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Dielectric properties of classical and quantized ionic fluids

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We study time-dependent correlation functions of classical and quantum gases using methods of equilibrium statistical mechanics for systems of uniform as well as nonuniform densities. The basis for our approach is the path integral formalism of quantum mechanical systems. With this approach the statistical mechanics of a quantum mechanical system becomes the equivalent of a classical polymer problem in four dimensions where imaginary time is the fourth dimension. Several nontrivial results for quantum systems have been obtained earlier by this analogy. Here, we will focus upon the presence of a time-dependent electromagnetic pair interaction where the electromagnetic vector potential that depends upon currents, will be present. Thus both density and current correlations are needed to evaluate the influence of this interaction. Then we utilize that densities and currents can be expressed by polarizations by which the ionic fluid can be regarded as a dielectric one for which a nonlocal susceptibility is found. This nonlocality has as a consequence that we find no contribution from a possible transverse electric zero-frequency mode for the Casimir force between metallic plates. Further, we establish expressions for a leading correction to *ab initio* calculations for the energies of the quantized electrons of molecules where now retardation effects also are taken into account.

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I. INTRODUCTION

Feynman found that the partition function of a quantum mechanical particle can be represented as a path integral in imaginary time that stretches from time 0 to time $\beta=1/k_BT$ where k_B is the Boltzmann constant and T is temperature [1]. With this a particle system in 3 dimensions becomes a "classical" polymer problem in 4 dimensions where the fourth dimension is imaginary time. The polymers are periodic in the fourth dimension such that end points at times 0 and β are tied together. To take the statistics or symmetry properties of fermions and bosons into account the end points of different polymers are tied together to form polymer coils. The path integral can also be regarded as a random walk problem whose properties has been studied and analyzed, and functional integration of it has been used to solve problems in statistical mechanics [2].

It was realized by Høye and Stell and by D. Chandler *et al.* that the polymer or a random walk picture could be utilized to evaluate the equilibrium properties of a fluid of quantized polarizable particles using methods of classical statistical mechanics [3,4]. Brevik and Høye then considered a pair of polarizable particles to evaluate their net attraction known as the Casimir force or van der Waals force [5] using methods of classical statistical mechanics as an alternative to the usual field theoretical approach to this problem. It was found that time dependent or retarded potentials could be used by this approach too. Further this approach was extended to the evaluation of the Casimir force between a pair of parallel dielectric plates to recover the well known Lifshitz result [6]. Later, this statistical mechanical derivation also gave new insight into a controversy with an ambiguity in the Lifshitz result for metallic surfaces [7]. This controversy has been heavily debated in later years [7,8]. In one way a zero-frequency transverse electric (TE) mode remains by which there is almost no temperature dependence of the Casimir force for low temperatures or small plate separations. By the statistical mechanical approach such a mode is clearly not present during derivations. To illustrate this absence of the TE mode a simple harmonic oscillator model with two oscillators interacting with a third one was studied in Ref. [7]. The absence of the TE mode is also supported by the works by Jancovici and Šamaj [9] and by Buenzli and Martin [10–12]. But the results of these latter works are restricted to the classical limit $\beta\rightarrow 0$. As a model for the metal plates they consider a classical Coulomb gas or plasma of free electrons where classical Debye-Hückel theory is used. The recent results by Høye [13] for ionic systems for more general densities and by Høye and Brevik [14] for dielectric plates with free charges are consistent with this.

In Ref. [12], the fully quantized version with the magnetic interactions of radiation included was also considered. With magnetic interactions it was found that the zero-frequency TE mode is still absent. The new feature of the present work in this respect is that the same result is derived for all temperatures.

However, recent experiments by Decca *et al.* seem to exclude the absence of the zero-frequency TE mode with high confidence [15]. More details on the experimental situation can be found in the review by Klimchitskaya *et al.* [16]. Thus there is a contradiction between experimental results and various theoretical results for media with free charges such as metals. This shows a need for further investigations on this issue.

Chandler and Wolynes considered the path integral formulation of fermion and boson fluids noting a very general isomorphism with a classical system of interacting polymers [17]. Further studies of boson and fermion fluids based on this isomorphism were made by Høye and Stell [18] where the equivalence of the path integral of quantized fermion and boson systems with classical polymer problems was noted. Due to the symmetry requirements of such fluids (exchange

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of identical particles) the equivalent polymers will be linked into polymer coils. With no pair interaction these coils form an ideal gas from which the well known pressures of the ideal fermion and boson gases are recovered.

The pair correlation function of free fermions and bosons in space and imaginary time can thus be evaluated using the polymer picture, and pair interactions can be taken into account. In Ref. [18] these were considered to be weak and of long range, and γ-ordering, where γ is the inverse range of interaction, was considered [19,20]. For Helmholtz free energy the leading order contribution beyond mean field theory is then the sum of ring graphs. The corresponding contribution to the correlation function or structure factor is the sum of chain graphs. These statistical mechanical methods have close relations to those developed by Alastuey, Ballenegger, Cornu, and Martin [21] who consider cluster expansions in terms of Mayer graphs and perform the resummation needed to replace the Coulomb potential with its shielded version. There is also some relation to the work by Alastuey and Martin who also note the classical analogy [22]. Finally, there is certain similarity to the recent work by Šamaj who considers current-current correlation functions in media coupled to radiation [23]. However, the formalism he uses is different and is based upon previous works by Rytov by using a macroscopic theory of thermal fluctuations of the electromagnetic field in conductors and dielectric media [24].

In a recent work, we investigated how dynamic properties in the linear response regime could be described by applying the methods of classical statistical mechanics upon the path integral [25]. One feature is that dynamic properties, that otherwise require kinetic theory, are kept even after the classical limit has been taken. This was verified by comparing with known results of kinetic theory of which the ideal gas free motion is the most simple. Then the gas particles were perturbed by a pair interaction like the electrostatic Coulomb interaction, and the γ-ordering mentioned above was applied. Results based upon the Vlasov equation for a classical plasma was recovered in this way [26]. Also the corresponding version with quantized electrons was in full agreement with an earlier result for small wave vectors [27]. Based on this and previous knowledge from use of γ-ordering on classical fluids there was reason to expect that these methods would work well when applied to quantum mechanical systems more generally. Thus energy corrections to *ab initio* computations of molecular energies with the Hartree-Fock (HF) or density-functional theory (DFT) [28] as basis were established too for systems of nonuniform density with static or time independent interactions.

In this work results of Ref. [25] will be extended to the non-trivial situation with radiating electromagnetic interaction between charged particles. Due to the electromagnetic vector potential it is clear that current correlations are needed in some way [12]. Here, we are able to incorporate these correlations in the statistical mechanical formalism. Further the ionic fluid is identified with an equivalent polarizable fluid with a nonlocal dielectric tensor. With this we find there is no contribution to the Casimir force between metallic plates from a possible zero-frequency TE mode. Further the results of Ref. [25] for the energy correction to molecular energies are extended to the situation with radiating electromagnetic interaction where retardation effects are present. This energy correction can be regarded as a Casimir energy due to non-local correlations throughout the system since this energy is like the one that creates the Casimir force between dielectric or metallic plates.

In Sec. II, it is demonstrated by a simple example how the integrand of the path integral for a vector potential is determined by the Lagrangian of the system as expected. In Sec. III, the radiating electromagnetic interaction between charged particles is considered and explicit expressions for this interaction is established.

In Sec. IV, the polarization is introduced, and particle densities and currents are related to it. In this way an equivalent polarizable fluid is obtained. Further the interaction between charges through the electromagnetic scalar and vector potentials is replaced by the radiating dipole-dipole interaction.

In Sec. V, density, current, and polarization correlations of an uniform ideal classical gas are studied. Then the correlation functions of the components of the polarization vector can be directly related to the susceptibility tensor of the system, and explicit expressions are obtained. The susceptibility becomes nonlocal in space, and thus it does not support the presence of a zero-frequency TE mode.

In Sec. VI, the corresponding quantum mechanical correlation functions are obtained for fermions and bosons, and general expressions for nonuniform systems are considered. Then the correlation functions can be constructed from the one-particle eigenstates that can be obtained by the HF or DFT methods.

In Sec. VII, the quantum mechanical expressions are considered for a uniform system. Then Fourier transform in space can be used, and simpler expressions are obtained. In the limit $\hbar \to 0$ these expressions can be identified in a straightforward way with the classical ones of Sec. V.

In Sec. VIII, a leading energy correction to molecular energies by *ab initio* computations is established. This energy contribution can be regarded as a bulk Casimir energy. The results of this section extends those of Ref. [25] where only electrostatic interactions and density correlations were used. In Sec. VIII, radiating dipole interaction and polarization correlations are used, but for electrostatic interactions the results are the same as those of the reference.

II. VECTOR POTENTIAL AND PATH INTEGRAL

According to Ref. [1] the action that forms the exponent of the integrand in the path integral is determined by the Lagrangian of the system. This also holds with the electromagnetic vector potential. We want to demonstrate this explicitly by considering a simple one dimensional example with Lagrangian

$$L = \frac{1}{2}\dot{x}^2 + \dot{x}A. \tag{1}$$

The generalized momentum is $p = \partial L / \partial \dot{x} = \dot{x} + A$ by which the Hamiltonian becomes

$$H = p\dot{x} - L = \frac{1}{2}(p - A)^2. \tag{2}$$

With imaginary time $\tau = it$ the corresponding Schrödinger equation becomes (with $\hbar = 1$ and $m = 1$)

$$\frac{1}{2}\left(\frac{1}{i}\frac{\partial}{\partial x} - A\right)^2 \psi = -\frac{\partial \psi}{\partial \tau}. \tag{3}$$

Its solution with $\psi(x) = \delta(x)$ for $\tau = 0$ is

$$\psi = \frac{1}{\sqrt{2\pi\tau}}\exp(\tau L) \tag{4}$$

provided τ is small (or A is constant). This is in accordance with Eq. (1), which can be written

$$L = \frac{1}{2}\left(\frac{x}{t}\right)^2 + \frac{x}{t}A = \frac{1}{\tau}\left(-\frac{x^2}{2\tau} + ixA\right). \tag{5}$$

In general there are other terms in L. However, for a small step $\tau \to 0$ in imaginary time, expression Eq. (4) is still the solution.

III. ELECTROMAGNETIC INTERACTION

With electromagnetic scalar and vector potentials $\Phi(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$ the contribution to the Lagrangian from interaction with particles at positions $\mathbf{r}_i$ is

$$L_{int} = q\sum_i \left[-\Phi(\mathbf{r}_i,t) + \frac{1}{c}\mathbf{v}_i \cdot \mathbf{A}(\mathbf{r}_i,t)\right], \tag{6}$$

where q is particle charge, $\mathbf{v}_i = \dot{\mathbf{r}}_i$ is velocity of particle i, and c is velocity of light. Here Gaussian units are used.

The free electromagnetic field also contributes to the Lagrangian. But it is bilinear in the field by which it is equivalent to a set of harmonic oscillators. Thus as has been implicitly understood earlier, these degrees of freedom can be integrated out explicitly [5–7]. The net result is that the free field contribution is unaffected by the presence of the particles while L_{int} will be a sum of pair interactions mediated by the electromagnetic field. In addition there can be external static fields such as the electrostatic one from atomic nuclei. With external fields that vary in space, the system will be non uniform such as the electron clouds of molecules.

The fields in Eq. (6) (apart from external ones) are created by the charged particles of the system. (Possible contributions from magnetic moments are disregarded here.) These fields are obtained by solving Maxwell's equations of electromagnetism

$$\nabla \mathbf{E} = 4\pi\rho$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \mathbf{B} = 0, \tag{7}$$

where $\mathbf{E}$, $\mathbf{B}$, ρ, and $\mathbf{j}$ are electric field, magnetic field, charge density, and current density respectively. In terms of the electromagnetic potentials one further has

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{8}$$

With this one obtains the usual wave equations

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Phi = -4\pi\rho$$

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{A} = -\frac{4\pi}{c}\mathbf{j} \tag{9}$$

provided the Lorentz gauge condition

$$\frac{1}{c}\frac{\partial \Phi}{\partial t} + \nabla\mathbf{A} = 0 \tag{10}$$

is used. We find it convenient to use this gauge to get the solution for the fields on a simple form. However, one may use a different gauge by adding contributions $-c^{-1}\partial\chi/\partial t$ and $\nabla\chi$ to the fields Φ and $\mathbf{A}$ respectively where χ is a scalar function. By partial integration and use of the condition of charge conservation given by Eq. (14) below, it is seen that this will not change the total interaction given by Eq. (20) in the next section.

By Fourier transform in both time and space one finds the solution

$$\hat{\Phi}(\mathbf{k},\omega) = \hat{\psi}(k,\omega)\hat{\rho}$$

$$\hat{\mathbf{A}}(\mathbf{k},\omega) = \frac{1}{c}\hat{\psi}(k,\omega)\hat{\mathbf{j}}, \tag{11}$$

where the hat denotes Fourier transform with respect to time ($k = |\mathbf{k}|$), and where

$$\hat{\psi}(k,\omega) = \frac{4\pi}{k^2 - (\omega/c)^2}. \tag{12}$$

In $\mathbf{r}$-space the $\hat{\psi}$ becomes ($r = |\mathbf{r}|$)

$$\hat{\psi}(r,\omega) = \frac{e^{-i(\omega/c)r}}{r} \tag{13}$$

for $\mathrm{Im}(\omega) < 0$. It can be noted that this solution also fulfills the gauge condition Eq. (10) due to the condition of charge conservation

$$\frac{\partial \rho}{\partial t} + \nabla\mathbf{j} = 0. \tag{14}$$

The $\hat{\psi}(r_{ij},\omega)$ will be the Fourier transform of the interaction between a pair of unit charges located at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. According to Eq. (6) the current also contributes to the interaction. The current density from a charge density $\rho(\mathbf{r})=q\delta(\mathbf{r}-\mathbf{r}_0)$ is $\mathbf{j}=q\mathbf{v}\delta(\mathbf{r}-\mathbf{r}_0)$. Thus the full pair interaction becomes $(\mathbf{v}=\dot{\mathbf{r}})$

$$\varphi(12,t)=q^2\psi(r_{12},t)\left(1-\frac{\dot{\mathbf{r}}_1\cdot\dot{\mathbf{r}}_2}{c^2}\right). \tag{15}$$

With the path integral imaginary time is used. However, we only need its Fourier transform which according to Eq. (A8) in Appendix immediately follows from Eq. (13) by replacing ω with $K=i\hbar\omega$. Thus

$$\hat{\psi}(r,K)=\frac{e^{-Kr/(\hbar c)}}{r}, \tag{16}$$

where $K=2\pi n/\beta$ with n integer. However, in Eq. (16) the K should be interpreted as $K=|K|$ (along the real axis). The reason is that one can put $K=(\varepsilon^2+K^2)^{1/2}$ with $\varepsilon\to 0$ and then take the continuation of this function when passing between the branch points $K=\pm i\varepsilon$ [5]. Further, for a uniform system the Fourier transform Eq. (12) can be used with $K=i\hbar\omega$ to get

$$\hat{\psi}(k,K)=\frac{4\pi}{k^2+K^2/(\hbar c)^2}. \tag{17}$$

IV. EQUIVALENT POLARIZABLE FLUID

By γ-ordering the leading contribution to the pair correlation function beyond the reference system is given by the chain graphs with potential bonds and hypervertices [19,20]. The contribution to the free energy is given by the corresponding ring graphs. In both cases the vertices of the graphs are hypervertices commonly formed by the density-density correlation function of a reference system. However, in the present case velocities are involved in the pair interaction. We will find that the classical polymer picture of the path integral can be extended to this situation. By this both density-current and current-current correlations will be needed to obtain all contributions from the vertices of the graphs. This will give a 4×4 matrix of correlation functions to be used at each vertex. However, this can be simplified. On physical grounds there is reason to expect an ionic system to be essentially a dielectric one. We will show that this is actually the situation with a dielectric constant that in general is a nonlocal tensor.

A dielectric fluid can be described by the polarization $\mathbf{P}=\mathbf{P}(\mathbf{r},t)$. From Maxwell's equations for dielectric media one finds that induced charge density ρ and current density $\mathbf{j}$ can be expressed as

$$\rho=-\nabla\mathbf{P}\quad\text{and}\quad\mathbf{j}=\frac{\partial\mathbf{P}}{\partial t}. \tag{18}$$

It is easily seen that these relations fulfill Eq. (14) for charge conservation.

With relations Eq. (18) it will be possible to relate the various correlation functions to a susceptibility tensor of the system. This will be considered in the following sections. Below in this section we will show that the ionic interaction can be replaced with the one of a dielectric fluid.

On the microscopic level the charge and current densities can be written $(\mathbf{r}_i=\mathbf{r}_i(t))$

$$\rho(\mathbf{r},t)=q\sum_i\delta(\mathbf{r}-\mathbf{r}_i)\quad\text{and}\quad\mathbf{j}(\mathbf{r},t)=q\sum_i\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i). \tag{19}$$

By integration of Eq. (6) over imaginary time $\tau(=it/\hbar)$ the total interaction of polymer pairs in the path integral is obtained. With Eqs. (11), (13), and (19) this can be written

$$U=-\int_0^\beta\int_0^\beta L_{int}d\tau_1d\tau_2=\int_0^\beta\int_0^\beta\int\int\left[\rho_1\psi(r_{12},t_{12})\rho_2-\frac{1}{c^2}\mathbf{j}_1\psi(r_{12},t_{12})\mathbf{j}_2\right]d\mathbf{r}_1d\mathbf{r}_2d\tau_1d\tau_2, \tag{20}$$

where $\rho_i=\rho(\mathbf{r}_i,t_i)$, $\mathbf{j}_i=\mathbf{j}(\mathbf{r}_i,t_i)$ $(i=1,2)$, $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$, and $t_{12}=t_2-t_1$. Here it should be noted that the time dependence in imaginary time is very different from the one in real time. However, their Fourier transforms are the same as mentioned in connection with Eq. (16) [5]. Thus for simplicity we here keep the same notation for functions in real and imaginary time.

By use of Eq. (18) the charge and current densities in expression Eq. (20) can be substituted by the polarization. Partial integrations then give

$$U=\int_0^\beta\int_0^\beta\int\int\left[\frac{\partial^2\psi}{\partial x_{1i}\,\partial x_{2j}}P_{1i}P_{2j}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t_1\,\partial t_2}\mathbf{P}_1\cdot\mathbf{P}_2\right]d\mathbf{r}_1d\mathbf{r}_2d\tau_1d\tau_2, \tag{21}$$

where summation convention is used $(\Sigma_{ij},i,j=1,2,3)$. With this expression for U the total interaction is written in terms of the radiating dipole-dipole interaction integrated together with the polarization. Thus for a pair of dipole moments $\mathbf{s}_1$ and $\mathbf{s}_2$ this will represent a pair interaction

$$\varphi(12,t_{12})=\frac{\partial^2\psi}{\partial x_{1i}\,\partial x_{2j}}s_{1i}s_{2j}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t_1\,\partial t_2}\mathbf{s}_1\mathbf{s}_2. \tag{22}$$

Its Fourier transform with respect to (relative) time is

$$\hat{\varphi}(12,\omega)=\frac{\partial^2\hat{\psi}}{\partial x_{1i}\,\partial x_{2j}}s_{1i}s_{2j}-\left(\frac{\omega}{c}\right)^2\hat{\psi}\mathbf{s}_1\cdot\mathbf{s}_2. \tag{23}$$

For uniform systems the Fourier transform with respect to space is used. One finds

$$\hat{\varphi}(12,\omega)=\hat{\psi}(k,\omega)\left[(\mathbf{k}\mathbf{s}_1)(\mathbf{k}\mathbf{s}_2)-\left(\frac{\omega}{c}\right)^2\mathbf{s}_1\cdot\mathbf{s}_2\right]. \tag{24}$$

With $\hat{\psi}$ given by Eq. (12) this expression is precisely the Fourier transform of the radiating dipole-dipole interaction as given by Eq. (6.3) in Ref. [6]. To evaluate the leading contributions from chain graphs and ring graphs we need the susceptibility tensor related to dipole-dipole correlations. With Eq. (18) these correlations can be related to density and current correlations.

V. CLASSICAL CASE

In this section, we will obtain the susceptibility for the situation where the reference system is an ideal classical gas. To do so, we utilize the well-known dynamical properties for this situation where different particles are uncorrelated. Thus we are left with the self-correlation. For free particle motion this will be

$$n(t,r) = \rho \int \delta(\mathbf{r} - \mathbf{v}t) f_0(v) d\mathbf{v}, \tag{25}$$

where $f_0(v)$ is Maxwell's velocity distribution

$$f_0(v) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta m v^2/2}. \tag{26}$$

Note that here and below, we find it convenient to redefine ρ to mean particle density with corresponding redefinitions of current and polarization.

In this section, we will further limit ourselves to the uniform case, and Fourier transform of Eq. (25) gives

$$\tilde{n}(t,k) = \rho \int f_0 e^{i\mathbf{kv}t} d\mathbf{v}. \tag{27}$$

According to Kubo the corresponding response function is given by $(t>0)$ [29]

$$\tilde{\phi}(t,k) = -\beta \frac{\partial}{\partial t} \tilde{n}(t,k) = -\beta\rho \int i\mathbf{kv} f_0 e^{i\mathbf{kv}t} d\mathbf{v}. \tag{28}$$

Finally, Fourier transform with respect to time gives $[\mathrm{Im}(\omega)<0]$

$$\begin{aligned}\hat{\phi}(\omega,k) &= \int_0^\infty \tilde{\phi}(t,k) e^{-i\omega t} dt = -\beta\rho \int \frac{i\mathbf{kv} f_0 d\mathbf{v}}{i\omega - i\mathbf{kv}} \\ &= -\frac{1}{2}\beta\rho \int \left[\frac{\mathbf{kv}}{\omega - \mathbf{kv}} - \frac{\mathbf{kv}}{\omega + \mathbf{kv}}\right] f_0 d\mathbf{v} \\ &= -\beta\rho \int \frac{(\mathbf{kv})^2 f_0 d\mathbf{v}}{\omega^2 - (\mathbf{kv})^2},\end{aligned} \tag{29}$$

where the symmetry of the Maxwell distribution f_0 is utilized.

The velocity-velocity correlation function is now obtained by multiplying the integrand of Eq. (25) with $v_i v_j$ where $v_i (i=1,2,3)$ is the component of the velocity in direction i. Its Fourier transform is

$$\tilde{n}_{ij}(t,k) = \rho \int v_i v_j f_0 e^{i\mathbf{kv}t} d\mathbf{v}. \tag{30}$$

To obtain the appropriate response function it now turns out that a subtle and delicate problem arises at $t=0$. Consider the Hamiltonian Eq. (2) with $-pF(t)$ as perturbing term [i.e., $F(t)=A$]. According to Kubo [29] and thus from Eq. (A1) in Appendix this term will again perturb p by an amount

$$\langle \Delta p \rangle = \int_\infty^t \phi_{pp}(t-t') F(t') dt, \tag{31}$$

where the ϕ_{pp} is the momentum-momentum response function. However, for $F(t)=0$ (no perturbation) the momentum is the same as the velocity by which ϕ_{pp} in accordance with Eq. (A7) will be the derivative of Eq. (30) (for $t \geq 0$). It turns out that we need the function that gives the perturbation in velocity, i.e., we need $\langle \Delta \dot{x} \rangle = \langle \Delta p \rangle - F(t)$ [see above Eq. (2)]. This will also be consistent with the quantum mechanical path integral. The required modification is then obtained by including a δ-function at $t=0$. This δ-function would also be the derivative of the jump in $\tilde{n}_{ij}$ at $t=0$ if $\tilde{n}_{ij}$ were put equal to zero for $t<0$. Thus the sought response function is

$$\begin{aligned}\tilde{\phi}_{ij}(t,k) &= -\beta \frac{\partial}{\partial t} \tilde{n}_{ij}(t,k) - \beta \tilde{n}_{ij}(t,k)\delta(t) \\ &= -\beta\rho \int v_i v_j [i\mathbf{kv} e^{i\mathbf{kv}t} + \delta(t)] f_0 d\mathbf{v}.\end{aligned} \tag{32}$$

Fourier-transformed with respect to t it becomes

$$\begin{aligned}\hat{\phi}_{ij}(\omega,k) &= -\beta\rho\omega \int \frac{v_i v_j f_0 d\mathbf{v}}{\omega - \mathbf{kv}} = -\frac{1}{2}\beta\rho\omega \int \left[\frac{1}{\omega - \mathbf{kv}}\right. \\ &\quad \left. + \frac{1}{\omega + \mathbf{kv}}\right] v_i v_j f_0 d\mathbf{v} = -\beta\rho\omega^2 \int \frac{v_i v_j f_0 d\mathbf{v}}{\omega^2 - (\mathbf{kv})^2}.\end{aligned} \tag{33}$$

The response function Eq. (33) can be directly related to the corresponding function P_{ij} for the polarization, which with interaction Eq. (24) is proportional to the susceptibility χ_{ij} [30]. In Ref. [30] the dipolar interaction is modified with a parameter Θ to create a family of mean field results for the dielectric constant. Interaction Eq. (24) corresponds to $\Theta = 1$. One finds

$$\chi_{ij} = 4\pi q^2 P_{ij}, \tag{34}$$

where q is the electric charge of each particle. From Eq. (18) one can conclude

$$\hat{P}_{ij}(\omega,k) = \frac{1}{\omega^2} \hat{\phi}_{ij}(\omega,k) = -\beta\rho \int \frac{v_i v_j f_0 d\mathbf{v}}{\omega^2 - (\mathbf{kv})^2}, \tag{35}$$

which also is consistent with the other relation $\hat{\phi}(\omega,k) = \Sigma_{ij} k_i k_j \hat{P}_{ij}$ with $\hat{\phi}$ given by Eq. (29). (These relations follow from Fourier transforms with $\mathbf{r} = \mathbf{r_2} - \mathbf{r_1}$ and $t = t_2 - t_1$.)

Expression Eq. (35) together with Eq. (34) gives the susceptibility of the ionic fluid. Due to its k-dependence the χ_{ij} is clearly nonlocal. It is now of interest to investigate its small ω properties in view of the extensive discussions about the possible contribution from of a TE zero mode $(\omega=0)$ to the Casimir force between metallic plates at finite temperatures [8]. First of all with $\omega=0$ we have the electrostatic situation where only the first term of the interaction Eq. (24) is present. Then only the response function

$$\hat{\phi}(0,k)=\sum_{ij}k_ik_j\hat{P}_{ij}=\beta\rho\int f_0 d\mathbf{v} \tag{36}$$

is needed. This gives a longitudinal susceptibility

$$\tilde{\chi}(k)=4\pi q^2\frac{\hat{\phi}(0,k)}{k^2}=\frac{\kappa^2}{k^2}, \tag{37}$$

where κ is the inverse Debye shielding length with

$$\kappa^2=4\pi\beta\rho q^2. \tag{38}$$

This is nothing but the electrostatic result obtained earlier [13,14].

However, for nonzero frequencies this is modified. If the k-dependence is neglected one from Eqs. (34) and (35) easily finds [with $\langle v_x^2\rangle=1/(m\beta)$]

$$\chi_{xx}=\chi_{yy}=\chi_{zz}=-\frac{\omega_p^2}{\omega^2},\quad \text{with}\quad \omega_p^2=\frac{4\pi\rho q^2}{m}. \tag{39}$$

This is the well-known susceptibility of the plasma model where ω_p is the plasma frequency. A problem with this result is that it suggests that the last term of the interaction Eq. (24) also may contribute for $\omega=0$ since it then stays finite in the limit $\omega\to 0$. This again is the basis for the extensive discussion about the possible contribution from a TE zero mode to the Casimir force. Thus for small k we will consider the integral Eq. (35) more closely in the limit $K=i\hbar\omega\to 0$

With polar coordinates one has $v_z=v\cos\theta$, and with new variable of integration $x=\cos\theta$ we with Eq. (35) will get the integral (with z axis along $\mathbf{k}$)

$$I=\int_{-1}^{1}\frac{dx}{1+(ax)^2}=\frac{1}{a}\arctan a\to\begin{cases}\pi/a, & a\to\infty\\ 1, & a\to 0\end{cases}, \tag{40}$$

where $a=\hbar kv/K$. With this we can obtain the average of the diagonal elements of the polarizability tensor as $(K=i\hbar\omega)$

$$\chi=\frac{1}{3}(\chi_{xx}+\chi_{yy}+\chi_{zz})=\frac{\omega_p^2}{\omega^2}I\sim\begin{cases}1/\omega k, & \omega/(kv)\to 0\\ 1/\omega^2, & \omega/(kv)\to\infty\end{cases}, \tag{41}$$

where v will be an average velocity of magnitude $v\sim(\beta m)^{-1/2}\sim T^{1/2}$.

Result [Eq. (41)] is similar to the Drue model for metals where $\chi\sim 1/(\omega^2+i\gamma\omega)$. Thus, we can conclude that there will be no zero frequency TE mode contribution. Of course there might be a contribution for $k=0$, but if so, this would be of measure zero. Now at $T=0$ the $v=0$ for a classical gas. But, in the quantum mechanical case, $v>0$ also at $T=0$ for fermions. For bosons in the condensed phase one will again have $v=0$ at $T=0$. On the other hand there is also a self-interaction upon the particles due to the radiation reaction [30,31]. The damping of oscillations due to the latter has not been accounted for above.

VI. QUANTUM MECHANICAL CORRELATION FUNCTIONS

As mentioned before the path integral of the quantum mechanical problem at thermal equilibrium is equivalent to a classical polymer problem. Considered as a polymer problem the Schrödinger equation solves in imaginary time the random walks formed by the polymers in the resulting external field. Here we will consider the general situation of nonuniform systems such as the electron clouds of molecules.

By using HF or DFT one can form the density-density correlation function along closed polymers and polymer coils (due to exchange effects for bosons and fermions) in terms of one-particle eigenfunctions. As in Ref. [25] it is given by

$$S(\lambda,\mathbf{r}_1,\mathbf{r}_2)=\zeta\sum_{mn}f_mf_nF_{mn}(\lambda,\mathbf{r}_1,\mathbf{r}_2), \tag{42}$$

where

$$F_{mn}(\lambda,\mathbf{r}_1,\mathbf{r}_2)=\phi_m(\mathbf{r}_1)e^{-(\beta-\lambda)E_m}\phi_m^*(\mathbf{r}_2)\phi_n(\mathbf{r}_2)e^{-\lambda E_n}\phi_n^*(\mathbf{r}_1), \tag{43}$$

$$f_n=\frac{1}{1\pm\zeta e^{-\beta E_n}},\quad \text{and}\quad \zeta=e^{\beta\mu}. \tag{44}$$

The μ is the chemical potential. The plus sign in Eq. (44) is for fermions, while the minus sign is for bosons. The f_n factors include the sums of path integral polymers that are tied into coils. Expression Eq. (43) is the product of quantum mechanical propagators (for states n and m) from position $\mathbf{r}_1$ to position $\mathbf{r}_2$ in imaginary time λ and then back to $\mathbf{r}_1$ in imaginary time $\beta-\lambda$. Note the $S(\lambda,\mathbf{r}_1,\mathbf{r}_2)$ is the correlation function for particles with equal spins as ideal fermions with different spins are uncorrelated before particle interactions are included. It may further be noted that compared with Ref. [25], the terms of the right hand side of expression Eq. (43) are arranged in opposite order. This is made in view of Eqs. (A4)–(A8) in Appendix where a previous mistake is corrected. Then operators when utilized in expression Eq. (43) will act in the usual way from left to right.

If one now first assumes that the perturbing pair interaction is the one given by Eq. (15) without its velocity-dependent part, then further evaluations to obtain the resulting correlation function and free energy change will be as given by Eqs. (5.8)–(5.16) in Ref. [25] except for replacing the static interactions $\psi(r)$ or $\tilde{\psi}(k)$ with $\hat{\psi}(r,K)$ or $\hat{\psi}(k,K)$ which are given by Eqs. (16) or (17).

However, with the velocity dependent part of the electromagnetic interaction Eq. (15) present one will find that velocity or current correlations will be needed. Also velocity-density correlations will be needed. But the latter can be avoided by using the polarization of Sec. IV. Thus a correlation function for polarizations is needed. It can be obtained by starting with the density-density correlation function Eq. (42) as basis. Then the velocity operators $\dot{\mathbf{r}}_1$ and $\dot{\mathbf{r}}_2$ are inserted in expression Eq. (43), and in the path integral $\dot{x}$ means

$$\dot{x}\to x/t=(x_2-x_1)/t=i\hbar(x_2-x_1)/\tau,\qquad \tau\to 0 \tag{45}$$

as expressed by Eq. (5) (where $\hbar=1$ was used). In the short time interval τ the evolution of the path integral is dominated by solution Eq. (4) (with $A=0$) independent of other perturbations. Thus we have $(\hbar=1,\ m=1)$

$$\phi_m^*(x)\dot{\phi}_n(x) \to \int_{-\infty}^{\infty} \phi_m^*(x_2) i \frac{u}{\tau} \frac{1}{\sqrt{2\pi\tau}} e^{-u^2/(2\tau)} \phi_n(x_1) du, \tag{46}$$

where $u=x_2-x_1$. Further with $x_2=x+u/2$ and $x_1=x-u/2$ we can expand

$$\phi\left(x \pm \frac{u}{2}\right) = \phi(x) \pm \frac{u}{2}\phi'(x) + \ldots \tag{47}$$

by which we find ($\tau \to 0$)

$$\phi_m^*(x)\dot{\phi}_n(x) \to \frac{1}{2i}[\phi_m^*(x)\phi_n'(x) - \phi_m'^*(x)\phi_n(x)]. \tag{48}$$

This is the standard expression for the velocity in quantum mechanics. So when $\hbar$ and the particle mass m are reintroduced, and the ith component of the velocity is considered one finds

$$\begin{aligned} j_{imn}(\mathbf{r}) &= \phi_m^*(x)\dot{\phi}_n(x) \\ &= \frac{\hbar}{2im}\left[\phi_m^*(\mathbf{r})\frac{\partial}{\partial x_i}\phi_n(\mathbf{r}) - \phi_n(\mathbf{r})\frac{\partial}{\partial x_i}\phi_m^*(\mathbf{r})\right]. \end{aligned} \tag{49}$$

This combined with expressions Eqs. (42) and (43) yields the velocity-velocity correlation function along the path integral polymer as

$$S_{ij}(\lambda,\mathbf{r}_1,\mathbf{r}_2) = \sum_{mn} J_{ijmn} e^{-\beta E_m} e^{\lambda\Delta_{mn}}$$

where

$$J_{ijmn} = \zeta f_n f_m j_{inm}(\mathbf{r}_1) j_{jmn}(\mathbf{r}_2) \quad \text{and} \quad \Delta_{mn} = E_m - E_n. \tag{50}$$

As discussed in connection with Eq. (32) in the classical case one again encounters a problem for $t=0$, i.e., for $\lambda=0$, where a δ-function will be needed. Here, we find it convenient to solve this problem by first establishing the corresponding correlation function for polarizations. It is obtained by integrating Eq. (50) twice with respect to λ and then multiply with $\hbar^2$ to obtain

$$P_{ij}(\lambda,\mathbf{r}_1,\mathbf{r}_2) = \hbar^2 \sum_{mn} J_{ijmn} \frac{e^{-\beta E_m} e^{\lambda\Delta_{mn}}}{\Delta_{mn}^2}. \tag{51}$$

If the eigenfunctions can be made real, as we will assume in this section, one notes that $j_{imn}(\mathbf{r})=-j_{inm}(\mathbf{r})$. Then Eq. (51) can be symmetrized to be written as

$$P_{ij}(\lambda,\mathbf{r}_1,\mathbf{r}_2) = \hbar^2 \sum_{mn} J_{ijmn} \frac{e^{-\beta E_m} e^{\lambda\Delta_{mn}} + e^{-\beta E_n} e^{-\lambda\Delta_{mn}}}{2\Delta_{mn}^2}. \tag{52}$$

The current-current correlation function is now found by the second derivative of expression Eq. (52) with respect to t_1 and t_2 with $\lambda=i(t_2-t_1)/\hbar$. Noting that S_{ij} is periodic in λ with period β (closed polymers) one gets a δ-function at $\lambda=0$ to obtain

$$\begin{aligned} S_{ij}(\lambda,\mathbf{r}_1,\mathbf{r}_2) = \sum_{mn} J_{ijmn} \Bigg[&\frac{1}{2}(e^{-\beta E_m} e^{\lambda\Delta_{mn}} + e^{-\beta E_n} e^{-\lambda\Delta_{mn}}) \\ &- \frac{1}{\Delta_{mn}}(e^{-\beta E_n} - e^{-\beta E_m})\delta(\lambda) \Bigg]. \end{aligned} \tag{53}$$

This relation between current and polarization correlations is like relation Eq. (35) a consequence of relations Eq. (18).

From Eqs. (42), (43), (52), and (53) the Fourier transforms with respect to imaginary time are easily obtained ($\omega^2=-(K/\hbar)^2$),

$$\begin{aligned} S(K,\mathbf{r}_1,\mathbf{r}_2) = \zeta \sum_{mn} &\frac{\Delta_{mn}(e^{-\beta E_n} - e^{-\beta E_m})}{\Delta_{mn}^2 + K^2} \\ &\times f_m f_n \phi_m(\mathbf{r}_1)\phi_m^*(\mathbf{r}_2)\phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1), \end{aligned} \tag{54}$$

$$S_{ij}(K,\mathbf{r}_1,\mathbf{r}_2) = \omega^2 \hat{P}_{ij}(K,\mathbf{r}_1,\mathbf{r}_2), \tag{55}$$

$$\hat{P}_{ij}(K,\mathbf{r}_1,\mathbf{r}_2) = \hbar^2 \sum_{mn} J_{ijmn} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{\Delta_{mn}(\Delta_{mn}^2 + K^2)}. \tag{56}$$

Result Eq. (54)) is Eq. (5.14) of Ref. [25]. while Eqs. (55) and (56) are new results. To obtain Eq. (54), the symmetry of Eq. (52) is also utilized in Eq. (42).

We can now show that P_{ij} is consistent with the density-density correlation function S. From relation Eq. (18) between density and polarization (per unit charge) one should have

$$S = \frac{\partial^2}{\partial x_{1i}\,\partial x_{2j}} P_{ij}, \quad \left(\sum_{ij}\right). \tag{57}$$

With Eq. (49) we then have derivatives

$$\begin{aligned} &\frac{\hbar}{2im}\frac{\partial}{\partial x_i}\left(\phi_m^*\frac{\partial}{\partial x_i}\phi_n - \phi_n\frac{\partial}{\partial x_i}\phi_m^*\right) \\ &= \frac{\hbar}{2im}\left(\phi_m^*\frac{\partial^2\phi_n}{\partial x_i\,\partial x_i} - \phi_n\frac{\partial^2\phi_m^*}{\partial x_i\,\partial x_i}\right) = \frac{1}{i\hbar}\Delta_{mn}\phi_m^*\phi_n, \end{aligned} \tag{58}$$

which follow from the one-particle Schrödinger equation. Here, it can be noted that this does not quite hold for the Hartree-Fock equation due to its exchange term. However, current correlations can only influence radiation corrections that are expected to be small anyway, so we will disregard this inaccuracy. Thus with Eqs. (49)–(52), (54), and (55) it is found that S as given by Eq. (42) is recovered.

VII. UNIFORM SYSTEM

For a uniform system, i.e., constant density, with ideal gas as a reference system the wave functions are plane waves

$$\phi(\mathbf{r}) \propto e^{i\mathbf{k}_n\mathbf{r}}. \tag{59}$$

with energy eigenvalues $E_n=E(k_n)$ where

$$E(k) = \frac{1}{2m}(\hbar k)^2 \tag{60}$$

This is to be inserted in Eq. (43) to obtain the correlation function Eq. (42). Then one can Fourier transform in space with respect to the relative separation $\mathbf{r}_2-\mathbf{r}_1$, and it is convenient to regard Eq. (43) as a product of two functions that can be transformed separately. The resulting Fourier transform thus becomes a convolution in $\mathbf{k}$-space, and we have transforms ($\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$)

$$\int \phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)e^{i\mathbf{k}''\mathbf{r}}d\mathbf{r} \propto \delta(\mathbf{k}''-\mathbf{k}_m)$$

$$\int \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)e^{i\mathbf{k}'\mathbf{r}}d\mathbf{r} \propto \delta(\mathbf{k}'+\mathbf{k}_n). \tag{61}$$

With this the resulting Fourier transform is obtained by the replacements

$$\mathbf{k}_m = \mathbf{k}'' \quad \text{and} \quad \mathbf{k}_n = -\mathbf{k}' \tag{62}$$

in the exponential terms of Eq. (54). So the Fourier transform becomes

$$\hat{S}(K,k) = \int \frac{\Delta^2}{\Delta^2+K^2} L d\mathbf{k}'. \tag{63}$$

where $\Delta=E(k'')-E(k')$ and $\mathbf{k}''=\mathbf{k}-\mathbf{k}'$. Further

$$L = \frac{\zeta}{(2\pi)^3}\frac{X-Y}{\Delta(1\pm\zeta X)(1\pm\zeta Y)} \tag{64}$$

where

$$X = F_\beta(k') \quad \text{and} \quad Y = F_\beta(k''), \quad \text{with} \quad F_\lambda(k) = \exp(-\lambda E(k)). \tag{65}$$

This is the same as Eq. (3.4) in Ref. [25]. except that there the symmetry in $\mathbf{k}'$ and $\mathbf{k}''$ was not utilized.

As in Ref. [25], one may again take the classical limit to obtain its Eq. (3.6) which is nothing but Eq. (29) (with $\hat{S} = \hat{\phi}$) if the symmetry of Eq. (52) had been utilized in the reference too. In the classical limit, $Ld\mathbf{k}' \to \beta\rho f_0 d\mathbf{v}$ and $\Delta \to -\hbar\mathbf{k}\mathbf{v}$, with $\mathbf{v}=\hbar\mathbf{k}'/m$.

The results for current and polarization correlations can now be obtained in a straightforward way. With the plane wave Eq. (59) the current element Eq. (49) becomes

$$j_{imn}(\mathbf{r}) = \frac{\hbar}{2m}(k_{in}+k_{im})\phi_m^*\phi_n. \tag{66}$$

Here $j_{inm}=j_{imn}$, and with $E(-k)=E(k)$ the symmetry used in Eq. (52) will also hold for the plane waves.

Now comparing expressions Eqs. (50) and (51) for P_{ij} and expressions Eqs. (42) and (43) for S one notes that they differ only by the product of the factors $(\hbar/\Delta_{mn})^2$, $\hbar(k_{in}+k_{im})/(2m)$, and $\hbar(k_{jn}+k_{jm})/(2m)$. Further by Fourier transform one has the replacements Eq. (62). Thus in light of result Eq. (63) the Fourier transform of Eq. (52) in imaginary time becomes

$$\hat{P}_{ij}(K,\mathbf{k}) \int \left[\frac{\hbar}{2m}(k_i''-k_i')\right]\left[\frac{\hbar}{2m}(k_j''-k_j')\right]\frac{\hbar^2}{\Delta^2+K^2}L d\mathbf{k}', \tag{67}$$

and in view of Eq. (55)

$$\hat{S}_{ij}(K,\mathbf{k}) = \omega^2 \hat{P}_{ij}(K,\mathbf{k}). \tag{68}$$

With $\mathbf{k}=\mathbf{k}''+\mathbf{k}'$ one can easily verify that

$$\hat{S}(K,k) = k_i k_j \hat{P}_{ij}(K,\mathbf{k}) \quad \left(\sum_{ij}\right) \tag{69}$$

consistent with relation Eq. (18) for density and polarization.

As for $\hat{S}$ above we again find it useful to consider the classical limit $\hbar \to 0$. Then

$$\frac{\hbar}{2m}(k_i''-k_i') = \frac{\hbar}{2m}(k_i-2k_i') \to -\frac{\hbar k_i'}{m} = -v_i, \tag{70}$$

and $\Delta \to -\hbar\mathbf{k}\mathbf{v}$. So compared with the limiting procedure of Eq. (63), the limit of Eq. (67) has the additional factor $v_i v_j \hbar^2/\Delta^2 = v_i v_j/(\mathbf{k}\mathbf{v})^2$. Thus the classical result Eq. (35) for $\hat{P}_{ij}$ is recovered as it differs from Eq. (29) by this factor.

From the limiting process it is seen that the main difference between the quantum mechanical treatment and the classical one for small k is the factor L given by (64) which in the classical case becomes the Maxwell velocity distribution f_0 (times a constant). But the frequency distribution remains essentially the same. Thus the analysis at the end of Sec. V in the classical case remains mainly the same in the quantum mechanical case. So more generally we can conclude there is no contribution to the Casimir force between metallic plates from a possible TE zero frequency mode [7,8].

VIII. CASIMIR ENERGY CONTRIBUTION TO *AB INITIO* COMPUTATIONS

In Ref. [25], the leading energy correction to molecular energies by *ab initio* computations was established. Standard methods here are the HF and DFT that are used to perform quantum mechanical computations on interacting electrons of atoms and molecules [28]. In Ref. [25], the interaction was assumed to be time-independent like the electrostatic one. The resulting pair correlation function is then the sum of chain bond graphs while the corresponding free energy correction is the sum of ring graphs to a leading order. At $T=0$ the free energy correction is just the ground state energy correction. One can note that this correction is related to nonlocal correlations which in the classical limit correspond to Debye-Hückel theory for ionic fluids or plasmas where Debye shielding also is taken into account.

With the new results obtained above the results of Ref. [25] can be extended to incorporate the time-dependent electromagnetic interaction. It is straightforward to replace the static charge-charge interaction with a time-dependent one as that requires no further modification. However, the electromagnetic interaction is also an interaction between currents. In the preceding sections we have seen how the path integral and its statistical mechanical interpretation as a classical polymer problem can include current correlations. Then with relations Eq. (18) densities and currents can be replaced by polarization by which the ionic fluid can be regarded as a polarizable fluid with susceptibility given by Eq. (34). This is again the correlation function P_{ij} for polarizations which is given by Eq. (56) for nonuniform systems, and which simplifies to Eq. (67) for uniform systems.

For a polarizable fluid one needs the dipolar interaction which follows from Eq. (23) or (24) with the dipole moments $\mathbf{s}_1$ and $\mathbf{s}_2$ deleted (since in the present case P_{ij} will replace the usual dipole correlations $\rho\langle s_i s_j\rangle$ at the hypervertices of graphs). In the uniform case the Fourier transform Eq. (24) can be used, and one has the interaction

$$\hat{\varphi}_{ij}(K,\mathbf{k}) = q^2\hat{\psi}(k,\omega)\left[k_i k_j - \left(\frac{\omega}{c}\right)^2\delta_{ij}\right] \tag{71}$$

with $\hat{\psi}(k,\omega)$ given by Eq. (12) and $K=i\hbar\omega$. In the nonuniform case the $\mathbf{r}$-dependent version Eq. (23) is needed. With $\hat{\psi}$ given by Eq. (13) or (16) one finds for the radiating dipole interaction

$$\hat{\varphi}_{ij}(K,\mathbf{r}) = q^2\Bigg[-\left(\frac{1}{r^5}+\frac{\nu}{r^4}+\frac{\nu^2}{3r^3}\right)e^{-\nu r}(3x_i x_j - r^2\delta_{ij}) + \frac{2\nu^2}{3r}e^{-\nu r}\delta_{ij} + \frac{4\pi}{3}\delta(\mathbf{r})\delta_{ij}\Bigg], \tag{72}$$

with $\nu=i\omega/c=K/(\hbar c)$ and $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$. The δ-function follows from $\nabla^2(1/r)=-4\pi\delta(\mathbf{r})$. One might think that the δ-function could give rise to divergence problems. However, as Eq. (72) is equivalent to the Coulomb interaction of the ionic system (for $\nu=0$), this should not be the case for the leading contribution considered below. Moreover, as done in Ref. [30] and indicated above Eq. (34), the δ-function may be multiplied with a parameter Θ. Also when solving for instance the well-known mean spherical approximation for dipolar hard spheres, the Θ will be implicitly defined by the hard sphere condition and the δ-function will be spread out within the hard sphere diameter.

To obtain the free energy change from the ring graphs one can now follow the method given in Sec. V of Ref. [25]. This means replacing the quantities $\hat{S}(K,k)$ and $\tilde{\psi}(k)$ of the reference with the matrices $\hat{P}_{ij}(K,\mathbf{k})$ and $\hat{\varphi}_{ij}(K,\mathbf{k})$ given by Eqs. (67) and (71), respectively, in the uniform case. In the nonuniform case $\hat{S}(K,\mathbf{r}_1,\mathbf{r}_2)$ and $\psi(r)$ are similarly replaced by matrices $\hat{P}_{ij}(K,\mathbf{r}_1,\mathbf{r}_2)$ and $\hat{\varphi}_{ij}(K,\mathbf{r})$ given by Eqs. (56) and (72). Due to relations Eqs. (57) and (69), it is easily seen that the above reduces to the situation studied in the reference when the interaction is electrostatic.

With interactions Eqs. (71) or (72) retardation effects are taken into account. The perturbing free energy correction is the same as a Casimir free energy contribution to molecular energies. Then for short separations r between two molecules it is well known that electrostatic van der Waals forces have energy $\propto 1/r^6$ while for larger separations retardation effects are important to give energy $\propto 1/r^7$. It is reason to expect that related behavior will be reflected within large molecules too.

IX. SUMMARY

Quantum mechanical systems at thermal equilibrium are through the path integral representation equivalent to classical polymer problems in four dimensions where the fourth dimension is imaginary time. Thus, one has correlation functions both in space and imaginary time. In this work we find that this equivalence also can include current correlations. These are needed to incorporate the radiating electromagnetic interaction within the formalism. Then for an ionic fluid we find it convenient to consider an equivalent polarizable fluid by introducing polarization. Polarization correlations and susceptibility are first established for a classical (ideal gas reference) fluid, and then corresponding results are obtained for the fully quantized fluid. From the non-local susceptibility obtained one finds that there will be no TE zero-mode contribution to the Casimir force between metallic plates, i.e., plates filled with an ionic fluid. Then it is shown how this can be used to evaluate a leading energy correction to *ab initio* computations of molecular energies (for nonuniform systems). This energy due to correlations between distant particles can be regarded as a Casimir free energy contribution to the system as it has the same origin as the Casimir free energy between separate dielectric or metallic plates.

APPENDIX: CORRELATION FUNCTIONS AND RESPONSE FUNCTIONS

Let the Hamiltonian H of a system at thermal equilibrium be perturbed by an amount $-AF(T)$. This will give a response

$$\langle\Delta B\rangle = \int_{-\infty}^{0}\phi_{BA}(t-t')F(t')dt' \tag{A1}$$

of a dynamical quantity B. Here A and B are time independent operators, and $F(t)$ is a time dependent function. The ϕ_{AB} is the response function given by Eq. (2.16) on page 139 of Ref. [29]. as

$$\phi_{BA}(t) = \frac{1}{i\hbar}Tr(\rho[A,B(t)]) \tag{A2}$$

where here ρ is the canonical equilibrium density matrix

$$\rho = \frac{1}{Z}e^{-\beta H}, \quad Z = Tr(e^{-\beta H}).$$

The B in the commutator is the time-dependent operator

$$B(t) = e^{\lambda H}Be^{-\lambda H} \tag{A3}$$

where $\lambda = it/\hbar$ is imaginary time. Earlier we unfortunately made a mistake here by defining λ with opposite sign [5]. The purpose with imaginary time is that it transforms the Schrödinger equation to an equation that describes diffusion for increasing λ. However, this mistake did not influence the results of previous applications since the operators A and B were equal (apart from a possible constant). With the change of sign of λ the correlation function along a polymer formed by the quantum mechanical paths is given by

$$g(\lambda) = Tr(\rho B(t)A) = \frac{1}{Z}Tr(e^{-(\beta-\lambda)H}Be^{-\lambda H}A). \tag{A4}$$

(With the λ used earlier the $B(t)$ and A were interchanged in this expression.) Further

$$Tr(\rho AB(t)) = \frac{1}{Z}Tr(e^{-\beta H}Ae^{\lambda H}Be^{-\lambda H}) = \frac{1}{Z}Tr(e^{\lambda H}Be^{-(\beta+\lambda)H}A) = g(\beta+\lambda) \tag{A5}$$

by which the response function can be written as

$$\phi_{BA}(t) = \frac{1}{i\hbar}(g(\beta+\lambda) - g(\lambda)). \tag{A6}$$

The classical limit $\hbar \to 0$ and $\beta \to 0$ can now be taken ($t = -i\hbar\lambda \geq 0$),

$$\phi_{BA}(t) = \frac{\beta}{i\hbar}\left[\frac{d}{d\lambda}g(\lambda) + \cdots\right] \to -\beta\frac{d}{dt}n(t) \tag{A7}$$

where $n(t)$ is the real time classical correlation function.

In Appendix B of Ref. [5]. the crucial identity

$$\hat{\phi}_{BA} = \hat{g}(K) \tag{A8}$$

was obtained where now

$$K = i\hbar\omega, \tag{A9}$$

and the Fourier transforms are

$$\hat{\phi}_{BA}(\omega) = \int_0^\infty \phi_{BA}(t)e^{-i\omega t}dt \quad \text{and} \quad \hat{g}(K) = \int_0^\beta e^{iK\lambda}d\lambda. \tag{A10}$$

The $\hat{g}(K)$ is defined only for $K = 2\pi n/\beta$ with n integer, but in relation Eq. (A8) its analytic continuation is used. In general $\hat{g}(K)$ is analytic for $|\mathrm{Im}(K)| < C$ with $C > 0$, and the integral for $\hat{\phi}_{BA}(\omega)$ converges for $\mathrm{Im}(\omega) < 0$, i.e., $\mathrm{Re}(K) > 0$. Thus Eq. (A8) is valid where these regions overlap.

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