($j = a, b$). $J(z(t)) \equiv J(t)$ is a coupling strength, where $z(t)$ is an externally imposed classical trajectory for the intermolecular separation. The operator $B \equiv q_a q_b$ generates intermolecular correlations. The bilinear intermolecular coupling of Hamiltonian (1) is paradigmatic of intermolecular forces: nonretarded interactions between arbitrary three-dimensional charge distributions can always be written as a sum of terms of the form of Eq. (1).

The key quantities in our theory are nonlinear response functions, $R^{(n)}(t, \tau_n, \dots, \tau_1)$, that relate the expectation value of the correlation, $\langle B(t) \rangle$, to the coupling at past times, $J(\tau)$, via:

$$\begin{aligned} \langle B(t) \rangle = & \int_{-\infty}^t d\tau_1 R^{(1)}(t, \tau_1) J(\tau_1) \\ & + \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 R^{(2)}(t, \tau_2, \tau_1) J(\tau_2) J(\tau_1) \\ & + \dots \end{aligned} \quad (2)$$

The n th order response function is most simply expressed as a multitime correlation function of superoperators in Liouville space. For any Hilbert space operator, X , we define the Liouville space superoperators X_+ and X_- by their action on the elements of the density matrix, ρ (which is written as a *vector* in Liouville space): $X_+ \rho \Leftrightarrow \frac{1}{2}(X\rho + \rho X)$, and $X_- \rho \Leftrightarrow [X, \rho]$. We further define an

interaction picture for superoperators, such that $\hat{X}_{\pm}(t) \equiv e^{i\mathcal{L}_0 t/\hbar} X_{\pm} e^{-i\mathcal{L}_0 t/\hbar}$, where \mathcal{L}_0 is the Liouville superoperator corresponding to some reference Hamiltonian. Using this notation and a reference Liouvillian $\mathcal{L}_0 = H_{a-} + H_{b-}$, the n th order response function becomes

$$R^{(n)} = \left(\frac{i}{\hbar}\right)^n \left\langle \Theta \hat{B}_+(t) \hat{B}_-(\tau_n) \cdots \hat{B}_-(\tau_1) \right\rangle_0, \quad (3)$$

where the Θ operator is 1 if $t > \tau_n > \cdots > \tau_1$, and 0 otherwise, and the expectation value is evaluated on the initial two-body density matrix, ρ_0 , of the uncoupled molecules.

We now relate $R^{(n)}$ to the properties of the *individual* molecules. Using superoperator algebra, the following substitutions may be made in Eq. (3): $B_+ \rightarrow q_{a+} q_{b+}$ and $B_- \rightarrow q_{a+} q_{b-} + q_{a-} q_{b+}$. The expression for $R^{(n)}$ then factors into a sum of 2^n terms. Each term splits into a product of two multitime correlation functions: one that depends only on $\hat{q}_{a\pm}(t)$ and ρ_{a0} , and one that depends only on $\hat{q}_{b\pm}(t)$ and ρ_{b0} . Depending on the sequence of $+$, $-$ superoperators, each multitime correlation function is related to either a nonlinear response function, molecular fluctuations in the initial state, or the response of the fluctuations to a perturbation. In contrast to the eigenstates used in standard perturbation theory, correlation functions are easier to calculate, are directly related to experimental observables, and can accommodate interactions with a bath.

As an example of the factorization of Eq. (3), the linear response function factors to

$$R^{(1)} = G_a^{+-} G_b^{++} + G_a^{++} G_b^{+-}, \quad (4)$$

where the Green functions are $G_j^{+-}(t, \tau_1) \equiv \frac{i}{\hbar} \langle \Theta \hat{q}_{j+}(t) \hat{q}_{j-}(\tau_1) \rangle_{j0}$ and $G_j^{++}(t, \tau_1) \equiv \langle \hat{q}_{j+}(t) \hat{q}_{j+}(\tau_1) \rangle_{j0}$, with $j = (a, b)$. The quantity G_j^{+-} is the response function of coordinate $\langle q_j(t) \rangle$ to a perturbation $V_j = -f_j(t) q_j$. The quantity G_j^{++} is a measure of the steady-state fluctuations of coordinate q_j . When ρ_0 does not evolve with time (i.e., $\mathcal{L}_0 \rho_0 = 0$), then the Green functions may be written as functions of a single variable, $t_1 \equiv t - \tau_1$, as may the response function $R^{(1)}$.

The steady-state van der Waals energy is obtained by an adiabatic switching of the coupling, J . In this process

the work and change in energy are equal and are given by $U = \int (\partial H / \partial J) dJ = - \int \langle B \rangle dJ$. The intermolecular correlation, $\langle B(t) \rangle$, is related to $J(t)$ by Eq. (2), or its frequency domain equivalent: $\langle \tilde{B}(\omega) \rangle = \chi^{(1)}(\omega) \tilde{J}(\omega) + \chi^{(2)}(-\omega; \omega_1, \omega_2) \tilde{J}(\omega_1) \tilde{J}(\omega_2) + \cdots$, where $\chi^{(n)}$ is the frequency domain analog of $R^{(n)}$. In the adiabatic limit, U depends on the response functions at zero frequency: $U = -\frac{1}{2} \chi^{(1)}(0) |J|^2 - \frac{1}{3} \chi^{(2)}(0; 0, 0) |J|^3 - \cdots$.

When the trajectory $z(t)$ causes J to vary with time (e.g., close encounters of gas-phase molecules), then the interaction energy is not defined, but the intermolecular force, given by $f(t) = \langle B(t) \rangle \partial_z J(t)$, is meaningful. The linear response function, $\chi^{(1)}(\omega) \equiv \chi'(\omega) + i\chi''(\omega)$, provides the leading contribution to the force. When J changes slowly (but not infinitely slowly), then the force has the form $f = A(z) - \Gamma(z)\dot{z}$ where the conservative part of the force is

$$A(z) = \frac{\partial}{\partial z} \frac{1}{2} \chi_B'(0) J^2, \quad (5)$$

and the friction coefficient is

$$\Gamma(z) = \left(\frac{\partial J}{\partial z} \right)^2 \frac{\partial \chi_B''(\omega)}{\partial \omega} \Big|_{\omega=0}. \quad (6)$$

If $J(t)$ is harmonically modulated at frequency ω , then $\chi'(\omega)$ is related to the time-averaged force and $\chi''(\omega)$ is related to the time-averaged dissipation. A Kramers Kronig relation connects $\chi'(\omega)$ and $\chi''(\omega)$.

Our first application is to the interaction of systems at different temperatures, β_a^{-1} and β_b^{-1} . In the case of local thermal equilibrium, the Green functions G_j^{+-} and G_j^{++} are directly related to response functions:

$$G_j^{+-}(t_1) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \alpha_j(\omega) e^{-i\omega t_1} d\omega, \quad (7)$$

$$G_j^{++}(t_1) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \alpha_j''(\omega) \coth\left(\frac{\hbar\omega\beta_j}{2}\right) e^{-i\omega t_1} d\omega, \quad (8)$$

where $\alpha_j(\omega) \equiv \alpha_j'(\omega) + i\alpha_j''(\omega)$ is the generalized linear polarizability of the molecule j . Equation (7) follows from the definition of the polarizability and Eq. (8) is a statement of the fluctuation dissipation theorem. Using Eqs. (7) and (8), the Fourier transform of Eq. (4) is

$$\chi^{(1)}(\omega) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega' \left[\coth\left(\frac{\hbar\beta_b\omega'}{2}\right) \alpha_a(\omega - \omega') \alpha_b''(\omega') + \coth\left(\frac{\hbar\beta_a\omega'}{2}\right) \alpha_a''(\omega') \alpha_b(\omega - \omega') \right]. \quad (9)$$

For the special case $\beta_a = \beta_b$ and $\omega = 0$, $\chi^{(1)}(0)$ may be evaluated via contour integration. The free energy, $\Delta F = -\frac{1}{2} \chi^{(1)}(0) |J|^2$ is given by the McLachlan formula:

$$\Delta F = -k_B T J^2 \sum_{n=0}^{\infty} \alpha_a(i\omega_n) \alpha_b(i\omega_n), \quad (10)$$

where the prime means that the $n = 0$ term is to be multiplied by $1/2$, $\omega_n = 2\pi n k_B T / \hbar$ are the Matsubara

frequencies, and $\alpha_j(\omega)$ is the linear polarizability of molecule j .

For the general case $\beta_a \neq \beta_b$ and $\omega \neq 0$, it is necessary to adopt a model for α_a and α_b and then to evaluate Eq. (9) numerically. As a simple illustration, we model a and b each as a damped harmonic oscillator, representing an electronic or vibrational transition. The polarizability of molecule j is given by a Lorentzian line shape centered

at frequency ω_j with a linewidth γ . Figure 1 shows the steady-state interaction energy [$U \propto -\chi^{(1)}(0)$] as a function of the resonant frequencies ω_a and ω_b and inverse temperatures β_a and β_b . The equilibrium force ($\beta_a = \beta_b$) displays no resonance at $\omega_a = \omega_b$, since it depends only on $(\omega_a + \omega_b)^{-1}$. The nonequilibrium force ($\beta_a \neq \beta_b$) has a contribution proportional to $(\omega_a - \omega_b)^{-1}$, which yields a *chemically specific* resonance in the force, which can be either attractive or repulsive.

Figure 2 shows $\chi'(\omega)$ (related to the force) and $\chi''(\omega)$ (related to the dissipation) for fixed resonant frequencies, ω_a and ω_b , when the coupling, $\tilde{J}(\omega)$, is harmonically modulated. At finite temperature, resonances in the force occur at $\omega = \pm\omega_a \pm \omega_b$. Even if ω_a and ω_b are too high for the nuclei to respond, their difference could be at a mechanically relevant frequency. Furthermore, the present formalism includes contributions to the force from low-frequency vibrational modes, which could readily couple to intermolecular motions.

When $\beta_a = \beta_b$, the dissipation, $\chi''(\omega)$, is positive for all $\omega > 0$. However, if $\omega_a > \omega_b$ and $\beta_a \omega_a < \beta_b \omega_b$, then the dissipation is *negative* for some $\omega > 0$, implying that energy is transferred from the oscillators to the source driving J . We thus have a heat engine, in which the van der Waals force is the energy transducer. Extraction of energy from the system is accompanied by heat flow from the hotter to the colder particle. The dissipative component of the van der Waals force allows for conversion between *intramolecular* excitation and *intermolecular* work, mediated purely by the fluctuating electromagnetic field. Such a mechanism is required for the system to reach thermal equilibrium.

We next consider an electronically excited molecule interacting with a ground state molecule. Several authors have studied this scenario for interaction of simple few-level systems [14–16]. Niemax measured van der Waals

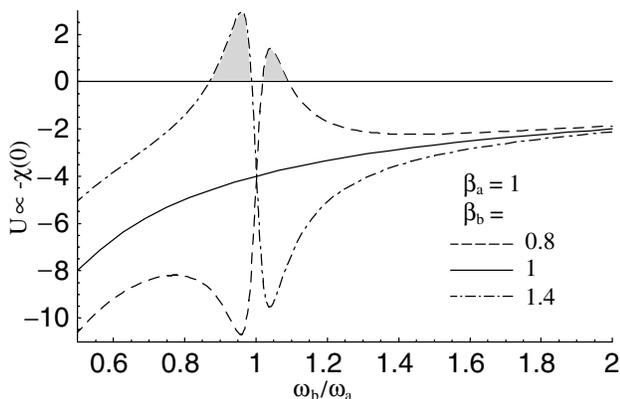


FIG. 1. Interaction energy of two harmonic oscillators as a function of their resonant frequencies, ω_b/ω_a and their temperatures, β_b/β_a . The nonequilibrium force ($\beta_a \neq \beta_b$) has a resonance that is absent from the equilibrium force. In the shaded regions the steady-state force is *repulsive*. The dimensionless parameters are $\beta_a \hbar \omega_a = 1$ and $\beta_a \hbar \gamma = 0.03$

forces between excited atoms in the gas phase and found that the force was up to 4 orders of magnitude stronger than the ground state force [9]. We show that in the regime where the Förster theory is valid, the interaction energy is proportional to the rate of FRET.

The Förster theory addresses the rate of energy transfer between an excited donor, d , weakly coupled to a ground state acceptor, a . We consider the same scenario, but calculate the interaction energy. The Green functions of the acceptor, G_a^{+-} and G_a^{++} , are given by Eqs. (7) and (8). The donor is not in thermal equilibrium, so Eqs. (7) and (8) do not apply; instead the donor Green functions are related to its emission spectrum. Assuming $\hbar \omega_0 \gg k_B T$, where ω_0 is a representative transition frequency of the donor or acceptor, we have

$$\tilde{G}_d^{\pm}(\omega) = \frac{3\pi\epsilon_0 \hbar c^3}{\omega^3 n(\omega) \tau_d} \left[\frac{1}{2} (\sigma_d(\omega) \pm \sigma_d(-\omega)) \right], \quad (11)$$

where $n(\omega)$ is the index of refraction of the medium containing the donor, τ_d is the donor lifetime, and $\sigma_d(\omega)$ is the normalized donor emission spectrum.

Under steady-state coupling, the interaction energy is given by $U_{\text{FRET}} = -\frac{1}{2} \chi_B^{(1)}(0) J^2$. Treating J as a coupling between point dipoles, the interaction energy evaluates to:

$$U_{\text{FRET}} = -\frac{3\hbar c^3 \kappa^2}{16\pi\epsilon_0 r^6 \tau_d} \int_0^\infty \frac{\sigma_d(\omega) \alpha'_a(\omega)}{n^5(\omega) \omega^3} d\omega, \quad (12)$$

where $\kappa \equiv 3(\hat{n}_a \cdot \hat{r})(\hat{n}_d \cdot \hat{r}) - \hat{n}_a \cdot \hat{n}_d$ is a geometrical factor arising from the relative orientations of the donor transition dipole, \hat{n}_d , and the acceptor transition dipole, \hat{n}_a . This interaction energy bears a striking resemblance to the Förster expression for the rate of FRET. The principle difference is that Eq. (12) contains the real part of the acceptor polarizability, $\alpha'_a(\omega)$, while the Förster expression contains the imaginary part, $\alpha''_a(\omega)$.

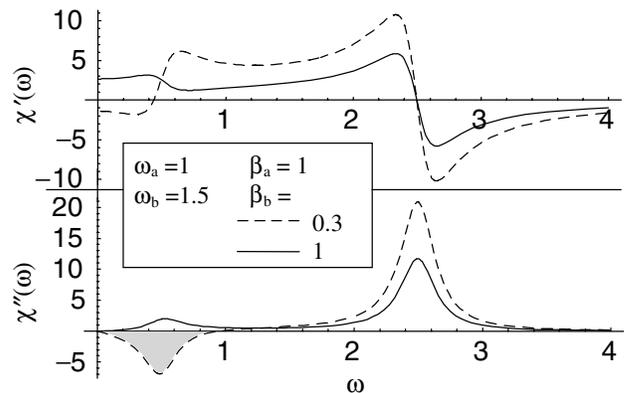


FIG. 2. Reversible [$f_r \propto \chi'(\omega)$] and irreversible [$f_i \propto \chi''(\omega)$] components of the intermolecular force for harmonically modulated coupling $\tilde{J}(\omega)$. Resonances in the force occur at $\omega = \pm\omega_a \pm \omega_b$. The shaded region indicates a domain of *negative dissipation*. The dimensionless parameters are $\beta_a \hbar \omega_a = 1$, $\beta_a \hbar \omega_b = 1.5$, and $\beta_a \hbar \gamma = 0.08$

The connection between energy transfer and the intermolecular force may be made more explicit by defining a two-dimension transition density, $K(\omega, \omega')$, that corresponds to the rate of FRET that would occur if the absorption spectrum of the acceptor, $\alpha_a''(\omega')$, were shifted along the frequency axis to coincide with the emission spectrum of the donor, $\sigma_d(\omega)$. It is easy to compute $K(\omega, \omega')$ from a known donor emission spectrum and acceptor absorption spectrum. In terms of $K(\omega, \omega')$,

$$K_{\text{FRET}} = \int_0^\infty \int_0^\infty K(\omega, \omega') \delta(\omega' - \omega) d\omega' d\omega \quad (13)$$

and

$$U_{\text{FRET}} = -\frac{\hbar}{\pi} \int_0^\infty \wp \int_0^\infty \frac{\omega' K(\omega, \omega')}{\omega'^2 - \omega^2} d\omega' d\omega. \quad (14)$$

If one calculates a self-energy of the donor due to the presence of the acceptor, then the rate of FRET is given by the imaginary part of the self-energy and the FRET force is given by the real part. Alternatively, the FRET force may be thought of as optical trapping of the acceptor by the near-field radiation from the excited donor. We have discussed these alternative viewpoints in [6].

We have simulated the interaction of two identical two level systems, subject to inhomogeneous broadening from a bath described by an overdamped Brownian oscillator [17]. The α_a'' and σ_d in this model are Gaussians with variance Δ and centers at ω_0 and $\omega_0 - 2\lambda$, respectively. 2λ is the Stokes shift, related to the strength of the coupling to the bath, and $\Delta^2 = 2\lambda/\hbar\beta$ is the linewidth parameter. When J does not depend on time, the leading term in the interaction free energy is of the form $U = -\frac{1}{2}J^2/\delta$, where δ is a measure of the detuning. For ground state interactions, $\delta = \hbar\omega_0$. For the excited state interaction, the detuning is entirely due to interactions with a bath, and we find $\delta = k_B T$. Typically $\hbar\omega_0 \gg k_B T$, so the excited state force far exceeds its ground state counterpart. These results are valid for times long compared to the relaxation time, Δ (typically picoseconds in water), but short compared to the spontaneous lifetime (typically nanoseconds). In the weak-coupling limit, spontaneous emission by the donor occurs independently of FRET, and leads to a decreasing probability over time that the donor is in the excited state. Also, our formalism holds only for $J < k_B T$. For stronger couplings, excitonic effects are important and the perturbation theory which is the basis of our approach is invalid.

The present formulation extends the McLachlan expression to include time-dependent coupling, nonequilibrium states, and the role of optical nonlinearities. Thermal, optical, or chemical excitation leads to stronger and more specific long-range forces. While the applications considered here are towards toy models, the formalism is amenable to use in quantum chemistry codes for including details of molecular structure.

The ground state interaction [Eq. (10)] is insensitive to the details of the spectral densities because it is highly off-resonant, reminiscent of the off-resonant Stark shift in nonlinear spectroscopy. The nonequilibrium forces, in contrast, [Eqs. (9) and (12)] depend on the overlap of absorption and resonant emission spectra at real frequencies. The ability to generate *resonant* van der Waals forces may be of practical use.

Several systems might demonstrate dramatic effects of nonequilibrium van der Waals forces that may be addressed by our formalism. Such forces may play a role in interactions of biomolecules within a cell and affect the mechanical properties of the active medium in a laser. The possibility of greatly reduced, or even negative, friction between systems at different temperatures or under optical excitation may be useful in the design of micromechanical systems.

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- [1] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1991).
 - [2] D. Langbein, *Theory of van der Waals Attraction*, Springer Tracts in Modern Physics Vol. 72 (Springer-Verlag, New York, 1974).
 - [3] H. van Amerongen, L. Valkunas, and R. van Grondelle, *Photosynthetic Excitons* (World Scientific, Singapore, 2000).
 - [4] N. Mataga, in *Molecular Interactions*, edited by H. Ratajczak and W.J. Orville-Thomas (John Wiley and Sons, New York, 1981), Vol. 2, Chap. 12.
 - [5] P. R. Selvin, *Nat. Struct. Biol.* **7**, 730 (2000).
 - [6] A. E. Cohen and S. Mukamel, *J. Phys. Chem. A* **107**, 3633 (2003).
 - [7] M. Kardar and R. Golestanian, *Rev. Mod. Phys.* **71**, 1233 (1999).
 - [8] E. Sassaroli, Y.N. Srivastava, and A. Widom, *Phys. Rev. A* **50**, 1027 (1994).
 - [9] K. Niemax, *Phys. Rev. Lett.* **55**, 56 (1985).
 - [10] M. J. Stephen, *J. Chem. Phys.* **40**, 669 (1964).
 - [11] E. A. Power and T. Thirunamachandran, *Phys. Rev. A* **51**, 3660 (1995).
 - [12] A. D. McLachlan, *Proc. R. Soc. London A* **271**, 387 (1963).
 - [13] A. D. McLachlan, *Proc. R. Soc. London A* **274**, 80 (1963).
 - [14] E. A. Power and T. Thirunamachandran, *Chem. Phys.* **171**, 1 (1993).
 - [15] F. G. Bass and V. Z. Lozovski, *Phys. Rev. B* **58**, 10721 (1998).
 - [16] E. A. Power and T. Thirunamachandran, *Chem. Phys.* **198**, 5 (1995).
 - [17] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).