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**Out-of-equilibrium relaxation of the thermal Casimir effect in a model polarizable material**David S. Dean,<sup>1,2</sup> Vincent Démery,<sup>2</sup> V. Adrian Parsegian,<sup>3</sup> and Rudolf Podgornik<sup>4,5</sup><sup>1</sup>*Université de Bordeaux and CNRS, Laboratoire Ondes et Matière d'Aquitaine (LOMA), UMR 5798, F-33400 Talence, France*<sup>2</sup>*Laboratoire de Physique Théorique (IRSAMC), Université de Toulouse, UPS and CNRS, F-31062 Toulouse, France*<sup>3</sup>*Department of Physics, University of Massachusetts, Amherst, Massachusetts 01003-9337, USA*<sup>4</sup>*Department of Theoretical Physics, J. Stefan Institute, SI-1000 Ljubljana, Slovenia*<sup>5</sup>*Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia*

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Relaxation of the thermal Casimir or van der Waals force (the high temperature limit of the Casimir force) for a model dielectric medium is investigated. We start with a model of interacting polarization fields with a dynamics that leads to a frequency dependent dielectric constant of the Debye form. In the static limit, the usual zero frequency Matsubara mode component of the Casimir force is recovered. We then consider the out-of-equilibrium relaxation of the van der Waals force to its equilibrium value when two initially uncorrelated dielectric bodies are brought into sudden proximity. For the interaction between dielectric slabs, it is found that the spatial dependence of the out-of-equilibrium force is the same as the equilibrium one, but it has a time dependent amplitude, or Hamaker coefficient, which increases in time to its equilibrium value. The final relaxation of the force to its equilibrium value is exponential in systems with a single or finite number of polarization field relaxation times. However, in systems, such as those described by the Havriliak-Negami dielectric constant with a broad distribution of relaxation times, we observe a much slower power law decay to the equilibrium value.

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**I. INTRODUCTION**

Despite the success of theoretical calculations on the equilibrium Casimir force [1–3], aspects of the out-of-equilibrium behavior still are poorly understood and are the subject of controversy and debate. A number of approaches have been adopted to compute thermal fluctuation induced forces out of equilibrium in simple models of soft matter systems and binary liquids. For example, the stress tensor has been used to compute the force [4–8] in a variety of nonequilibrium contexts. While it is clear that, in such systems, computations using the stress tensor yield the average value of the force at thermal equilibrium, it seems, nevertheless, that more information is needed regarding the dynamics of the field theory representing the critical or fluctuating field [9], in particular, how the value of the field at a surface changes when the surface is moved. An alternative approach is to define an energetic interaction of the field with a surface and then to define forces via the principle of virtual work [10,11]. Yet another is to define the force at a surface by a local kinetic argument, for instance, by using the ideal gas form for the pressure as a function of the local density field [12,13]. There are notable differences in out-of-equilibrium forces computed using the approaches above, and relatively few systems have been studied explicitly. However, studies of free Gaussian field theories undergoing model A (nonconserved) dynamics have been carried out. Model A dynamics for the field is basically a diffusion equation driven by white noise, and the thermal Casimir forces are found to tend toward the equilibrium value with diffusive scaling [6,7,10,11]. As well as studying the approach to equilibrium for dynamics obeying detailed balance, one can examine what happens when the noise is nonthermal, for instance, colored. In this case, the steady state Casimir interaction, under model A-type dynamics, tends to acquire an additional screening due to temporal correlations in the noise [4,10,11]. We also note that the Parisi-Wu stochastic

quantization scheme can be used to extract equilibrium results for the quantum Casimir force via a Langevin dynamics approach [14].

In the case of quantum electrodynamics, the definition of the instantaneous force can be derived from the stress tensor as it is defined physically within the theory of electromagnetism via the force acting on charges and currents just as was done in the first Lifshitz paper on the equilibrium van der Waals force [15]. The study of the out-of-equilibrium quantum electromagnetic Casimir effect is, however, much more complicated than the equilibrium thermal Casimir effect, and a number of physical assumptions need to be made if one wants to study dynamics or nonequilibrium situations. One approach is to use generic models of fluctuating electrodynamics (or stochastic Maxwell equations) *à la* Rytov *et al.* [16] where the field is driven by randomly fluctuating current densities or dipole fields [17–25]. The out-of-equilibrium context analyzed in the above papers is where the interacting media have different temperatures. In some cases, there can be a long range bulk induced interaction between the media, essentially due to the difference in their blackbody radiations. A similar bulk effect was found in Ref. [5] for the thermal Casimir effect in fluctuating scalar fields in the presence of temperature gradients. Another interesting aspect of these nonequilibrium papers is that the radiative heat transfer between bodies at different temperatures also can be studied. Whereas, the theory of fluctuating electrodynamics is very general and applies to materials of generic dielectric properties, there, nevertheless, are certain local equilibrium or fluctuation dissipation properties that need to be assumed in these theories. The goal of this paper is not to study nonequilibrium steady states but rather to address the question of how the Casimir force evolves in time to its equilibrium value, for instance, when two dielectric 89 slabs are brought suddenly into proximity.

Specifically, we will examine the out-of-equilibrium behavior of the thermal part of the electrodynamic Casimir force

(corresponding to thermal van der Waals interactions). Our approach will be based on a specialized form of fluctuating electrodynamics based on the full  $n$ -body dipolar interaction between two model dielectric media. The question we will address in this paper is how the thermal van der Waals interaction between two media relaxes to its equilibrium value. Some physical properties of the thermal Casimir interaction look less mysterious when studied in this setting, and we show that the thermal Casimir interaction is induced by the correlations between the polarization fields of the two media. For a single type of polarization field, our model corresponds to a Debye-type dielectric material. However, if we assume that there is a distribution of polarization fields with different relaxation times and dielectric susceptibilities, then any dielectric function can be obtained by taking a suitable distribution. Thus, although our model only applies to Debye-like dielectrics, it can be applied to any dielectric function as results of our computations only depend on the frequency dependent dielectric function. Furthermore, as we are interested in the approach to the equilibrium force, we argue that the slowest relaxing polarizability fields will be the thermal ones (zero Matsubara frequency term), and among these, thermal modes, those with the slowest dynamics should exhibit a Debye relaxation.

The dynamics we assume for the microscopic model for a polarizable dielectric media is overdamped stochastic dynamics for the polarization field. In the static limit, the force between such media corresponds to the zero frequency Matsubara term in the interaction energy between dielectric media as found in the Lifshitz theory [1]. We show here how the thermal van der Waals force between two objects emerges via the correlation of dipoles in the interacting media. Within this formalism, we can see how the force evolves with time toward its equilibrium value, for instance, for two slabs brought into close proximity where they initially had infinite separation. We also can see how, on upon changing the temperature of the system, the van der Waals force evolves from its initial equilibrium value at the initial temperature to the final equilibrium value at a different temperature. Although the model is simple and restricted to the nonquantum part of the van der Waals interaction, it may give useful intuition about fluctuation induced forces out of equilibrium. An appealing aspect of this approach is that the Laplace transform (with respect to time) of the dynamical force can be expressed in terms of static results that can be obtained via well established equilibrium methods.

We note that the study of the quantum Casimir-Polder interaction between atoms and surfaces has been studied in a number of out-of-equilibrium contexts [26–29]. Specifically, one can study the evolution of a quantum state of the system that is not a stationary state and also modifications of the Casimir-Polder force due to the atom's motion. The study here, thus, is more conceptually related to these studies as we study the evolution of an initially out-of-equilibrium state to the thermal equilibrium one.

## II. MODEL OF POLARIZABLE MEDIA

In this section, we define a simple model for the polarizable media and their dielectric properties, showing that the dielec-

tric response functions are a linear combination of Debye-like terms. We then show how the average force between two such media in thermal equilibrium is identical to the thermal Casimir or van der Waals force as predicted by Lifshitz theory. The argument we present is for the normal thermal Casimir interaction between two semi-infinite dielectric slabs. However, the argument clearly generalizes for the force in any direction on dielectric bodies separated by vacuum.

Consider a system with an ensemble of local polarization fields  $\mathbf{p}_\nu(\mathbf{x})$  at point  $\mathbf{x}$  in the medium. The index  $\nu$  corresponds to a type or species of polarization field, which notably has its own polarizability per unit volume denoted by  $\chi_\nu(\mathbf{x})$ . We consider two semi-infinite regions (slabs)  $V^+$  and  $V^-$  defined via the sign of the coordinate  $z$  such that  $z > 0$  in  $V^+$  and  $z < 0$  in  $V^-$ . The two regions  $V^+$  and  $V^-$  will be separated in the  $z$  direction by a distance  $L$ . In this notation, the total energy for a given configuration of the dipole fields is

$$H = \frac{1}{2} \int d\mathbf{x} d\mathbf{y} \sum_{\nu\nu'} \mathbf{p}_\nu(\mathbf{x}) \cdot A_{\nu\nu'}(\mathbf{x}, \mathbf{y}, L) \mathbf{p}_{\nu'}(\mathbf{y}), \quad (1)$$

where

$$A_{\nu\nu'}(\mathbf{x}, \mathbf{y}) = \frac{\delta(\mathbf{x} - \mathbf{y}) I \delta_{\nu\nu'}}{\chi(\mathbf{x})} + D(\mathbf{x}, \mathbf{y}, L). \quad (2)$$

In the first term,  $I$  is the identity matrix in three-dimensional space, and the polarization energy, Eq. (1), corresponds to the classical harmonic energy needed to generate a local polarization field. In the second term,  $D$  is the interaction between the dipoles in two semi-infinite regions, which we write in terms of the standard dipole-dipole coupling,

$$D_0(\mathbf{x} - \mathbf{y}) = -\nabla_i \nabla_j G(\mathbf{x} - \mathbf{y}), \quad (3)$$

where  $G$  is the Green's function for the electrostatic field *in vacuo* obeying

$$\epsilon_0 \nabla^2 G(\mathbf{x}) = -\delta(\mathbf{x}). \quad (4)$$

Writing the energy in the above manner means that the separation ( $L$ ) dependent part of the energy is encoded in the dipolar interaction term  $D$ . This interaction is given by

$$D(\mathbf{x}, \mathbf{y}, L) = D_0(\mathbf{x} - \mathbf{y}), \quad (5)$$

when  $\mathbf{x} \in V^+$  and  $\mathbf{y} \in V^+$  or when  $\mathbf{x} \in V^-$  and  $\mathbf{y} \in V^-$ ,

$$D(\mathbf{x}, \mathbf{y}, L) = D_0(\mathbf{x} - \mathbf{y} - L\hat{\mathbf{z}}), \quad (6)$$

when  $\mathbf{x} \in V^-$  and  $\mathbf{y} \in V^+$ , and

$$D(\mathbf{x}, \mathbf{y}, L) = D_0(\mathbf{x} + L\hat{\mathbf{z}} - \mathbf{y}), \quad (7)$$

when  $\mathbf{x} \in V^+$  and  $\mathbf{y} \in V^-$ .

Notice that the  $L$  dependence for slabs will be replaced by another general relative coordinate for bodies of arbitrary geometry, for instance, the distance between the center of two spheres or the distance between the center of a sphere and a semi-infinite plane.

Before proceeding with the analysis of Casimir interactions between two slabs, let us consider the dielectric properties of the bulk systems. We will assume that each dipole field obeys Langevin dynamics and that the only coupling between the different polarization fields is their mutual dipole-dipole interactions. The dynamical equations for each field in the

presence of a uniform time dependent electric field  $\mathbf{E}$ , thus, is given by

$$\frac{\partial p_{iv}(\mathbf{x})}{\partial t} = -\kappa_v(\mathbf{x}) \frac{\delta H}{\delta p_{iv}(\mathbf{x})} + \kappa_v(\mathbf{x}) E_i(t) + \zeta_{vi}(\mathbf{x}, t), \quad (8)$$

where  $\kappa_v$  is a local diffusion constant for each polarization field and determines the time scale of relaxation of the field. The noise  $\zeta_{vi}(\mathbf{x}, t)$  is of a white noise type and has a space-time correlation function,

$$\langle \zeta_{vi}(\mathbf{x}, t) \zeta_{v'j}(\mathbf{x}', t') \rangle = 2T \delta_{ij} \kappa_v(\mathbf{x}) \delta_{vv'} \delta(\mathbf{x} - \mathbf{x}'), \quad (9)$$

where  $T$  is the temperature (imposed on the polarization field by the local bulk environment) and the weighting  $\kappa_v$  assures that detailed balance holds, i.e., that the dynamics eventually leads to thermal equilibrium at temperature  $T$ .

In a bulk system (where  $\kappa_v$  and  $\chi_v$  are constant), we determine the dielectric properties of the model by computing the response to a spatially uniform applied electric field  $\mathbf{E}(t) = \mathbf{E} \exp(i\omega t)$ . The average response of each polarizability field is uniform in space, and the interactions between dipoles average to zero. The average value of each polarizability field then is given by

$$\langle \mathbf{p}_v(t) \rangle = \frac{\chi_v}{1 + \frac{i\omega\chi_v}{\kappa_v}} \mathbf{E} \exp(i\omega t), \quad (10)$$

and, thus, the average total electric displacement is

$$\mathbf{D}(t) = \epsilon_0 \mathbf{E}(t) + \sum_v \langle \mathbf{p}_v(t) \rangle. \quad (11)$$

This allows us to read off the frequency dependent dielectric response as

$$\epsilon(\omega) = \epsilon_0 + \sum_v \frac{\chi_v}{1 + i\omega\chi_v\kappa_v}, \quad (12)$$

which is obviously just a superposition of Debye-like dielectric responses. The frequency dependent dielectric response, thus, depends on both the polarizabilities  $\chi_v$  and the dynamical variable  $\kappa_v$ . The static dielectric constant, however, depends only on the static polarizabilities,

$$\epsilon(0) = \epsilon_0 + \sum_v \chi_v. \quad (13)$$

### III. EQUILIBRIUM VAN DER WAALS INTERACTION

After having established the basic bulk dielectric properties of our model, we will show how they enter the equilibrium van der Waals or thermal Casimir effect between two semi-infinite dielectric slabs.

The force between two semi-infinite slabs separated by a distance  $L$  for any configuration of the polarizability fields in the two slabs is given by

$$f = -\frac{\partial H}{\partial L} = -\frac{1}{2} \sum_{vv'} \int dx dy \mathbf{p}_v(\mathbf{x}) \cdot \frac{\partial}{\partial L} A(\mathbf{x}, \mathbf{y}, L) \mathbf{p}_{v'}(\mathbf{y}), \quad (14)$$

since only the dipole interaction term  $D$  depends on  $L$ . The local polarizability only depends on the coordinates within

the two volumes  $V^+$  and  $V^-$ . The equilibrium value for the average force may be obtained using the fact that

$$\langle p_v(\mathbf{x}) p_{v'}(\mathbf{y}) \rangle = T [A^{-1}(\mathbf{x}, \mathbf{y}, L)]_{vv'}, \quad (15)$$

and, thus,

$$\langle f \rangle = -\frac{T}{2} \text{Tr} \left( A^{-1} \frac{\partial}{\partial L} A \right), \quad (16)$$

where  $\text{Tr}$  indicates the trace over the operator, the spatial, and the species indices. This average force, thus, may be written as

$$\langle f \rangle = -\frac{T}{2} \frac{\partial}{\partial L} \text{Tr} \ln[A] = -\frac{\partial F}{\partial L}, \quad (17)$$

which of course agrees with the standard statistical mechanical definition if  $F = -T \ln(Z)$  is interpreted as the free energy obtained from the partition function,

$$Z = \int d[\mathbf{p}] \exp(-\beta H). \quad (18)$$

This partition function can be written in a standard way by introducing a Hubbard-Stratonovich auxiliary field  $\phi$ , which physically can be identified with  $i\psi$  where  $\psi$  is the fluctuating electrostatic potential to decouple the dipolar interaction. This gives up to a constant factor independent of  $L$ ,

$$Z = \int \prod_v d[\mathbf{p}_v] d[\phi] \exp \left( -\frac{\beta}{2} \int \epsilon_0 [\nabla \phi(\mathbf{x})]^2 + \beta \int_{z<0} d\mathbf{x} i \sum_v \mathbf{p}_v(\mathbf{x}) \cdot \nabla \phi(\mathbf{x}) - \sum_v \frac{\mathbf{p}_v(\mathbf{x})^2}{2\chi_v(\mathbf{x})} + \beta \int_{z>L} d\mathbf{x} i \sum_v \mathbf{p}_v(\mathbf{x}) \cdot \nabla \phi(\mathbf{x}) - \sum_v \frac{\mathbf{p}_v(\mathbf{x})^2}{2\chi_v(\mathbf{x})} \right). \quad (19)$$

We note that the variables  $\chi_v$  are not necessarily the same in regions  $z < 0$  and  $z > L$  as, in general, they correspond to two different materials. As the integrals over  $\mathbf{p}_v$  now are decoupled, they may be carried out to yield, again up to constants independent of  $L$ , the standard form of the partition function for the thermal Casimir contribution for van der Waals interactions between dielectric media,

$$Z = \int d[\phi] \exp \left( -\frac{\beta}{2} \int d\mathbf{x} \epsilon(\mathbf{x}, 0) [\nabla \phi(\mathbf{x})]^2 \right). \quad (20)$$

Here,  $\epsilon(\mathbf{x}, 0) = \epsilon_0 + \sum_v \chi(\mathbf{x})$  for  $z < 0$  and  $z > L$ , i.e., in the volumes  $V^+$  and  $V^-$  and  $\epsilon(\mathbf{x}) = \epsilon_0$  for  $z \in [0, L]$ , i.e., the vacuum between the two media. We also see that the variables  $\epsilon(\mathbf{x}, 0)$  are simply the local static dielectric constants as defined by Eq. (13). This form of the partition function corresponds to the one stemming from the Lifshitz theory of the Casimir force for the thermal van der Waals component of the interaction. As mentioned above, the resulting expression for the partition function is, in fact, valid for any geometry and configuration of dielectric bodies if they are separated by vacuum—the partition function depends on the position of the dielectrics only through the local value of the dielectric constant in space.

The partition function in Eq. (20) can be evaluated exactly for systems where  $\epsilon(\mathbf{x})$  depends only on the coordinate  $z$  (slablike configurations), whereas, for other geometries, it can be evaluated via different approximation schemes, such as the

proximity force approximation or using systematic multipolar expansions.

#### IV. DYNAMICS

We now turn to the problem of the dynamical evolution of the force. In the absence of an applied field, the polarization dynamics can be written as

$$\frac{\partial p_{iv}(\mathbf{x})}{\partial t} = -\kappa_v(\mathbf{x}) \frac{\delta H}{\delta p_{iv}(\mathbf{x})} + \zeta_{iv}(\mathbf{x}, t), \quad (21)$$

where  $\kappa_v(\mathbf{x})$  determines the local relaxation in the region  $\mathbf{x}$  of space. The condition of detailed balance implies that the noise correlator obeys

$$\langle \zeta_{iv}(\mathbf{x}, t) \zeta_{jv'}(\mathbf{x}', t') \rangle = 2T R_{ivjv'}(\mathbf{x}, \mathbf{x}'), \quad (22)$$

where the operator  $R$  is given by

$$R_{ivjv'}(\mathbf{x}, \mathbf{x}') = \kappa_v(\mathbf{x}) \delta_{ij} \delta_{vv'} \delta(\mathbf{x} - \mathbf{x}'). \quad (23)$$

In operator notation, the dynamical equations can be written as

$$\frac{\partial \mathbf{p}(\mathbf{x})}{\partial t} = -R A \mathbf{p}(\mathbf{x}) + \zeta(\mathbf{x}, t). \quad (24)$$

The average value of the dynamical force, Eq. (14), can be obtained from the time correlation function of the dipole field defined as

$$\langle p_{iv}(\mathbf{x}, t) p_{jv'}(\mathbf{x}', t) \rangle = C_{ivjv'}(\mathbf{x}, \mathbf{x}', t), \quad (25)$$

so that the time dependent average force is given by

$$\langle f(t, L, T) \rangle = -\frac{1}{2} \text{Tr} C(t) \frac{\partial}{\partial L} A. \quad (26)$$

The evolution equation for  $\mathbf{p}$ , being of first order in time, can be integrated to give an explicit form for the correlation function,

$$C(t) = \exp(-tRA)C(0)\exp(-tAR) + TA^{-1}[1 - \exp(-2tAR)], \quad (27)$$

in operator notation, where  $C(0)$  is the value of the correlation function at  $t = 0$ . We notice here that the force between the two regions depends on the cross correlation between them. If, at  $t = 0$ , the two regions are brought into proximity from a long distance, the cross correlation at  $t = 0$  is zero, and only the second term in Eq. (27) remains. In the absence of initial correlations, the Laplace transform of  $C$ ,

$$\mathcal{L}C(s) = \int_0^\infty dt C(t) \exp(-st) \quad (28)$$

is given by

$$\mathcal{L}C(s) = \frac{T}{s} \left[ A + \frac{sR^{-1}}{2} \right]^{-1}. \quad (29)$$

This means that the Laplace transform of the time dependent average force can be written as

$$\mathcal{L}\langle f \rangle(s) = -\frac{T}{2s} \text{Tr} \left[ A + \frac{sR^{-1}}{2} \right]^{-1} \frac{\partial}{\partial L} A. \quad (30)$$

Two points should be noted at this stage: (i) the operator  $R$  does not depend on the distance between the two regions  $V^+$  and  $V^-$ , and (ii) its inverse is simply

$$R^{-1}(\mathbf{x}, \mathbf{x}')_{ivjv'} = \frac{\delta_{ij} \delta_{vv'}}{\kappa_v(\mathbf{x})} \delta(\mathbf{x} - \mathbf{x}'). \quad (31)$$

The first of these points means that we can write

$$\mathcal{L}\langle f \rangle(s) = -\frac{1}{s} \frac{\partial F_s}{\partial L} = \frac{T}{s} \frac{\partial}{\partial L} \ln(Z_s), \quad (32)$$

where

$$Z_s = \int \prod_v d[\mathbf{p}_v] \exp[-\beta H_d(s)], \quad (33)$$

and  $H_d(s)$  is an effective dynamical Hamiltonian given by

$$H_d(s) = H + \frac{s}{4} \sum_v \frac{\mathbf{p}_v^2(\mathbf{x})}{\kappa_v(\mathbf{x})}. \quad (34)$$

It can be written as a static Hamiltonian with local dynamical polarizabilities,

$$\frac{1}{\chi_v(\mathbf{x}, s)} = \frac{1}{\chi_v(\mathbf{x})} + \frac{s}{2\kappa_v(\mathbf{x})}, \quad (35)$$

which, in turn, leads to local *dynamic* dielectric constants given by

$$\epsilon_d(\mathbf{x}, s) = \epsilon_0 + \sum_v \frac{\chi_v(\mathbf{x})}{1 + \frac{s\chi_v(\mathbf{x})}{2\kappa_v(\mathbf{x})}}. \quad (36)$$

The observant reader immediately recognizes a similarity between the form of Eq. (36) for the dynamical dielectric constant and the frequency dependent dielectric constant predicted by the dielectric response model from Eq. (12), indeed, we find that  $\epsilon_d(s) = \epsilon(-i\frac{s}{2})$ . Thus, for the computation of the thermal van der Waals forces in this model, knowledge of the frequency dependent dielectric constants allows one to predict the temporal evolution of the force toward its equilibrium value. Although the computation above was carried out with slab geometries in mind, it is easy to see that it applies for general geometries where dielectric objects are separated by vacuum. This means that we can write the time dependent force as

$$\langle f(t) \rangle = -\frac{\partial F(t, L)}{\partial L}, \quad (37)$$

where  $F(t, L)$  is an effective time dependent free energy given by

$$F(t, L) = -T \mathcal{L}^{-1} \frac{1}{s} \ln \left[ Z \left( \epsilon \left( -i\frac{s}{2} \right) \right) \right], \quad (38)$$

where  $\mathcal{L}^{-1}$  indicates the inverse Laplace transform and the notation  $\epsilon(is/2)$  denotes that the frequency dependent dielectric constant is taken in all regions at the value  $-is/2$ . The pole at  $s = 0$  yields the equilibrium free energy and, thus, the equilibrium force. We notice again, as in the static case, that the dynamical computation also applies to an arbitrary geometry of dielectric bodies separated by vacuum.

In the above, one can invert the Laplace transform using the Bromwich integration formula to get

$$F(t, L) = -T \int_{-i\infty}^{i\infty} \frac{ds}{2\pi is} \exp(st) \ln \left[ Z \left( \epsilon \left( -i\frac{s}{2} \right) \right) \right], \quad (39)$$

where the integration is to the right of the imaginary axis (as all singularities are at negative  $s$ ). One can remove the term with the pole at  $s = 0$  by hand to write

$$F(t, L) = F_{eq}(L) - T \int_{-i\infty}^{i\infty} \frac{ds}{2\pi i s} \exp(st) \times \left[ \ln \left[ Z \left( \epsilon \left( -i \frac{s}{2} \right) \right) \right] - \ln[Z(\epsilon(0))] \right], \quad (40)$$

where

$$F_{eq}(L) = -T \ln[Z(\epsilon(0))] \quad (41)$$

is the equilibrium free energy  $F_{eq}(L) = \lim_{t \rightarrow \infty} F(t, L)$ . In the above formula, the remaining contour integral is now free of singularities on the imaginary axis, and therefore, we may write it as a Fourier transform by performing the substitution  $s = 2i\omega$ ,

$$F(t, L) = F_{eq}(L) - T \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i \omega} \exp(2i\omega t) [\ln[Z(\epsilon(\omega))] - \ln[Z(\epsilon(0))]]. \quad (42)$$

The above results can be generalized to the situation where the two bodies are initially in equilibrium (at fixed distance  $L$ ) at a temperature  $T_0$ , and then the temperature is changed to  $T$ . We can write the force for two slabs as the sum of two components,

$$\langle f(L, t, T_0 \rightarrow T) \rangle = \langle f(L, T_0) \rangle_{eq} + \frac{(T - T_0)}{T} \langle f^{(0)}(t, L, T) \rangle, \quad (43)$$

where  $\langle f(L, T_0) \rangle_{eq}$  is the equilibrium force at temperature  $T_0$  and  $\langle f^{(0)}(L, t, T) \rangle$  is the time dependent force for two initially uncorrelated bodies at temperature  $T$ . The result for uncorrelated bodies at temperature  $T$  obviously can be extracted from the above result by setting  $T_0 = 0$ .

## V. ANALYTICAL RESULTS FOR SLAB GEOMETRIES

Here, we consider the case of two parallel semi-infinite slabs of dielectric constants  $\epsilon_1$  and  $\epsilon_2$  (we take subscripts 1 and 2 to refer to regions  $V^-$  and  $V^+$ , respectively). Whereas, we claim that our results are applicable to general geometries, we restrict our analysis to the interaction between semi-infinite slabs as the static results necessary to extract the dynamical results are simplest in this case, and we do not have to resort to approximations.

The *dynamical free energy*,

$$F_s = -T \ln \left\{ Z \left[ \epsilon \left( -i \frac{S}{2} \right) \right] \right\} \quad (44)$$

can then be read off from standard equilibrium results and is given by

$$F_s = \frac{TS}{16\pi L^2} \int_0^\infty u du \ln \left[ 1 - \Delta_1 \left( -i \frac{S}{2} \right) \Delta_2 \left( -i \frac{S}{2} \right) \times \exp(-u) \right], \quad (45)$$

where  $S$  is the area of the slabs and

$$\Delta_i(\omega) = \frac{\epsilon_i(\omega) - \epsilon_0}{\epsilon_i(\omega) + \epsilon_0}. \quad (46)$$

The time dependent force for two initially uncorrelated slabs, thus, is of the form

$$\langle f(L, t, T) \rangle = -\frac{TS}{L^3} H(t), \quad (47)$$

where  $H(t)$  is a time dependent Hamaker coefficient whose Laplace transform is given by

$$\mathcal{L}H(s) = -\frac{1}{8\pi s} \int_0^\infty u du \ln \left[ 1 - \Delta_1 \left( -i \frac{S}{2} \right) \Delta_2 \left( -i \frac{S}{2} \right) \times \exp(-u) \right]. \quad (48)$$

The above expression for the time dependent Hamaker coefficient can then be written in terms of the polylogarithmic function  $\text{Li}_3(z) = \sum_{n=1}^{\infty} z^n/n^3$  to give

$$\mathcal{L}H(s) = \frac{1}{8\pi s} \text{Li}_3 \left[ \Delta_1 \left( -i \frac{S}{2} \right) \Delta_2 \left( -i \frac{S}{2} \right) \right]. \quad (49)$$

The static equilibrium value simply is recovered from the pole at  $s = 0$  outside and is given by

$$H_{eq} = \frac{1}{8\pi} \text{Li}_3[\Delta_1(0)\Delta_2(0)]. \quad (50)$$

Equation (47) represents an interesting and fundamental result for slab geometries. It states that the nonequilibrium force has the same separation dependence as the equilibrium force, but its Hamaker coefficient is time dependent. Dynamic effects do not modify the spatial dependence of the van der Waals force, and the force is instantaneously long range. This decoupling of the spatial and temporal behaviors of the force is in sharp contrast to that of the critical Casimir force for free scalar fields (again, in a parallel plate geometry) with Dirichlet or Neumann boundary conditions undergoing model A dynamics. In that case, the average force exhibits diffusive scaling, behaving as  $f(L, t) = t^{-\alpha} g(L/\sqrt{t})$  [6,7,10,11]. We finally note that the mapping of the Laplace transform of the time dependent force onto an effective equilibrium problem is reminiscent of the results found in Refs. [10,11] when a similar correspondence occurs for the time dependent thermal Casimir force for a free scalar field.

Let us now investigate some special cases of the above general results.

### A. Short time behavior for Debye-type dielectrics

To begin with, we consider the temporal evolution of the Hamaker coefficient in the simplest case where the two bounding surfaces are described by identical Debye-type dielectric responses and the time evolution is limited to short time scales. Assuming that there is only one dipole type in each dielectric slab, we, thus, have

$$\epsilon_i \left( -i \frac{S}{2} \right) = \epsilon_0 + \frac{\chi_i}{1 + \frac{S\chi_i}{2\kappa_i}}. \quad (51)$$

By dimensional analysis, we see that we can write  $\kappa_i = \frac{\chi_i}{\tau_i}$ , where  $\tau_i$  is a microscopic polarization relaxation time in slab  $i$ . This change in notation then yields the familiar Debye formula for the dielectric constant,

$$\epsilon(\omega) = \epsilon_0 + \frac{\Delta\epsilon}{1 + i\omega\tau}, \quad (52)$$

where  $\epsilon(0) - \epsilon_0 = \Delta\epsilon = \chi$ . From this, we obtain

$$\epsilon\left(-i\frac{s}{2}\right) = \epsilon_0 + \frac{\epsilon_i - \epsilon_0}{1 + \frac{s\tau_i}{2}}, \quad (53)$$

which, in turn, yields

$$\Delta_i\left(-i\frac{s}{2}\right) = \frac{\epsilon_i - \epsilon_0}{\epsilon_i + \epsilon_0 + \epsilon_0\tau_i s}. \quad (54)$$

At short times, the temporal behavior of  $H(t)$  can be obtained by looking at the large  $s$  behavior of  $\mathcal{L}H(s)$ . In this limit, we have that

$$\Delta_i\left(-i\frac{s}{2}\right) \approx \left(\frac{\epsilon_i - \epsilon_0}{\epsilon_0}\right) \frac{1}{s\tau_i}. \quad (55)$$

As the  $\Delta_i(-i\frac{s}{2})$  are small, and we are effectively in the dilute two body limit, this means that the correlations other than the two body ones set in at later time scales. We, thus, find

$$\mathcal{L}H(s) \approx \frac{(\epsilon_1 - \epsilon_0)(\epsilon_2 - \epsilon_0)}{8\pi s^3 \tau_1 \tau_2 \epsilon_0^2}, \quad (56)$$

and, thus, inverting the Laplace transform, we find that, at short times,

$$H(t) \approx \frac{(\epsilon_1 - \epsilon_0)(\epsilon_2 - \epsilon_0) t^2}{16\pi \tau_1 \tau_2 \epsilon_0^2}. \quad (57)$$

The above initial growth is quadratic in time, reflecting the need for the polarization fields to become correlated. This result can be generalized straightforwardly to several polarization types  $\nu_i$  in each slab, and we find that, at early times,

$$H(t) \approx \frac{t^2}{16\pi \epsilon_0^2} \sum_{\nu_1 \nu_2} \frac{\chi_{\nu_1} \chi_{\nu_2}}{\tau_{\nu_1} \tau_{\nu_2}}. \quad (58)$$

From this expression, one obviously discerns the pairwise nature of the interaction between the distinct polarization types  $\nu_1$  and  $\nu_2$  in slabs 1 and 2.

### B. Long time behavior for Debye-type dielectrics

Next, we consider the long time behavior of the Hamaker coefficient in the case of two identical Debye-type materials. As we know the initial (and final equilibrium) values of the force, we can examine its full temporal evolution by analyzing the temporal derivative  $\dot{H}(t) = dH/dt$ . As the initial value of  $H$  is zero, standard results on Laplace transforms give

$$\mathcal{L}\dot{H}(s) = \frac{1}{8\pi} \text{Li}_3\left[\Delta_1\left(-i\frac{s}{2}\right) \Delta_2\left(-i\frac{s}{2}\right)\right]. \quad (59)$$

In this case, we have

$$\Delta_1\left(-i\frac{s}{2}\right) = \Delta_2\left(-i\frac{s}{2}\right) = \frac{\epsilon - \epsilon_0}{\epsilon_0\tau} \frac{1}{s+a} \quad \text{with } a = \frac{\epsilon + \epsilon_0}{\epsilon_0\tau}. \quad (60)$$

Now, by using the series representation of  $\text{Li}_3$ , we can invert the Laplace transform term by term to find

$$\begin{aligned} \dot{H}(t) &= \frac{1}{8\pi} \sum_{n=1}^{\infty} \left(\frac{\epsilon - \epsilon_0}{\epsilon_0\tau}\right)^{2n} \frac{t^{2n-1} \exp(-at)}{n^3(2n-1)!} \\ &= \frac{1}{4\pi t} \exp(-at) R\left(\frac{(\epsilon - \epsilon_0)t}{\epsilon_0\tau}\right), \end{aligned} \quad (61)$$

where

$$\begin{aligned} R(u) &= \sum_{n=1}^{\infty} \frac{u^{2n}}{n^2(2n)!} = 4 \int_0^u ds [\ln(u) - \ln(s)] \frac{\cosh(s) - 1}{s} \\ &\simeq 2 \frac{\exp(u)}{u^2} \quad \text{for } u \rightarrow \infty. \end{aligned} \quad (62)$$

The asymptotic form for  $u \rightarrow \infty$  was derived by expressing  $R(u)$  in terms of hypergeometric functions. Putting this all together yields, for large  $t$ ,

$$\dot{H}(t) \approx \frac{\tau^2}{2\pi t^3} \left(\frac{\epsilon_0}{\epsilon - \epsilon_0}\right)^2 \exp\left(-\frac{2t}{\tau}\right). \quad (63)$$

Therefore, at late times, the asymptotic form of the time dependence of the Hamaker coefficient turns out to be

$$H(t) \approx H_{eq} - \frac{\tau^2}{4\pi t^2} \left(\frac{\epsilon_0}{\epsilon - \epsilon_0}\right)^2 \exp\left(-\frac{2t}{\tau}\right). \quad (64)$$

The apparent divergence in the second term above, when  $\epsilon \rightarrow \epsilon_0$ , appears strange at first sight, however, we must bare in mind that the asymptotic expansion we carried out to obtain this result depended on the variable  $u = (\epsilon - \epsilon_0)t/\tau\epsilon_0$  being large. We numerically can verify the validity of the asymptotic expansion by comparison with a direct numerical evaluation of Eq. (61). It is found to be correct, but its realm of validity is for very large values of  $u$  of the order of 50. The asymptotic expansion, thus, is of limited use and just shows that, at very late times, the final relaxation to the equilibrium Hamaker coefficient is exponential with time scale  $\tau^* = \tau/2$ , interestingly independent of  $\epsilon$ .

A particularly nontrivial point about the above calculation is that, although the pairwise approximation is valid for the equilibrium Hamaker coefficient when  $\Delta\epsilon = \epsilon - \epsilon_0$  is small, the pairwise approximation cannot be used to extract the temporal behavior of the out-of-equilibrium Hamaker coefficient. This is because  $\Delta\epsilon$  appears multiplied by time  $t$ , and thus, the product of the two eventually must become large. Thus, even when the final equilibrium result is dominated by pairwise interactions, the dynamical evolution to the equilibrium actually depends crucially on the full  $n$ -body interactions.

In the case where the two media are of Debye type but with different dielectric parameters, the inversion of the Laplace transform of  $\dot{H}(s)$  is more complicated, and, in general, we have not been able to find an analytical expression as in the case where both slabs are composed of identical dielectric media. However, in the case where the media are such that

$$a = a_1 = \frac{\epsilon_1 + \epsilon_0}{\tau_1\epsilon_0} = a_2 = \frac{\epsilon_2 + \epsilon_0}{\tau_2\epsilon_0}, \quad (65)$$

this means that  $\Delta_1(-i\frac{s}{2})$  and  $\Delta_2(-i\frac{s}{2})$  have the same poles (at  $s = -a_1 = -a_2$ ), and we obtain

$$\dot{H}(t) = \frac{1}{4\pi t} \exp(-at) R\left(\frac{\sqrt{(\epsilon_1 - \epsilon_0)(\epsilon_2 - \epsilon_0)}t}{\epsilon_0\sqrt{\tau_1\tau_2}}\right). \quad (66)$$

Here, the late time relaxation to the equilibrium Hamaker coefficient is again exponential with time scale  $\tau^* = 1/[a - \sqrt{(a - \frac{2}{\tau_1})(a - \frac{2}{\tau_2})}]$ , which we see is dependent on the dielectric constant but only through variable  $a$ .

A subvariant of this situation, which can be resolved analytically, is the case where one of the systems has a much shorter relaxation time than the other, for instance,  $\tau_2 \ll \tau_1$ . In the inversion of the Laplace transform, we may use the approximation,

$$\Delta_2\left(-i\frac{s}{2}\right) = \frac{\epsilon_2 - \epsilon_0}{\epsilon_2 + \epsilon_0 + \epsilon_0\tau_2s} \approx \frac{\epsilon_2 - \epsilon_0}{\epsilon_2 + \epsilon_0} = \Delta_2(0), \quad (67)$$

i.e., this is essentially the assumption that the polarization field in slab 2 instantaneously equilibrates with the electric field produced by the polarization field of the slab. In addition, the approximation is valid only for times  $t$  such that  $t \gg \tau_1$ . Within this approximation, we find that

$$\dot{H}(t) = \frac{1}{8\pi t} \exp(-a_1 t) W\left(\frac{\Delta_2(\epsilon_1 - \epsilon_0)t}{\epsilon_0\tau_1}\right), \quad (68)$$

where

$$W(u) = \sum_{n=1}^{\infty} \frac{u^n}{n!n^2} \simeq \frac{\exp(u)}{u^2} \quad \text{for } u \rightarrow \infty, \quad (69)$$

in the large  $u$  limit. Thus, for large  $t$ , we remain with

$$H(t) \approx H_{eq} - \frac{\tau_1^2}{4\pi t^2} \left(\frac{\epsilon_0}{\Delta_2(\epsilon_1 - \epsilon_0)}\right)^2 \exp\left(-\frac{2t(\epsilon_1 + \epsilon_2)}{\tau_1(\epsilon_2 + \epsilon_0)}\right). \quad (70)$$

Therefore, even though the relaxation time of slab 2 is very small and the overall relaxation time scale is set by  $\tau_1$ , i.e., of the relaxation time of slab 1, the relaxation time of the full Hamaker coefficient scales with  $\tau_1$  but also depends on the dielectric properties of slab 2 through the factor  $\frac{(\epsilon_1 + \epsilon_2)}{(\epsilon_2 + \epsilon_0)}$ .

### C. Havriliak-Negami-type dielectrics

It is possible to obtain non-Debye-like behavior of the dielectric constant by choosing a suitable distribution of polarizability and relaxation times for the associated polarization fields, i.e., by assuming the existence of a distribution,

$$\rho(\chi, \tau) = \sum_{\nu} \delta(\tau - \tau_{\nu}) \delta(\chi - \chi_{\nu}), \quad (71)$$

such that

$$\epsilon(\omega) = \epsilon_0 + \int d\tau d\chi \rho(\chi, \tau) \frac{\chi}{1 + i\omega\tau}. \quad (72)$$

A very general phenomenological formula for the dielectric constant is the Havriliak-Negami formula [30,31],

$$\epsilon(\omega) = \epsilon_0 + \frac{\Delta\epsilon}{[1 + (i\omega\tau_0)^{\alpha}]^{\beta}}, \quad (73)$$

with  $\alpha \in [0, 1]$  and  $\beta > 0$ . The Havriliak-Negami form reduces to the Debye model in the case where  $\alpha = \beta = 1$ . When  $\beta = 1$ , it gives the Cole-Cole formula, and when  $\alpha = 1$ , it gives the Cole-Davidson formula. We should note that the Havriliak-Negami dielectric function can be written explicitly as a superposition of individual Debye relaxations, and thus, the study of this functional form within the dynamical formalism presented here is justified. In terms of our model, this model is composed of polarization fields of the same polarizability

$\chi$  ( $= \Delta\epsilon = \epsilon - \epsilon_0$ ) but with different relaxation times  $\tau$ . This means that the dielectric function can be written in the form

$$\epsilon(\omega) = \epsilon_0 + \Delta\epsilon \int d\tau \rho(\tau) \frac{\chi}{1 + i\omega\tau}, \quad (74)$$

where

$$\rho(\tau) = \frac{1}{\tau\pi} \frac{\left(\frac{\tau}{\tau_0}\right)^{\alpha\beta} \sin(\beta\theta)}{\left[\left(\frac{\tau}{\tau_0}\right)^{2\alpha} + 2\left(\frac{\tau}{\tau_0}\right)^{\alpha} + 1\right]^{\beta/2}}$$

and  $\theta = \tan^{-1}\left[\frac{\sin(\pi\alpha)}{\left(\frac{\tau}{\tau_0}\right)^{\alpha} + \cos(\pi\alpha)}\right]$ . (75)

In the short time limit (corresponding to large  $s$ ), we find

$$\mathcal{L}H(s) \approx \frac{2^{\alpha_1\beta_1 + \alpha_2\beta_2 - 5} \Delta\epsilon_1 \Delta\epsilon_2}{\pi s^{1 + \alpha_1\beta_1 + \alpha_2\beta_2} \tau_{01}^{\alpha_1\beta_1} \tau_{02}^{\alpha_2\beta_2} \epsilon_0^2}, \quad (76)$$

which, after inverting the Laplace transform, gives for short times,

$$H(t) \approx \frac{2^{\alpha_1\beta_1 + \alpha_2\beta_2 - 5} t^{\alpha_1\beta_1 + \alpha_2\beta_2} \Delta\epsilon_1 \Delta\epsilon_2}{\pi \Gamma(\alpha_1\beta_2 + \alpha_2\beta_2 + 1) \tau_{01}^{\alpha_1\beta_1} \tau_{02}^{\alpha_2\beta_2} \epsilon_0^2}, \quad (77)$$

where  $\Gamma(z)$  is the Euler  $\gamma$  function. Thus, we see that exponents  $\alpha$  and  $\beta$  in the Havriliak-Negami formula control the early time growth exponent, which depends on the product of the two  $\alpha\beta$ . We also can verify that this general formula agrees with Eq. (58) in the Debye case where all  $\alpha$  and  $\beta$  are equal to 1.

The late time decay to the equilibrium Hamaker coefficient between two slabs with Havriliak-Negami dielectric functions can be extracted from the small  $s$  expansion of  $\mathcal{L}H(s)$ , and we find

$$H(t) \approx H_{eq} - \frac{\epsilon_0}{\pi} \text{Li}_2[\Delta_1(0)\Delta_2(0)]$$

$$\times \left[ \frac{\beta_1}{(\epsilon_1 + \epsilon_0)\Gamma(-1 - \alpha_1)} \left(\frac{\tau_{01}}{2t}\right)^{\alpha_1} + \frac{\beta_2}{(\epsilon_2 + \epsilon_0)\Gamma(-1 - \alpha_2)} \left(\frac{\tau_{02}}{2t}\right)^{\alpha_2} \right]. \quad (78)$$

Thus, the late time decay is dominated by the term above with the smaller value of  $\alpha_i$ . This form of the Hamaker coefficient relaxation is very different from the pure Debye exponential relaxation, Eq. (64), and obviously shows a long time algebraic tail. Thus, we see that the time needed to relax to equilibrium in this case can be much longer than the microscopic time scales  $\tau_{0i}$  that set the characteristic time of Hamaker coefficient relaxation in the pure Debye model.

## VI. NUMERICAL RESULTS

In this section, we numerically compute the time evolution of the Hamaker coefficient to its equilibrium value by numerically inverting the Laplace transform  $H(s)$ .

### A. Debye dielectrics

The most complete analytical results we have obtained are for the temporal evolution of the Hamaker constant for two Debye dielectrics composed of the same material. We have a



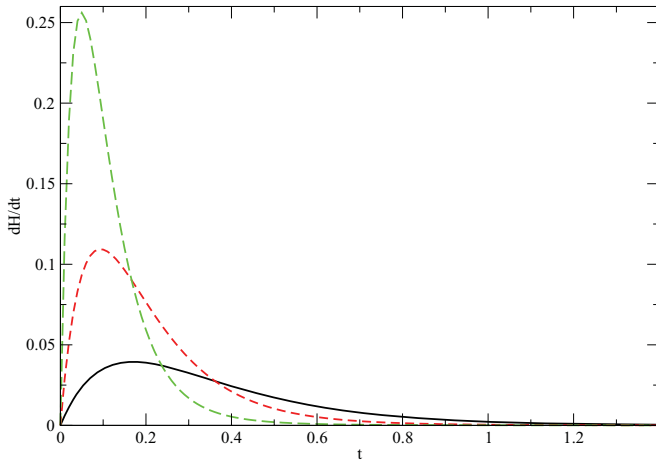


FIG. 1. (Color online) Time derivative of the Hamaker constant  $\dot{H}(t)$  for initially uncorrelated Debye slabs made up from identical media all with  $\tau = 1$  and (i)  $\epsilon = 5\epsilon_0$  (solid black line) (ii)  $\epsilon = 10\epsilon_0$  (short dashed red line), and (iii)  $\epsilon = 20\epsilon_0$  (long dashed green line).

closed form expression for the temporal derivative  $\dot{H}(t)$  given by Eq. (61). In Fig. 1, we have compared the analytical form of Eq. (61) with the result obtained by numerical inversion of the Laplace transform for  $\dot{H}(t)$  for the cases  $\tau = 1$  and  $\epsilon = 5, 10$ , and  $20$ . Only the analytical curves are shown as the accord with the analytical formula is perfect. The figure shows that the temporal derivative increases most rapidly at short times for the systems of higher dielectric constant as predicted by Eq. (56). However, the final relaxation is slowest for the systems of lower dielectric constants.

Now, we consider a pure Debye case where each slab is characterized by a single time scale  $\tau_i$  and dielectric constant  $\epsilon_i$ . We examine the case where  $\epsilon_1 = 10\epsilon_0$  and  $\epsilon_2 = 2\epsilon_0$  in the following three cases where (i)  $\tau_1 = 1, \tau_2 = 1$  (ii)  $\tau_1 = 1, \tau_2 = 0.1$ , and (iii)  $\tau_1 = 0.1, \tau_2 = 1$  (therefore, we are measuring time in units of the longer of times  $\tau_1$  and  $\tau_2$ ). Note that the equilibrium  $H_{eq}$  value of the Hamaker coefficient is the same in all of these cases. In Fig. 2, we plot the functions  $H(t)/H_{eq}$  for each case. We see that, in the last two cases where the shorter time scale  $\tau = 0.1$  is introduced, the approach to the equilibrium value is quicker. However, the quickest relaxation occurs when the shorter of the two relaxation times is associated with the more dilute dielectric medium, i.e., that with the lower dielectric constant.

### B. Havriliak-Negami dielectrics

We now consider the Havriliak-Negami form for the dielectric constant of two media. For simplicity, we consider media of the same type with a fixed  $\Delta\epsilon = \epsilon - \epsilon_0$ , and we use units such that  $\tau_0 = 1$ . The case where  $\Delta\epsilon = 3$  and when  $\beta = 1$  (the Cole-Cole) is shown in Fig. 3 for several values of  $\alpha$ . We see that, as  $\alpha$  decreases from 1 toward 0, the relaxation to the final equilibrium Hamaker coefficient (which is the same for all the curves as the static dielectric constants are the same) becomes increasingly slow as one would expect from Eq. (78). Also, numerical fitting of the late time decay toward 1 in Fig. 3 is compatible with the analytic prediction of the late time exponents given in Eq. (78). The initial behavior

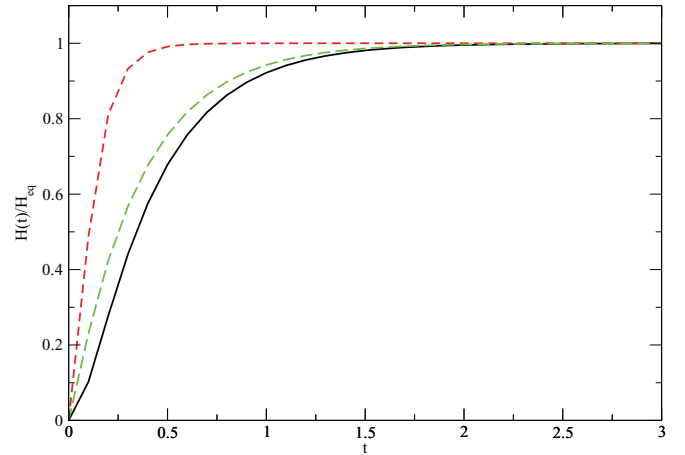


FIG. 2. (Color online) Time evolution of the Hamaker constant normalized by its equilibrium value for two initially uncorrelated slabs of pure Debye-type dielectric slabs 1 and 2 with  $\epsilon_1 = 10\epsilon_0, \epsilon_2 = 2\epsilon_0$ , and relaxation times (i)  $\tau_1 = 1, \tau_2 = 1$  (solid black line) (ii)  $\tau_1 = 1, \tau_2 = 0.1$  (short dashed red line), and (iii)  $\tau_1 = 0.1, \tau_2 = 1$  (long dashed green line).

is the inverse, the systems with smallest  $\alpha$  have a  $H(t)$  that grows faster in accordance with the predictions of Eq. (77). An interesting feature of Fig. 3 is that all the curves cross each other at the same isosbesticlike point in time at around  $t = 0.25$ .

In Fig. 4, we show the temporal evolution of  $H(t)$  for Cole-Davidson-type dielectrics for different values of  $\beta$  but with the same dielectric constants. As predicted from Eq. (77), the systems with the smaller values of  $\beta$  show the most rapid growth in  $H(t)$  at short times, but in contrast with the Cole-Cole case, these systems also converge most rapidly to the equilibrium value, and there is no isosbesticlike point in this case.

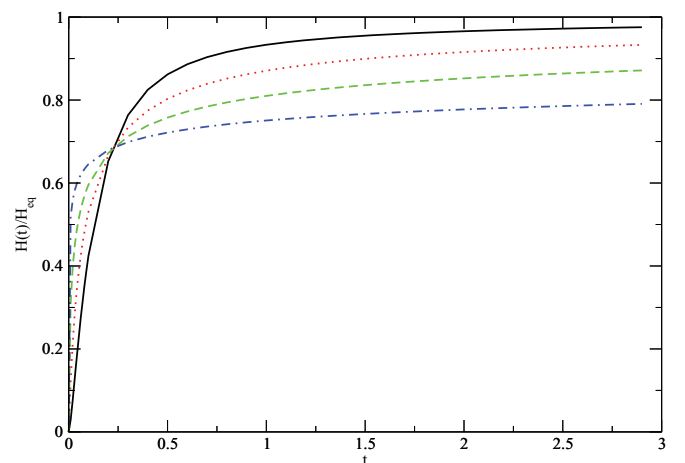


FIG. 3. (Color online) Time evolution of the Hamaker constant normalized by its equilibrium value for two identical initially uncorrelated Cole-Cole (Havriliak-Negami with  $\beta = 1$ ) dielectric slabs 1 and 2 with  $\epsilon = 10\epsilon_0$  and characteristic relaxation times  $\tau = 1$  for different values of  $\alpha$ : (i)  $\alpha = 0.8$  (solid black line), (ii)  $\alpha = 0.6$  (red short dashed line), (iii)  $\alpha = 0.4$  (green long dashed line), and (iv)  $\alpha = 0.2$  (blue dot-dashed line).

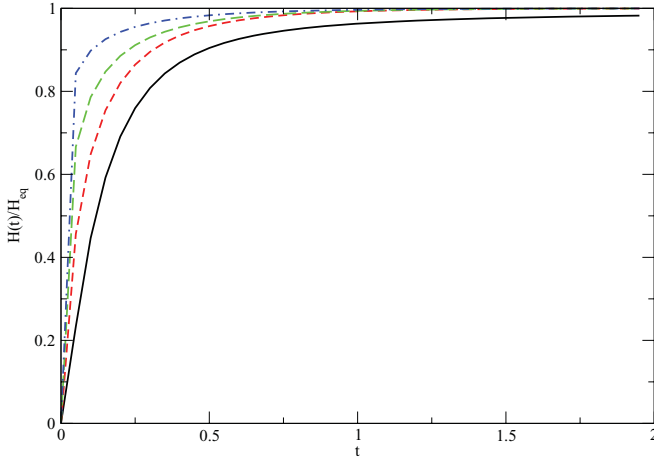


FIG. 4. (Color online) Time evolution of the Hamaker constant normalized by its equilibrium value for two identical initially uncorrelated Cole-Davidson (Havriliak-Negami with  $\alpha = 1$ ) dielectric slabs 1 and 2 with  $\epsilon = 10\epsilon_0$  and characteristic relaxation times  $\tau = 1$  for different values of  $\alpha$ : (i)  $\beta = 0.8$  (solid black line), (ii)  $\beta = 0.6$  (red short dashed line), (iii)  $\beta = 0.4$  (green long dashed line), and (iv)  $\beta = 0.2$  (blue dot-dashed line).

## VII. DISCUSSION

We have formulated a theory describing how the thermal van der Waals force between two dielectric objects evolves with time toward its equilibrium value. As an example of a general approach, we analyze the dynamics of the thermal Casimir or zero Matsubara frequency van der Waals interactions between two slabs brought into close proximity from an infinite separation, corresponding to the limit of the nonquantum part of the total van der Waals interaction. Despite these simplifications, our calculations give a useful intuition about fluctuation induced forces out of equilibrium. The particular strength of our approach is that the Laplace transform (with respect to time) of the dynamical force can be expressed in terms of equilibrium results available from a wide range of equilibrium methods.

We show that, for the zero frequency Matsubara term in planar geometry, the coarse-grained dynamics of the interacting dielectric media only enters via the Hamaker coefficient, whereas, the dependence on the spacing between the dielectric interfaces remains unchanged and coincides with the equilibrium scaling. This is a fundamental result but is limited to the high temperature part of the Casimir interaction. However, it is this part of the van der Waals interaction that is most important in (bio)colloid systems and nanosystems.

The time evolution of the thermal van der Waals force between two surfaces of area  $S$  at temperature  $T$  separated by  $L$ ,  $f(L, t, T)$ , then is given by

$$\langle f(L, t, T) \rangle = -\frac{TS}{L^3} H(t). \quad (79)$$

Whereas, the separation into an equilibrium separation scaling and a nonequilibrium Hamaker coefficient appears to be universal, the form of the time dependence of the Hamaker coefficient  $H(t)$  is specific and strongly is dependent on the dielectric response of the two bounding dielectric surfaces.

We have shown that, for Debye-type dielectric responses of the interacting materials with a relaxation time of  $\tau$ , the scaling of the Hamaker coefficient for short times is given by

$$H(t) \sim C_{<} t^2,$$

whereas, in the asymptotic time regime, we obtain  $H(t) \approx H_{eq} - \frac{C_{>}}{t^2} \exp(-\frac{2t}{\tau})$ . The time scale of these nonequilibrium effects in thermal Casimir interactions, thus, is determined by the (longest) dielectric relaxation time of the interacting media. This would render the practical observation of these nonequilibrium effects difficult in general, however, it may be possible to observe temporal evolution of the force for systems with extremely long relaxation times, such as polymers, colloids, and glassy systems.

Indeed, in the case of the non-Debye-like response that we have studied, i.e., the Havriliak-Negami dielectric response function (which commonly is applied to polymeric systems), we obtain a completely different asymptotic behavior of the Hamaker coefficient. Instead of an exponential scaling with time, a long algebraic tail is obtained instead. We derived the scaling form

$$H(t) \approx H_{eq} - \left(\frac{C_{>}}{2t}\right)^\alpha,$$

in the late time asymptotic regime where  $\alpha$  is one of the scaling exponents in the Havriliak-Negami dielectric response function. This long time algebraic tail in the relaxation of the nonequilibrium Hamaker coefficient leads to the conclusion that, for this particular dielectric model, it might be possible to observe long time nonequilibrium effects.

Variation in the form of the time evolution of the nonequilibrium Hamaker coefficient with the nature of the dielectric response of the interacting media makes it possible or, indeed, quite probable that, in some experiments where, at least indirectly, time dependent van der Waals interactions are probed, these effects may complicate a clear cut interpretation of the experiments. This would be especially true for the tapping mode atomic force microscopy (AFM) measurements of macromolecular interactions or any other situation involving time varying separation between the interacting dielectric interfaces. The AFM tapping mode vibration of the interacting surfaces together with the time evolution of the appropriate nonequilibrium Hamaker coefficients would lead to a nontrivial modification of the dependence of the magnitude of the van der Waals interaction on the dielectric characteristics of the interacting surfaces. In order to consider more experimentally appropriate geometries, it would be interesting to extend the results here to, for instance, sphere plane and sphere sphere geometries. In these systems, the corresponding static problems will involve more than one length scale, and the simple scaling seen for slab geometries will break down. Our results on slabs show that, even when the equilibrium problem can be treated in the pairwise limit, the dynamics involves many body effects. The standard approximations applied for equilibrium Casimir forces may well break down for the study of relaxation to equilibrium, and thus, one may have to resort to numerical methods [32–34] to compute the Laplace transform of the general result, Eq. (38), and then to numerically invert the Laplace transform to obtain the temporal dependence.

The nonequilibrium effects considered in this paper could possibly complicate the quantitative interpretation of experiments on van der Waals interactions in terms of the dielectric susceptibilities of the interacting interfaces. In order to interpret these experiments, one, thus, possibly would need to incorporate the theory presented above to extract quantitative measures of time-averaged van der Waals interactions. Nonequilibrium effects also potentially could be important for the functioning of Casimir ratchet devices where oscillating surfaces are used to obtain directed motion via the Casimir effect [35].

Another possible area of further analysis would be a comparison between these dynamical nonequilibrium van der Waals forces with the hydrodynamic drag forces of Stefan type. These forces have their origins in the flow of fluid from between the two interacting surfaces as they are pushed together [36]. The time dependence of the nonequilibrium van der Waals interaction and the specific model studied here also could be related to and could shed light on the phenomenon of drag induced on moving bodies by Casimir forces [37–40].

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