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## Van der Waals interactions: Corrections from radiation in fluids

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We consider induced van der Waals interactions with corrections due to radiation in fluids consisting of polarizable hard spheres. The fluctuating polarizations are quantized while the positions of particles are treated classically. First the well known result for the induced Casimir free energy for a pair of particles is used to establish the resulting free energy at low density. The Casimir interaction includes the full effect of the quantized radiating electromagnetic field. Then the situation with electrostatic dipole-dipole interactions is considered for general density. For this situation the induced interactions are the van der Waals interactions, and we evaluate numerically the free energy based upon analytic results obtained earlier. These analytic results were obtained by extending methods of classical statistical mechanics to the path integral of quantum mechanics. We have realized that these methods can be extended to time-dependent interactions too. Thus we here also make the extension to the radiating dipole-dipole interaction between pairs of particles to obtain explicit results for more arbitrary fluid densities, and radiation corrections to the induced free energy are found both analytically and numerically. *Copyright 2013 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4792939]*

### I. INTRODUCTION

Atoms and molecules are polarizable. Their polarizability can be related to fluctuating dipole moments, and with the electrostatic dipole-dipole interaction the well known attractive van der Waals force between pairs of particles is induced. It was noticed that there were deviations from this force, and by use of quantum electrodynamics the Casimir-Polder force was obtained where retardation effects were taken into account.<sup>1</sup> Further, the methods of the quantized electromagnetic field have been used to obtain the Casimir force for various situations.<sup>2-4</sup>

Methods of quantum mechanics are not easily extended to general fluid density. But Chandler *et al.* and Høye and Stell realized that the equilibrium properties of a fluid of quantized polarizable particles could be evaluated by using methods of classical statistical mechanics.<sup>5,6</sup> The basis for this was the path integral representation of quantum mechanics. Feynman found that the partition function of a quantum mechanical particle can be represented as a path integral in imaginary time  $\beta = 1/(k_B T)$  where  $k_B$  is Boltzmann's constant and  $T$  is temperature.<sup>7</sup> The path integral can be interpreted as a "classical" polymer in 4 dimensions where imaginary time is the fourth dimension with periodic boundary conditions at times 0 and  $\beta$ . It can also be regarded as a random walk whose properties have been studied and analyzed, and this has been used to solve problems in statistical mechanics.<sup>8</sup>

Brevik and Høye reconsidered the evaluation of the Casimir-Polder force by applying the statistical mechanical method of thermal equilibrium to the path integral.<sup>9</sup> Then it was realized that the method also was applicable to time-dependent interactions, and the Casimir-Polder force

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was recovered. The latter derivation coincides with the interpretation that the Casimir force can be related to fluctuating dipole moments. In this way the electromagnetic field is fully replaced by pair interactions between dipole moments.<sup>10,11</sup> The reason why this replacement is possible, is that the field is quantized as a set of harmonic oscillators. A related conclusion was earlier noted by McLachlan.<sup>2</sup>

The Casimir force becomes the van der Waals force when retardation effects are neglected, i.e. the static dipole-dipole interaction is used. Thus the former includes corrections to the latter from radiation. A purpose of the present work is to investigate these corrections for fluids where the particles form a network of interactions. To do so we extend the statistical mechanical theory for the Casimir force of a pair of particles. For low density one can simply add up pairs of particles. However, for higher densities the “classical” methods applied to the quantized polarizable fluid can be used.<sup>5,6</sup> We have realized that these methods also can be extended to the situation with radiating dipole-dipole interaction, and we do so in this work. This extension makes evaluations more demanding, and results of several previous works must be utilized and combined. But explicit results can still be obtained in terms of the solution of the Ornstein-Zernike integral equation where now a (transformed) direct correlation function is of Yukawa form outside hard cores.

A motivation for this work is to investigate the influence from radiation upon the free energy of fluids as just indicated. Due to the time dependence or retardation properties of the interaction it is not obvious how to perform evaluations at thermal equilibrium where also the particle structure at the molecular level also should be taken into account. We are not aware of other approaches that have obtained quantitative results for this problem. However, the statistical mechanical method that we will utilize and extend to the situation with radiating pair interactions, can deal with the particle nature on the molecular level to give quantitative results. To perform explicit evaluations the fluid is modified in a way typical for developments in fluid theory. Thus in the present case the molecules are approximated by hard spheres with fluctuating dipole moments located at their centers.

Another motivation for this work is to get some estimate of the influence from radiation on the energy of electrons in molecules. This is a noticeable effect for large molecules, and it lead to the evaluation of the Casimir-Polder force.<sup>1</sup> In this respect one of us in recent works has included van der Waals and Casimir energies as leading perturbations<sup>12-14</sup> to ab initio Hartree-Fock or density functional theory for molecular energies.<sup>15</sup> These energies can be expressed in terms of the occupied and excited eigenstates of the molecules. In Ref. 13 it was found that the system of electrons in molecules may be regarded as a dielectric fluid and radiation corrections can be taken into account. But incorporation of the van der Waals or Casimir energies in molecular evaluations will be demanding; so the influence of radiation is not easily obtained. However, the dielectric fluid studied in this work may be regarded as a strongly simplified model of a large molecule where the influence of radiation between the electrons is studied. The energy shifts from this influence are expected to be small since they are closely related to the Lamb shift as they both can be related to the consequences of the vacuum fluctuations of the electromagnetic field.<sup>16</sup> Our results will show that this is the case.

Perturbing contributions to molecular energies from non-local correlations are of central interest and various recipes have been used. One of them is the RPA (random phase approximation) which is in accordance with the van der Waals energy where radiation is absent.<sup>17,18</sup> This has been studied by Lein *et al.* for the uniform electron gas where simulation results with which to compare are available.<sup>19</sup> They point out that the RPA gives too low energy (a situation similar to classical Debye-Hückel theory). This is corrected by including a term in addition to the Coulomb interaction at short range. In Ref. 14 it was suggested in view of the statistical mechanical approach that this may be adjusted determined from a hard core condition upon the resulting correlation function as two electrons can not be on the same position due to the repulsive Coulomb interaction (and for equal spins). In any case this will need further investigations.

In Sec. II the expression for the Casimir free energy of a pair of polarizable particles is considered. By integration over separations outside the hard core diameter of the particles the induced free energy per particle for a fluid at low density is obtained. This is compared with the induced van der Waals free energy where radiation is disregarded.

In Sec. III a polarizable fluid at arbitrary density, where the particles interact via the electrostatic dipole-dipole interaction, is considered, and the van der Waals free energy is evaluated. For this

situation we study how the induced energy deviates from the value that would be obtained from a direct sum of low density pair energies.

In Sec. IV the polarizable fluid at arbitrary density, where the full radiating dipole-dipole interaction is present, is considered. The induced energy for this situation is evaluated, and we study how it deviates from the induced van der Waals free energy.

## II. A PAIR OF PARTICLES

The Casimir free energy between a pair of polarizable particles is given by Eq. (5.15) of Ref. 9 as

$$F = -\frac{3}{2\beta r^6} \sum_{n=-\infty}^{\infty} e^{-2\tau} \left[ 2 \left( 1 + \tau + \frac{1}{3} \tau^2 \right)^2 + \left( \frac{2}{3} \tau^2 \right)^2 \right] \alpha_K^2. \quad (2.1)$$

Here

$$\tau = \frac{|K|r}{\hbar c} \quad \text{with} \quad K = 2\pi n/\beta \quad (2.2)$$

where  $n$  is integer,  $r$  is separation between the particles,  $c$  is velocity of light, and  $K$  is the Matsubara frequency

$$K = i\hbar\omega \quad (2.3)$$

where  $\omega$  is the frequency and  $i$  is the imaginary unit. It is to be noted that imaginary values of  $\omega$  are used in expression (2.3) and other expressions below where real values of  $K$ , according to Eq. (2.2), are used. (The  $K$  was defined with opposite sign in Ref. 9. As noted in Refs. 13 and 14 that was a mistake that did not influence results so far. This sign will depend upon how the Fourier transform is defined with  $-i\omega t$  or  $i\omega t$  in the exponent, i.e.  $-i\omega t = iK\lambda$  with imaginary time  $\lambda = it/\hbar$  means  $K = i\hbar\omega$ .) Finally  $\alpha_K$  is the frequency dependent polarizability of the particles. When each particle is modeled as a simple harmonic oscillator, which will be used throughout this work, it is given by (with  $-(\hbar\omega)^2 = K^2$ )

$$\alpha_K = \frac{\alpha(\hbar\omega_0)^2}{K^2 + (\hbar\omega_0)^2} \quad (2.4)$$

where  $\alpha$  is the zero frequency polarizability and  $\omega_0$  is the eigenfrequency (which is real). The well known Casimir-Polder result (for  $T = 0$ ) is recovered when  $\alpha_K = \alpha$  for all  $K$ , i.e.  $\omega_0 \rightarrow \infty$ .<sup>1</sup> This and result (2.1) were earlier obtained by a Green function method.<sup>20</sup>

It can be remarked that the  $\alpha_K$  of Eq. (2.4) is a simplified version of real molecules as it contains only one resonance frequency. However, it can be replaced with any realistic polarizability by which results below will become less explicit. Further it can be noted that the polarizability  $\alpha$  is here used in Gaussian units since the dipole-dipole interaction defined through Eqs. (3.2)–(3.5) below (and Eq. (4.1) instead of (3.5) in the radiating case) are in Gaussian units as is commonly used in models of ionic and dielectric fluids. In SI units the corresponding polarizability is  $\alpha_{SI} = 4\pi\epsilon_0\alpha$  where  $\epsilon_0$  is the permittivity of vacuum.

Compared with the energy quantum  $\hbar\omega_0$  the thermal energy  $k_B T$  will be regarded as small. Thus we will consider  $T = 0$  to simplify. With this the summation in Eq. (2.1) is replaced by integration where

$$\frac{1}{\beta} \sum_{n=-\infty}^{\infty} \rightarrow \frac{1}{2\pi} \int_{-\infty}^{\infty} dK \rightarrow \frac{1}{\pi} \int_0^{\infty} dK. \quad (2.5)$$

We will consider fluids. Thus one should take the average over separations, and in the low density limit expression (2.1) is to be used for particle separations larger than the hard core diameter  $R$ . With number density of particles  $\rho$  the induced free energy per particle becomes (with factor 1/2

to avoid double counting of interactions)

$$f = \frac{1}{2}\rho \int F d\mathbf{r} = 2\pi\rho \int_R^\infty Fr^2 dr = -\frac{\rho\alpha^2\hbar\omega_0}{R^3} \int_0^\infty dK e^{-2z} \frac{2(1+z)^2 + z^3}{(K^2 + 1)^2} \quad (2.6)$$

where the replacement of integration variable

$$K \rightarrow \hbar\omega_0 K, \quad dK \rightarrow \hbar\omega_0 dK \quad (2.7)$$

has been made to simplify. Further with this

$$z = \gamma K, \quad \gamma = \frac{\omega_0 R}{c}. \quad (2.8)$$

Integral (2.6) can be verified by differentiation with respect to  $R \rightarrow r$  (and  $z \propto R$ ). The inverse of  $\gamma$  multiplied with  $2\pi$  is the wavelength of radiation relative to the hard core diameter at resonance frequency  $\omega_0$ . Thus for small molecules the  $\gamma$  and thus radiation effects will be small.

A limiting case of Eq. (2.6) is the electrostatic limit  $\gamma \rightarrow 0$  ( $z \rightarrow 0$ ) by which

$$f = f_0 = -\frac{\pi\rho\alpha^2\hbar\omega_0}{2R^3}. \quad (2.9)$$

Another limit is the Casimir  $\gamma \rightarrow \infty$  ( $\omega_0 \rightarrow \infty$ ) case where the denominator in Eq. (2.6) can be put equal to one to obtain

$$f = f_C = \frac{23}{4\pi\gamma} f_0 = -\frac{23\rho\hbar c\alpha^2}{8R^4}. \quad (2.10)$$

Eq. (2.9) is the van der Waals interaction  $F = -3\alpha^2\hbar\omega_0/(4r^6)$  integrated while Eq. (2.10) is the corresponding Casimir interaction  $F = -23\hbar c\alpha^2/(4\pi r^7)$  integrated. Eq. (2.6) may also be expanded for small  $\gamma$  to obtain

$$f = (1 - \gamma^2 + \dots)f_0. \quad (2.11)$$

The  $\gamma^2$  term of Eq. (2.11) represents the leading radiation correction to the free energy of van der Waals interactions. A notable feature of this correction is that it depends directly upon  $R$  since

$$\gamma^2 f_0 \propto \frac{\omega_0^3}{R}. \quad (2.12)$$

Thus the greater part of it must come from separations  $r$  close to the minimum  $r = R$ . Immediately this may be somewhat counterintuitive since with interaction  $F$  given by Eq. (2.1) the corresponding relative correction is largest for large  $r$  where retardation effects dominates, but clearly, this is outweighed by the rapid vanishing of the interaction for large  $r$ .

The  $f$  as given by Eq. (2.6) is evaluated numerically and the ratio  $f/f_0$  is shown in Fig. 1 as function of  $\lambda = 2\pi/\gamma = 2\pi c/(\omega_0 R)$ .

As a numerical example we will make estimates for Ar (argon) where the atoms interact via the Lennard-Jones potential  $\phi(r) = 4\varepsilon_{LJ}[(\sigma/r)^{12} - (\sigma/r)^6]$ . For Ar the critical temperature is  $T_c = 151$  K and  $\varepsilon_{LJ}/(k_B T_c) \approx 0.8$ . Thus with  $k_B = 1.38 \cdot 10^{-23}$  J/K

$$4\varepsilon_{LJ} = 6.67 \cdot 10^{-21} \text{ J} \approx 42 \text{ meV}. \quad (2.13)$$

The attractive part of  $\phi(r)$  is to be identified with the van der Waals interaction  $F$  given below Eq. (2.10). So with  $R \approx \sigma = 3.4 \text{ \AA}$  we have

$$4\varepsilon_{LJ} R^6 = \frac{3}{4} \hbar\omega_0 \alpha^2. \quad (2.14)$$

The dielectric constant may here be estimated with the Clausius-Mosotti relation  $(\varepsilon - 1)/(\varepsilon + 2) = (4\pi/3)\rho\alpha$ . With mass density  $1.4 \text{ g/cm}^3$ , atomic weight 39.95,  $\varepsilon = 1.6$  in liquid state, and

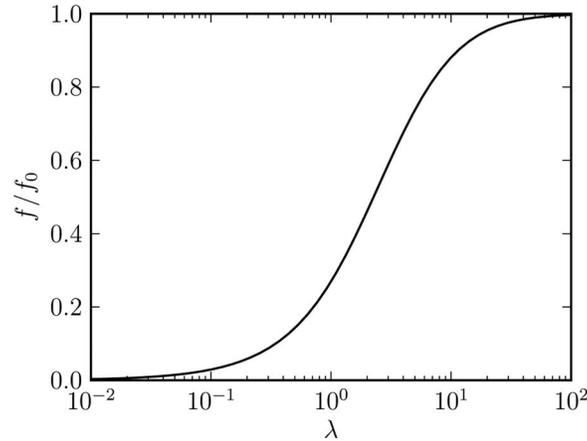


FIG. 1. Casimir free energy per particle  $f$  given by Eq. (2.6) divided by its electrostatic limit  $f_0$  given by Eq. (2.9) as function of dimensionless wavelength  $\lambda = 2\pi/(\omega_0 R)$  on logarithmic scale. The  $\omega_0$  is the oscillator eigenfrequency while  $R$  is the hard core diameter.

Avogadro's number  $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$  the particle density becomes  $\rho = 2.1 \cdot 10^{28} \text{ m}^{-3}$  by which

$$\rho R^3 = 0.82 \quad \text{and} \quad \frac{\alpha}{R^3} = \frac{3}{4\pi\rho R^3} \frac{\varepsilon - 1}{\varepsilon + 2} = 0.0485. \quad (2.15)$$

With Eq. (2.14) this gives

$$\hbar\omega_0 = \frac{16\varepsilon_{LJ}}{3(\alpha/R^3)^2} = 3.78 \cdot 10^{-18} \text{ J} \approx 24 \text{ eV}. \quad (2.16)$$

Thus with  $\hbar = 1.054 \cdot 10^{-34} \text{ Js}$  and  $c = 3.0 \cdot 10^8 \text{ m/s}$

$$\gamma = \frac{\hbar\omega_0 R}{\hbar c} = 4.1 \cdot 10^{-2}, \quad \gamma^2 = 1.7 \cdot 10^{-3}, \quad \text{and} \quad \lambda = \frac{2\pi}{\gamma} \approx 150. \quad (2.17)$$

For the van der Waals energy per particle (2.9) we get

$$f_0 = -\frac{\pi}{2} \hbar\omega_0 \left(\frac{\alpha}{R^3}\right)^2 \rho R^3 = -\frac{4\pi}{6} 4\varepsilon_{LJ} \rho R^3 \approx 72 \text{ meV}. \quad (2.18)$$

The repulsive part of the Lennard-Jones interaction when integrated for  $r > \sigma \approx R$  reduces this by one third. The change in free energy due to radiation is thus

$$\Delta f_{rad} = -\gamma^2 f_0 \approx 0.12 \text{ meV}. \quad (2.19)$$

For larger molecules the influence of radiation will increase due to larger molecular diameter  $R$  and thus increasing  $\gamma$ .

### III. ELECTROSTATIC INTERACTION

For higher densities and polarizabilities the resulting free energy will deviate from adding contributions from pairs of particles. However, the solution of the quantized polarizable fluid is then applicable.<sup>5,6</sup> By use of the path integral its solution turned out to be the one of the corresponding classical fluid for each Matsubara frequency  $K$ . Then the mean spherical approximation (MSA)<sup>21</sup> was used where the spatial positions of the particles were not quantized.

To sketch the solution we may merely consider the classical case which is for  $K = 0$ . This is based upon the solution of the Ornstein-Zernike equation with MSA boundary conditions<sup>22,23</sup>

$$h(12) = c(12) + \int \rho(\mathbf{s}_3) c(13) h(32) d\mathbf{s}_3 d\mathbf{r}_3 \quad (3.1)$$

where  $h(12)$  and  $c(12)$  are the pair correlation function and the direct correlation function respectively. Here the number  $i = 1, 2, 3$  denote the position  $\mathbf{r}_i$  and the dipole moment  $\mathbf{s}_i$  of particle  $i$ . The  $\rho(\mathbf{s}_3)$  is the density distribution of fluctuations of the dipole moment of particle  $i = 3$  in the harmonic oscillator potential. Further the dipole moment of each particle is modelled as a point dipole located at its center. With the MSA one can write

$$\begin{aligned} c(12) &= c_0(r) + \beta s_1 s_2 [c_\Delta(r)\Delta(12) + c_D(r)D(12)] \\ h(12) &= h_0(r) + \beta s_1 s_2 [h_\Delta(r)\Delta(12) + h_D(r)D(12)] \end{aligned} \quad (3.2)$$

with

$$\Delta(12) = \hat{s}_1 \cdot \hat{s}_2; \quad \text{and} \quad D(12) = 3(\hat{r}_1 \cdot \hat{s}_2)(\hat{r}_1 \cdot \hat{s}_2) - \hat{s}_1 \cdot \hat{s}_2. \quad (3.3)$$

where the hats denote unit vectors. The MSA boundary conditions for hard spheres of unit diameter are

$$\begin{aligned} c(12) &= -\beta\Phi(12) \quad \text{for} \quad r > 1 \\ h(12) &= -1 \quad \text{for} \quad r < 1 \end{aligned} \quad (3.4)$$

The condition on  $c(12)$ , where  $\Phi(12)$  is the pair interaction, is an approximation while the condition on  $h(12)$  is the exact hard core condition for spheres of unit diameter. With static dipole-dipole interaction this means

$$\begin{aligned} c_0(r) &= 0; \quad c_\Delta(r) = 0; \quad c_D(r) = 1/r^3 \quad \text{for} \quad r > 1 \\ h_0(r) &= -1; \quad h_\Delta(r) = 0; \quad h_D(r) = 0 \quad \text{for} \quad r < 1. \end{aligned} \quad (3.5)$$

With the MSA it is found that the resulting density distribution is such that ( $\rho = \int \rho(\mathbf{s}) d\mathbf{s}$ )<sup>22</sup>

$$R_0 = \beta\rho m^2 = \frac{3\rho\alpha}{1 + \alpha c_\Delta(0)}; \quad m^2 = \langle s^2 \rangle. \quad (3.6)$$

In Appendix A we give more details about the solution of the above MSA problem.

In the quantum mechanical case it turned out that the solution is a straightforward extension of the classical MSA problem above.<sup>5,6</sup> The main change is to extend the polarizability to non-zero Matsubara frequencies, i.e.  $\alpha \rightarrow \alpha_K$  with  $\alpha_K$  given by Eq. (2.4) in our case. But a general  $\alpha_K$  that represents a sum of harmonic oscillators, can be used. With this Eq. (3.6) is generalized to (with the rescaling (2.7) for  $K$ )

$$R_K = \frac{3\rho\alpha}{K^2 + 1 + \alpha c_\Delta^K(0)}, \quad (3.7)$$

and Eqs. (A18) and (A19) for the solution in Appendix A becomes (with  $c_\Delta(0) \rightarrow c_\Delta^K(0)$  etc.)

$$c_\Delta^K(0) = -2\kappa(q(2\xi) - q(-\xi)), \quad \xi = \frac{\pi}{6}\kappa R_K, \quad (3.8)$$

$$q(2\xi) - q(-\xi) = \frac{4\pi}{3}R_K, \quad (3.9)$$

where the parameter  $\kappa$  is defined by Eq. (A12) and  $q(x)$  is given by Eq. (A15). These quantities are the only ones needed in the electrostatic case at  $T = 0$ . From this one sees that

$$c_\Delta^K(0) = -16\xi. \quad (3.10)$$

Eq. (3.9) with expressions (3.7) and then (3.10) inserted gives the required equation for the parameter  $\xi = \xi(\rho, \alpha, K)$ .

For the quantized polarizable fluid the total internal energy per particle  $u_t$  is given by Eq. (76) in Ref. 6 as

$$\beta\rho u_t = 3\rho \sum_K \frac{1 + \alpha c_{\Delta}^K(0)}{K^2 + 1 + \alpha c_{\Delta}^K(0)} \quad (3.11)$$

when the replacement (2.7) for  $K$  is used. (In the reference  $1/\alpha = \sigma \hbar^2 \omega_0^2$ .) At  $T = 0$  one again can integrate, so with Eqs. (2.5) and (2.7)

$$u_t = 3\hbar\omega_0 \frac{1}{\pi} \int_0^{\infty} dK \frac{1 + \alpha c_{\Delta}^K(0)}{K^2 + 1 + \alpha c_{\Delta}^K(0)}. \quad (3.12)$$

With  $c_{\Delta}^K(0) = 0$  one gets the result for non-interacting oscillators (3 dimensions)

$$u_0 = 3\hbar\omega_0 \frac{1}{\pi} \int_0^{\infty} dK \frac{1}{K^2 + 1} = \frac{3}{2} \hbar\omega_0. \quad (3.13)$$

The difference gives the induced energy

$$u = u_t - u_0 = 3\hbar\omega_0 \frac{1}{\pi} \int_0^{\infty} dK \frac{K^2 \alpha c_{\Delta}^K(0)}{(K^2 + 1)(K^2 + 1 + \alpha c_{\Delta}^K(0))}. \quad (3.14)$$

At temperature  $T = 0$  this is also the induced free energy  $f = f(\rho)$  since the entropy vanishes at  $T = 0$  for quantized systems.

For general density the  $f$  must be evaluated numerically, but the low density limit may be checked against result (2.9). From Eq. (3.10)  $c_{\Delta}^K(0) = -16\xi$ , and from Eqs. (A12) and (3.5) in the limit  $\rho \rightarrow 0$  one finds  $\kappa \rightarrow 1/3$  as  $h_D \rightarrow c_D = 1/r^3$ , and from (3.9), (A15), and (3.7)  $24\xi + \dots = (4\pi/3)R_K$  by which  $16\xi \rightarrow (8\pi\rho\alpha/3)/(K^2 + 1)$ . Thus in this limit

$$f = u = -8\rho\alpha^2\hbar\omega_0 \int_0^{\infty} dK \frac{K^2}{(K^2 + 1)^3} = -\frac{\pi\rho\alpha^2\hbar\omega_0}{2} \quad (3.15)$$

which is result (2.9) for spheres of unit diameter  $R = 1$ .

In Figs. 2 and 3 the induced free energy (van der Waals energy) (3.14) divided by its low density expression (2.9) is shown as a function of density  $\rho$  and polarizability  $\alpha$  respectively. It is seen that this ratio decreases somewhat with respect to increasing density. This decrease is due to the interaction via many particles by which the direct pair interaction is modified into an effective one. The attractive part of the potential between neutral particles (e.g. the Lennard-Jones potential) is the above van der Waals interaction. Commonly it is assumed to be constant independent of density. Our results show that this is a reasonable approximation. Thus for the situation considered for Ar at the end of Sec. II with  $\alpha/R^3 \rightarrow \alpha = 0.0485$  and  $\rho R^3 \rightarrow \rho = 0.82$ , one from Figs. 2 or 3 finds the change  $\Delta f$  in the van der Waals interaction  $f$  compared to its low density value  $f_0$  to be

$$\Delta f = f - f_0 \approx -0.03 f_0 \approx 2 \text{ meV}. \quad (3.16)$$

It can be noted that our numerical results below are limited to  $\alpha = 1/8$  since for larger  $\alpha$  the MSA solution will fail to be unique. This value may reflect an instability of “close-packed” clusters in the fluid. The Clausius-Mosotti relation for the dielectric constant  $\epsilon$  on a regular cubic lattice would give  $(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)\rho\alpha = 1$  for  $\rho = 6/\pi$  when  $\alpha = 1/8$ , i.e.  $\epsilon \rightarrow \infty$ . Thus our results may cover realistic values of  $\alpha$  for fluids. (In SI units the limiting value  $\alpha/R^3 \rightarrow \alpha = 1/8$  corresponds to the polarizability  $\alpha_{SI} = 4\pi\epsilon_0\alpha = (\pi/2)\epsilon_0 R^3$ , where  $\epsilon_0$  is the permittivity of vacuum). Also our results cover densities of interest for fluids below close packing of hard spheres. The dielectric constant of the MSA fluid itself is given by  $\epsilon = q(2\xi)/q(-\xi)$  ( $K = 0$ ).<sup>22,24,25</sup> The problem with larger  $\alpha$  is connected to the properties of Eqs. (3.6) and (3.10) where one notes that  $R_0 \rightarrow \infty$  for  $\xi < 1/2$  when  $\alpha > 1/8$ . On the other hand the  $R_0$  of Eq. (A19) in Appendix A is finite for  $\xi < 1/2$  with  $q(2\xi)$  defined by Eq. (A15).

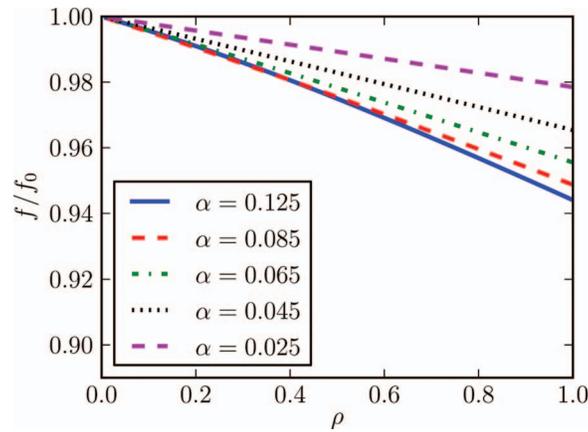


FIG. 2. Induced free energy (van der Waals energy) per particle  $f = f(\rho) = u$  in the electrostatic case as given by Eq. (3.14) divided by the low density limit  $f_0 = f(0)$  given by Eq. (2.9) (or Eq. (3.15) where  $R = 1$ ) as function of dimensionless density  $\rho R^3 \rightarrow \rho$ . The curves are for various values of the dimensionless polarizability  $\alpha/R^3 \rightarrow \alpha$  (in Gaussian units). In SI units the polarizability will be  $\alpha_{SI} = 4\pi\epsilon_0\alpha \rightarrow 4\pi\epsilon_0R^3\alpha$  where  $\epsilon_0 = 8.85 \cdot 10^{-12}$  As/(Vm) is the permittivity of vacuum.

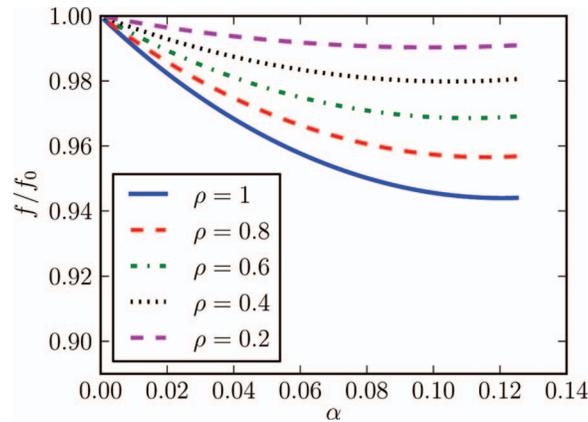


FIG. 3. Same as Fig. 2, but as function of polarizability  $\alpha/R^3 \rightarrow \alpha$  for various values of density  $\rho R^3 \rightarrow \rho$ .

#### IV. RADIATING INTERACTIONS

The quantum mechanical problem can be extended to time-dependent interactions as mentioned before. Within the MSA the problem again turns out to be solvable in terms of a simple fluid problem, i.e. hard spheres with added interaction of Yukawa form where also an analytic solution has been worked out. The  $c(12)$  and  $h(12)$  can still be written in the form (3.2), but the  $c_{\Delta}(r)$  and  $c_D(r)$  will change.<sup>24,25</sup> The radiating dipole-dipole interaction is a solution of Maxwell's equations, and with Eq. (5.10) of Ref. 9, one now instead of Eq. (3.5) will have<sup>26</sup>

$$c_{\Delta}(r) = -\frac{2}{3}z^2 \frac{e^{-zr}}{r}; \quad c_D(r) = \frac{e^{-zr}}{r^3} \left( 1 + zr + \frac{1}{3}(zr)^2 \right), \quad r > 1 \quad (4.1)$$

where  $z$  is given by Eq. (2.8) and  $r/R \rightarrow r$  such that again hard spheres of unit diameter are considered. (By a misprint the  $\psi_{\Delta K} = -c_{\Delta}$  has wrong sign in Ref. 9. As commented below Eq. (2.3) its  $K$  should have opposite sign too.) Like the static dipole-dipole interaction defined through Eqs. (3.2)–(3.5), the radiating one defined through Eqs. (3.2)–(3.4) is an interaction between pairs of particles. Radiation means exchange of energy between particles. But like the situation for one pair of particles in Sec. II such exchange does not enter evaluations at thermal equilibrium.

Now we apply transformation (A10) in Appendix A to the new  $c_D$  to obtain

$$\hat{c}_D(r) = \frac{1}{3}z^2 \frac{e^{-zr}}{r} \quad \text{for } r > 1. \quad (4.2)$$

It can be noted that the Yukawa form of  $\hat{c}_D(r)$  is an exact transformation of the radiating dipole-dipole interaction. Thus it does not serve as an approximation in the present case contrary to the typical situation by other applications in the statistical mechanics of fluids.

The definition (A12) of  $\kappa$  will remain. But with  $\tilde{c}_1$  and  $\tilde{c}_2$  given by Eq. (A8) the boundary conditions (A13) are modified into

$$\begin{aligned} \hat{c}_1(r) = 0 \quad \text{and} \quad \hat{c}_2(r) = -\frac{1}{3}z^2 \frac{e^{-zr}}{r} \quad \text{for } r > 1, \\ \hat{h}_1(r) = -2\kappa \quad \text{and} \quad \hat{h}_2(r) = \kappa \quad \text{for } r < 1. \end{aligned} \quad (4.3)$$

One can note that  $\hat{c}_1$  is unchanged. It corresponds to the longitudinal part of the dipolar interaction, i.e. the  $J_1$  term of Eq. (A5), while  $\hat{c}_2$  may be related to radiation of transverse waves, i.e. the  $J_2$  term. Again transformation (A14) in Appendix A is performed, and for  $C_1$  one has the same PY problem as before while for  $C_2$  one will get an MSA problem with one Yukawa term with boundary conditions (for density  $-\kappa R_K$ )

$$\begin{aligned} C_2(r) = K_y e^z \frac{e^{-zr}}{r}, \quad K_y = \frac{z^2}{3\kappa} e^{-z} \quad \text{for } r > 1, \\ H_2(r) = -1 \quad \text{for } r < 1. \end{aligned} \quad (4.4)$$

For  $q_1 = q(2\xi)$  the solution will be given by Eq. (A15) as before, but the  $q_2$  is replaced by  $a$  below. As found by Waisman the  $C_2(r)$  will have the following form for  $r < 1$ <sup>27,28</sup>

$$-C_2(r) = a + br + \frac{1}{2}xar^3 + v \frac{1 - e^{-zr}}{zr} + v^2 \frac{\cosh zr - 1}{2r K_y z^2 e^z} \quad (4.5)$$

with  $x = (\pi/6)n_2$  where  $n_2$  is number density. For the coefficients  $a$  and  $v$  one has the relations

$$\begin{aligned} a = a(x) = 1 - n_2 \tilde{C}_2(0) \\ v = v(x) = 24x K_y e^z \int_1^\infty r e^{-zr} g(r) dr \end{aligned} \quad (4.6)$$

where  $g(r) = H_2(r) + 1$ . Further from Eq. (4.5) one finds

$$-C_2(0) = a + v \quad (4.7)$$

The integral for  $v$  is proportional to the internal energy of the Yukawa fluid, and for low density and in the mean field limit  $z \rightarrow 0$  one finds with expression (4.4) inserted and with  $x = -\xi$

$$v = 24x K_y \frac{1+z}{z^2} \rightarrow -8\xi \frac{(1+z)e^{-z}}{\kappa} = -\frac{4\pi}{3} R_K (1 - \frac{1}{2}z^2 + \dots). \quad (4.8)$$

With expression (4.1) for  $c_D(r)$  one now will find from transformation (A10) that

$$\tilde{c}_D(0) = 0 \quad (4.9)$$

instead of Eq. (A19) with the consequence that Eq. (3.9) now turns into

$$q(2\xi) - a(-\xi) = 0. \quad (4.10)$$

This seems to be a discontinuous change of the equation, but it is not so. To see that one can take the  $z \rightarrow 0$  limit for which Eq. (4.8) gives  $v \rightarrow -(4\pi/3)R_K$ . In the electrostatic case with  $z = 0$  the  $\hat{c}_D(r)$  of Eq. (4.2) vanishes by which the  $v$  of Eq. (4.6) will vanish too. However, the  $-C_2(0) = q(-\xi)$  will have the limiting value of Eq. (4.7). Thus  $a + v \rightarrow q(-\xi)$ , ( $z \rightarrow 0$ ). With this

Eq. (4.10) becomes Eq. (3.9) in the limit  $z \rightarrow 0$ , and the discontinuity is avoided. Further, with use of Eq. (4.10), Eq. (3.8) will be modified to

$$c_{\Delta}^K(0) = 2\kappa(C_1(0) - C_2(0)) = -2\kappa(q(2\xi) - (a(-\xi) + v(-\xi))) = 2\kappa v(-\xi) \quad (4.11)$$

while Eq. (3.7) will remain unchanged.

Eq. (4.10) will be the equation to be solved for  $\xi$ . This is done together with Eq. (3.7) where Eq. (4.11) is inserted. Then the solution for  $a$  and  $v$  for the one Yukawa fluid problem is needed. Simplified expressions for this solution were worked out by Høye and Stell.<sup>28</sup> These expressions are used, and those needed here are given in Appendix B. Together they give a relation that are solved numerically with respect to the unknown parameter  $a$  ( $= a(-\xi)$ ). Then “reduced density”  $x = -\xi$  is assumed known. As shown in Appendix B the other quantities of interest can all be expressed explicitly in terms of  $a$  and  $\xi$ . With known  $a$  Eq. (4.10) may again be solved with respect to  $\xi$  in an iteration procedure.

When radiation is included expression (3.11) for the internal energy will be modified. The reason is the temperature dependence of the transformed interaction (4.3) outside the hard core. Thus we must turn to the free energy expression which is still valid. For the total free energy per particle  $f_i$  we can write

$$-\beta\rho f_i = I_0 + \sum_K (I_K^R + I_K) \quad (4.12)$$

where from Eqs. (66), (67), and (64) of the Ref. 6 one has (with  $\sigma\hbar^2\omega_0^2 = 1/\alpha$ )

$$I_K^R = \frac{3}{2}\rho \ln\left(\frac{\sigma R_K}{3\rho\eta^2}\right) + \frac{1}{2}R_K c_{\Delta}^K(0), \quad (4.13)$$

$$I_K = -\frac{1}{2}\frac{1}{(2\pi)^3} \int \{ \ln[1 - R_K \tilde{c}_1^K(k)] + 2 \ln[1 - R_K \tilde{c}_2^K(k)] \} d\mathbf{k} - \frac{1}{2}R_K c_{\Delta}^K(0). \quad (4.14)$$

Here  $I_K^R$  is the contribution from the reference system (with a modified  $R_K$  due to pair interactions) while  $I_K$  is the perturbation. To obtain expression (4.13) correctly the path integral was discretized such that

$$\beta = N\eta, \quad K = 2\pi n/\beta, \quad n = 0, 1, 2, \dots, N-1, \quad (4.15)$$

and the limit  $N \rightarrow \infty$  ( $\eta \rightarrow 0$ ) was considered. The  $I_0$  is merely hard spheres alone and will not contribute to the configurational internal energy as classical kinetic energy may be disregarded in this connection.

Again for  $T = 0$  it is convenient to consider the expression for the internal energy  $u_i$

$$\beta\rho u_i = -\sum_K (I_{K\beta}^R + I_{K\beta}), \quad I_{K\beta}^R = \beta \frac{\partial I_K^R}{\partial \beta}, \quad I_{K\beta} = \beta \frac{\partial I_K}{\partial \beta}. \quad (4.16)$$

Now with expression (4.15) one has

$$\beta \frac{\partial}{\partial \beta} = -K \frac{\partial}{\partial K} = \eta \frac{\partial}{\partial \eta}. \quad (4.17)$$

Further with Eq. (3.7) one can put  $R_K c_{\Delta}^K(0) = 3\rho - R_K(K^2 + 1)/\alpha$  for the last term of expression (4.13). With this substitution one will find that the partial differentiation with respect to  $R_K$  will vanish and thus will not contribute to  $u_i$ . This reflects the method used to differentiate the free energy in Ref. 6 where the density distribution  $\rho(\{\mathbf{s}_n\})$  of polymer configurations is considered constant (as it should) by differentiation with respect to temperature. (Here  $R_K/\eta$  is the corresponding quantity to be kept constant in this respect, according to its definition given by Eq. (47) of Ref. 6.) With this we find

$$-I_{K\beta}^R = 3\rho - \frac{1}{\alpha} K^2 R_K = 3\rho \frac{1 + \alpha c_{\Delta}^K(0)}{K^2 + 1 + \alpha c_{\Delta}^K(0)}, \quad (4.18)$$

$$-I_{K\beta} = \frac{1}{2} \frac{1}{(2\pi)^3} \left\{ \int \frac{R_K K \frac{\partial}{\partial K} \tilde{c}_1^K(k)}{1 - R_K \tilde{c}_1^K(k)} d\mathbf{k} + 2 \int \frac{R_K K \frac{\partial}{\partial K} \tilde{c}_2^K(k)}{1 - R_K \tilde{c}_2^K(k)} d\mathbf{k} \right\} - \frac{1}{2} R_K K \frac{\partial}{\partial K} c_{\Delta}^K(0). \quad (4.19)$$

When Eq. (4.18) alone is inserted in Eq. (4.16) the static result (3.11) is recovered in full. The reason for this is that here  $R_K$  is kept fixed by differentiation instead of  $R_K/\eta$  by which a contribution has moved from  $I_{K\beta}$  to  $I_{K\beta}^R$ . (If differentiation with respect to  $R_K$  had been included, one would get the integral  $\int [\tilde{h}_1(k) + 2\tilde{h}_2(k)] d\mathbf{k} = 0$  with use of Eq. (A9) and the core condition (A13) ( $\hat{c}_i(r) \rightarrow \hat{c}_i^K(r)$  etc.). Now one can write ( $i = 1, 2$ )

$$\frac{R_K}{1 - R_K \tilde{c}_i^K(k)} = R_K + R_K^2 \tilde{h}_i^K(k). \quad (4.20)$$

Inserted in the integrals of Eq. (4.19) the  $R_K$  term of Eq. (4.20) will give a common term multiplied with (cf. Eq. (A18))

$$\hat{c}_1^K(0) + 2\hat{c}_2^K(0) = c_{\Delta}^K(0) \quad (4.21)$$

which will cancel its last term. Integration in  $\mathbf{k}$ -space can be replaced with integration in  $\mathbf{r}$ -space, and we are left with

$$-I_{K\beta} = \frac{1}{2} R_K^2 \left[ \int \hat{h}_1^K(r) K \frac{\partial}{\partial K} \hat{c}_1^K(r) d\mathbf{r} + 2 \int \hat{h}_2^K(r) K \frac{\partial}{\partial K} \hat{c}_2^K(r) d\mathbf{r} \right]. \quad (4.22)$$

With boundary condition (4.3) on  $\hat{h}_i(r)$  the sum of integrals would vanish if  $\hat{c}_2(r)$  like  $\hat{c}_1(r)$  were non-zero only for  $r < 1$  since Eq. (A8) and condition (4.9) implies  $\tilde{c}_1(0) - \tilde{c}_2(0) = 0$ . Thus the net result is that only the part of  $\hat{c}_2^K(r)$  for  $r > 1$ , where  $\tilde{h}_2^K(r)$  deviates from its core condition, contributes to Eq. (4.22). So we get

$$-I_{K\beta} = R_K^2 \int_{r>1} [-\kappa + \hat{h}_2^K(r)] K \frac{\partial}{\partial K} \hat{c}_2^K(r) d\mathbf{r}. \quad (4.23)$$

For small  $z$  the first term is the leading one. Also in the low density limit  $\hat{h}_2(k) \rightarrow \hat{c}_2(k)$  by which simple explicit expressions can be obtained. However, the Fourier transform  $\tilde{h}_2(k)$  may be utilized to evaluate the last integral more generally.<sup>29</sup> A simpler method would be to evaluate the Laplace transform of  $r[-\kappa + \hat{h}_2(r)]$  (i.e. of  $r[H_2(r) + 1]$ ) and its derivative<sup>29</sup> since with Eqs. (2.8) and (4.3)

$$K \frac{\partial}{\partial K} \hat{c}_2^K(r) = z \frac{\partial}{\partial z} \hat{c}_2^K(r) = -\frac{2}{3} z^2 \frac{e^{-zr}}{r} + \frac{1}{3} z^3 e^{-zr}. \quad (4.24)$$

However, for simplicity we here will use  $\hat{h}_2(r) = \hat{c}_2(r)$  for all densities as  $z$  will be considered small, and we find

$$\begin{aligned} -I_{K\beta} &= 4\pi R_K^2 \left[ -\kappa z \int_{r>1} \hat{c}_2^K(r) r^2 dr + \frac{1}{2} z \frac{\partial}{\partial z} \int_{r>1} (\hat{c}_2^K(r))^2 r^2 dr \right] \\ &= 4\pi R_K^2 \left[ -\frac{1}{3} \kappa z^2 e^{-z} + \frac{1}{36} (3z^3 - 2z^4) e^{-2z} \right] \end{aligned} \quad (4.25)$$

where  $\kappa$  follows from its relation (3.8) to  $\xi$  and  $R_K$ . Again for non-interacting oscillators one has  $c_{\Delta}^K(0) = 0$  (and  $I_{K\beta} = 0$ ) with contribution  $u_0$  given by Eq. (3.13). When subtracting this from contribution (4.18) expression (3.14) for the static case is recovered. By including expression (4.25) to this the induced energy  $u$  and thus the induced free energy  $f$  is obtained

$$f = u = u_t - u_0 = \frac{\hbar\omega_0}{\pi\rho} \int_0^{\infty} \left[ \frac{3\rho K^2 \alpha c_{\Delta}^K(0)}{(K^2 + 1)(K^2 + 1 + \alpha c_{\Delta}^K(0))} - I_{K\beta} \right] dK. \quad (4.26)$$

It is of interest to show that the low density limit of this coincides with the Casimir energy. This is verified in Appendix C.

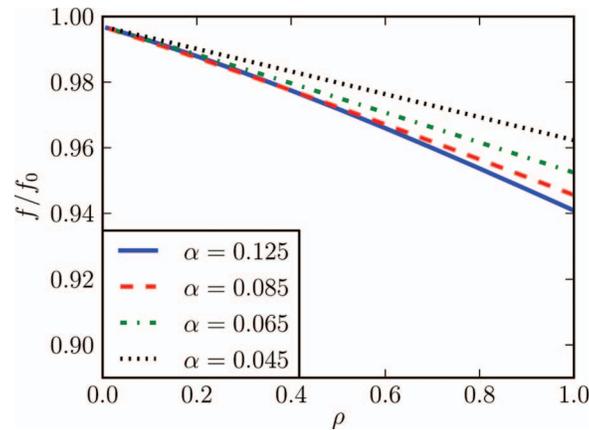


FIG. 4. Induced free energy (Casimir) per particle  $f = f(\rho) = u$  with radiating interaction as given by Eq. (4.26) divided by the low density limit  $f_0$  given by (2.9) (electrostatic case) as function of density. The curves for different polarizabilities  $\alpha$  are for dimensionless wavelength  $\lambda = 2\pi/(\omega_0 R) = 100$ .

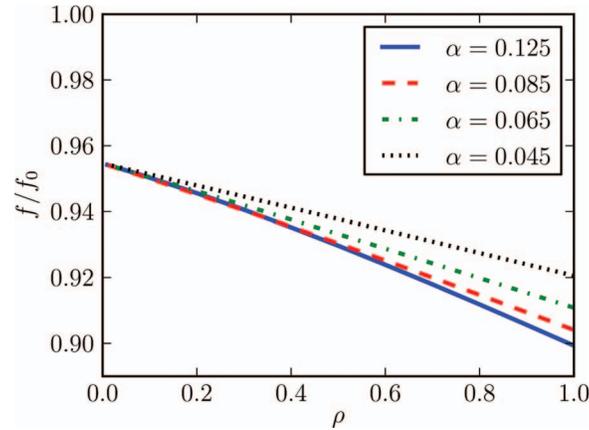


FIG. 5. The same as Fig. 4 for  $\lambda = 20$ .

In Figs. 4 and 5 the induced free energy (Casimir energy) (4.26) divided by the low density value (2.9) (static case) is shown as function of density for  $\lambda = 2\pi/\gamma = 2\pi c/(\omega_0 R) = 100$  and  $\lambda = 20$  respectively. When compared with the electrostatic case ( $\gamma = 0$ ) shown in Fig. 2 one sees a small change due to radiation effects.

In Figs. 6 and 7 the small difference  $\Delta f$  between the Casimir energy (4.26) and the van der Waals energy (3.14) divided by  $f_0$  given by Eq. (2.9) is shown for different values of  $\lambda$ . A notable feature of this difference relative to  $f_0$  is that it is almost independent of density and polarizability. This was not expected. However, by further considerations it seems to us that the physical interpretation of this unexpected independence can be understood from Eq. (2.11) where Eq. (2.12) is the perturbation from radiation. As commented below the latter equation, the largest correction from radiation comes from separations where particles are close to each other. In this way the influence from correlations with surrounding particles further away becomes small, and the correction becomes mainly the contribution from the direct sum of all separate pairs of particles like it is for low density. The counterintuitive aspect of this is that the relative influence from radiation upon the induced interaction dominates for large separations; but since the interaction decays rapidly with increasing separation anyway, this has little influence upon the resulting energy when integrated.

For the situation with liquid Ar considered at the end of Sec. II the correction from radiation can be read off from Figs. 6 or 7. As the relative change in free energy is almost independent of  $\rho$

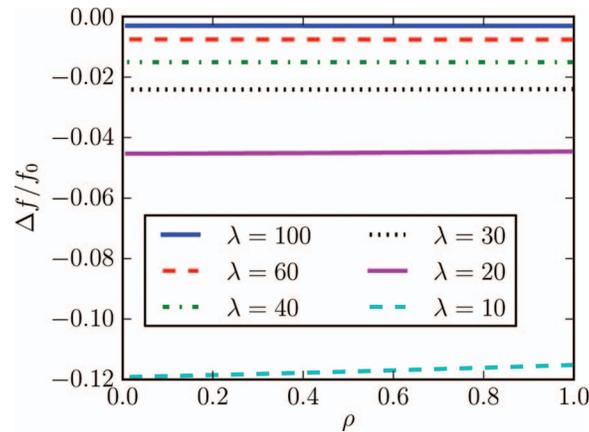


FIG. 6. The difference  $\Delta f$  between the induced Casimir free energy given by Eq. (4.26) and the van der Waals energy given by Eq. (3.14) divided by  $f_0$  given by Eq. (2.9) as function of dimensionless density. The curves for different values of  $\lambda = 2\pi/(\omega_0 R)$  are for dimensionless polarizability  $\alpha = 0.075$ . A notable feature of these curves is that there is almost no dependence upon  $\alpha$ .

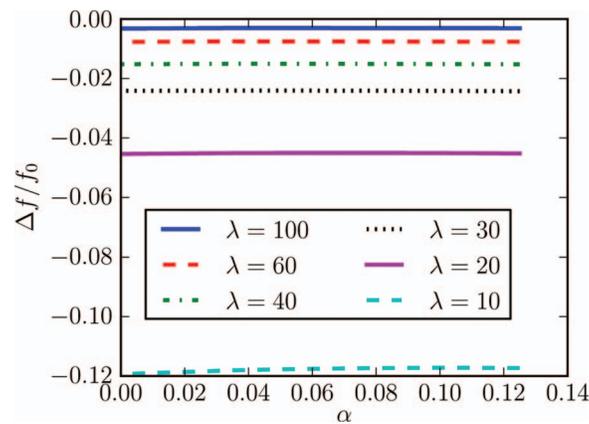


FIG. 7. The same as Fig. 6, but now as function of polarizability  $\alpha$  for density  $\rho = 0.5$ .

and  $\alpha$ , it remains essentially the same as already found at the end of that section for  $\lambda \approx 150$  where  $\Delta f_{rad} = 0.12$  meV was found.

## V. SUMMARY

We have studied corrections from radiation for a simplified fluid model consisting of hard spheres with fluctuating dipole moments located at their centers. The fluctuating dipole moments are quantized as harmonic oscillators. First the well established Casimir interaction between a pair of particles is studied. Its electrostatic limit is the induced van der Waals interaction. For low density of particles the contribution to the energy of the fluid is obtained by averaging the Casimir energy over particle positions. The influence of radiation or retardation effects depends upon the ratio of the hard sphere diameter and the characteristic wavelength of the electromagnetic radiation at the harmonic oscillator eigenfrequency. Then general fluid density is considered for the electrostatic case, and changes in the van der Waals interaction are found. The fluid model used, is the quantized polarizable fluid evaluated by a method based upon classical statistical mechanics. Finally radiation effects are taken into account by further extension of the polarizable fluid model. Results are presented in Figs. 1–7. As a general feature we find that the average van der Waals interaction per pair of particles decreases slightly with increasing particle density. Radiation effects are small, but will increase in

magnitude for increasing particle size relative to characteristic wavelength of radiation. As a specific example, numerical values are found for Ar in liquid state.

## APPENDIX A: SOLUTION STATIC CASE

The classical polarizable fluid may be regarded as a polar fluid with (fixed) dipole moment  $m$ . With this Eq. (3.1) can be written (with  $\rho(\mathbf{s}_3) \rightarrow \rho$ )

$$h(12) = c(12) + \rho \int c(13) * h(32) d\mathbf{r}_3 \quad (\text{A1})$$

where \* denotes the remaining integration over orientations of the dipole moment. Its Fourier transform is

$$\tilde{h}(12) = \tilde{c}(12) + \rho \tilde{c}(13) * \tilde{h}(32) \quad (\text{A2})$$

where the tilde denotes Fourier transform. We can write

$$\begin{aligned} \tilde{c}(12) &= \tilde{c}_0 + \beta m^2 (\tilde{c}_\Delta \Delta + \tilde{c}_D D) \\ \tilde{h}(12) &= \tilde{h}_0 + \beta m^2 (\tilde{h}_\Delta \Delta + \tilde{h}_D D) \end{aligned} \quad (\text{A3})$$

where  $\tilde{c}_\Delta = \tilde{c}_\Delta(k)$  etc. with Fourier variable  $\mathbf{k}$ . The  $\Delta = \Delta(12)$  as given by Eq. (3.3) and

$$D = \tilde{D}(12) = 3(\hat{k}_1 \hat{s}_2)(\hat{k}_1 \hat{s}_2) - \hat{s}_1 \hat{s}_2. \quad (\text{A4})$$

The  $c_0$  and  $h_0$  represent the reference system hard spheres and do not couple to the remaining terms by solution. The remaining terms decouple by introduction of<sup>24,25</sup>

$$J_1 = D + \Delta \quad \text{and} \quad J_2 = 2\Delta - D \quad (\text{A5})$$

by which ( $J_1 J_1 = J_1 * J_1$  etc.)

$$J_1 J_1 = J_1; \quad J_2 J_2 = J_2; \quad J_1 J_2 = 0. \quad (\text{A6})$$

Then we have

$$\begin{aligned} \tilde{c} &= \tilde{c}_0 + \tilde{c}_1 J_1 + \tilde{c}_2 J_2 \\ \tilde{h} &= \tilde{h}_0 + \tilde{h}_1 J_1 + \tilde{h}_2 J_2 \end{aligned} \quad (\text{A7})$$

where

$$\begin{aligned} \tilde{c}_1 &= (\tilde{c}_\Delta + 2\tilde{c}_D)/3; \quad \tilde{c}_\Delta = \tilde{c}_1 + 2\tilde{c}_2 \\ \tilde{c}_2 &= (\tilde{c}_\Delta - \tilde{c}_D)/3; \quad \tilde{c}_D = \tilde{c}_1 - \tilde{c}_2 \end{aligned} \quad (\text{A8})$$

with similar expressions for  $\tilde{h}_1$  and  $\tilde{h}_2$ . With this the Ornstein-Zernike equation (A2) separates into the following equations (besides the one for  $\tilde{c}_0$  and  $\tilde{h}_0$ )

$$\begin{aligned} \tilde{h}_1 &= \tilde{c}_1 + R_0 \tilde{c}_1 \tilde{h}_1 \\ \tilde{h}_2 &= \tilde{c}_2 + R_0 \tilde{c}_2 \tilde{h}_2 \end{aligned} \quad (\text{A9})$$

where  $R_0 = \beta \rho m^2$  as given by Eq. (3.6). With this the angular dependence has disappeared such that the  $\tilde{c}_D$  and  $\tilde{h}_D$  can be regarded as Fourier transforms of functions of spherical symmetry. These functions to be denoted by hats are obtained by the transform ( $c \rightarrow c_D, h_D$ )<sup>24,25</sup>

$$\begin{aligned} \hat{c}(r) &= c(r) - 3 \int_r^\infty c(r') r'^{-1} dr' \\ c(r) &= \hat{c}(r) - \frac{3}{r^3} \int_0^r \hat{c}(r') r'^2 dr'. \end{aligned} \quad (\text{A10})$$

Then boundary conditions (3.5) imply

$$\begin{aligned}\hat{c}_D(r) &= 0, & r > 1 \\ \hat{h}_D(r) &= -3\kappa, & r < 1\end{aligned}\quad (\text{A11})$$

where

$$\kappa = \int_1^{\infty} h_D(r)r^{-1} dr. \quad (\text{A12})$$

Thus with this and Eqs. (3.5) and (A8) the boundary conditions become

$$\begin{aligned}\hat{c}_1(r) &= 0 & \text{and} & \hat{c}_2(r) = 0 & \text{for } r > 1 \\ \hat{h}_1(r) &= -2\kappa & \text{and} & \hat{h}_2(r) = \kappa & \text{for } r < 1.\end{aligned}\quad (\text{A13})$$

With a final transformation

$$\begin{aligned}\hat{h}_1 &= 2\kappa H_1; & \hat{c}_1 &= 2\kappa C_1 \\ \hat{h}_2 &= -\kappa H_2; & \hat{c}_2 &= -\kappa C_2\end{aligned}\quad (\text{A14})$$

one obtains Ornstein-Zernike equations with the boundary conditions for hard spheres, the Percus-Yevick (PY) approximation, for two cases with densities  $2\kappa R_0$  and  $-\kappa R_0$  respectively.

From the solution of the hard spheres PY problem<sup>30</sup> one finds<sup>6,24,25</sup>

$$\begin{aligned}1 - n_i \tilde{C}_i(0) &= q_i, & (i = 1, 2) \\ q_i &= q(x_i) = \frac{(1 + 2x_i)^2}{(1 - x_i)^4}, & x_i = \frac{\pi}{6} n_i\end{aligned}\quad (\text{A15})$$

with number densities

$$n_1 = 2\kappa R_0 \quad \text{and} \quad n_2 = -\kappa R_0. \quad (\text{A16})$$

Further for hard spheres<sup>28,30</sup>

$$-C_i(0) = q_i \quad (\text{A17})$$

from which with use of Eqs. (A8) and (A14) one obtains

$$c_{\Delta}(0) = \hat{c}_1(0) + 2\hat{c}_2(0) = -2\kappa(q_1(2\xi) - q_2(-\xi)), \quad \xi = \frac{\pi}{6}\kappa R_0. \quad (\text{A18})$$

From the Fourier transform of  $c_D(r)$  ( $\rightarrow 1/r^3$ ,  $r \rightarrow \infty$ ) or by use of transformation (A10) one finds

$$\tilde{c}_D(0) = -\frac{4\pi}{3}.$$

Together with Eqs. (A8), (A14), and (A15) this gives  $R_0\tilde{c}_D(0) = 2\kappa R_0\tilde{C}_1(0) - (-\kappa R_0)\tilde{C}_2(0)$  or

$$q(2\xi) - q(-\xi) = \frac{4\pi}{3}R_0. \quad (\text{A19})$$

## APPENDIX B: SOLUTION RADIATING CASE

To obtain the solution of the one Yukawa problem with boundary condition (4.4) auxiliary quantities  $U_0$  and  $U_1$  are found. Eq. (2.31) of Ref. 28 then gives for  $U_0$

$$\begin{aligned}U_0 + A - p &= \frac{1}{2} \left( -p - z\sqrt{A} + \sqrt{p^2 + 2pz\sqrt{A} + z^2p} \right) \\ A &= (1 - x)^2 a; \quad p = (1 - x)^2 q(x) = \left( \frac{1 + 2x}{1 - x} \right)^2.\end{aligned}\quad (\text{B1})$$

Further its Eqs. (2.24) and (2.26) give for  $U_1$

$$U_1 = (2 - \sqrt{p})U_0 - \Gamma$$

$$2\sqrt{p}\Gamma = (U_0 + A - p)(U_0 + A) + \frac{1}{4}z^2(p - A). \quad (\text{B2})$$

With this the connection between  $a$  and  $K_y$  is given by its Eq. (2.38) as

$$K_y = \frac{z^2}{6x(z+2)^2} \left[ \frac{\sigma - \tau y}{(\sigma - \tau)y} \right]^2 U_0 \quad (\text{B3})$$

where from its Eqs. (2.35) and (2.36)

$$\sigma = \frac{1}{2z} \left[ \frac{z-2}{z+2} + e^{-z} \right]; \quad \tau = \frac{1}{2z} \left[ \frac{z^2+2z-4}{z^2+2z+4} + e^{-z} \right] \quad (\text{B4})$$

$$y = \frac{4+2z-z^2}{2(2+z)} \frac{U_0}{U_1}. \quad (\text{B5})$$

However,  $K_y$  depends upon  $\kappa$ , but with expressions (3.8) for  $\xi$  and (4.4) for  $K_y$  one notes that

$$6\xi K_y = \frac{\pi}{3} z^2 e^{-z} R_K. \quad (\text{B6})$$

Further expression (4.11) for  $c_{\Delta}^K(0)$  is to be inserted in expression (3.7) for  $R_K$ . Then the quantity  $v(-\xi)$  is needed, and Eq. (2.37) of the reference gives

$$v = v(x) = K_y \frac{1-y}{\sigma - \tau y}. \quad (\text{B7})$$

Eq. (B3) with Eqs. (B1), (B2), and (B4)–(B6) inserted for fixed  $x = -\xi$  gives the relation that can be solved numerically with respect to  $a = a(-\xi)$ . This is then used in Eq. (4.10) to obtain  $\xi$  by iterations. (Also Eq. (4.10) may be solved explicitly as  $\xi = \xi(a)$  by which  $a$  will be the only parameter to solve for.)

For small  $K_y \rightarrow 0$  ( $A \rightarrow p$ ,  $U_0 \rightarrow 0$ ) one may utilize a more transparent linearized version by which numerical solution of Eq. (B3) is avoided. The solution for this situation may be used as input for the non-linear case. Then Eq. (2.42) of Ref. 28 or Eqs. (B1) and (B2) above give a fixed ratio

$$\frac{U_1}{U_0} = 2 - \sqrt{p} - \frac{\frac{1}{4}z^2}{\sqrt{p} + \frac{1}{2}z} \quad (\text{B8})$$

to be used in Eq. (B7) via Eq. (B5) to determine  $v$ . Further its Eq. (2.39) or Eq. (B1) determine  $a$  since then

$$A - p = - \left[ 1 - \frac{\frac{1}{4}z^2}{(\sqrt{p} + \frac{1}{2}z)^2} \right] U_0 \quad (\text{B9})$$

where with known  $K_y$  and  $v$  the  $U_0$  follows from Eq. (2.34) of the reference as

$$U_0 = 6\xi K_y \left( \frac{z+2}{z} \right)^2 \left( 1 - \sigma \frac{v}{K_y} \right)^2. \quad (\text{B10})$$

With this the  $a(-\xi)$  is obtained by use of Eqs. (B8), (B5), (B7), and (B10) in Eq. (B9). This is further inserted in Eq. (4.10) to be solved numerically with respect to  $\xi$ .

### APPENDIX C: LOW DENSITY LIMIT

In the low density limit one finds from Eq. (3.7)  $R_K \rightarrow 3\rho\alpha/(K^2 + 1)$ , and a partial integration can be performed on the first part of integral (4.26) for the induced free energy to obtain

$$f = \frac{\hbar\omega_0}{\pi\rho} \int_0^\infty \left\{ \frac{1}{4} R_K^2 \left[ \frac{c_\Delta^K(0)}{R_K} + K \frac{\partial}{\partial K} \left( \frac{c_\Delta^K(0)}{R_K} \right) \right] - I_{K\beta} \right\} dK. \quad (\text{C1})$$

Then low density values of  $\kappa$  and  $c_\Delta(0)$  are needed. The  $\kappa$  is most easily obtained from its definition (A12), and with  $h_D(r) \rightarrow c_D(r)$  expression (4.1) gives

$$\kappa = \frac{1}{3}(1+z)e^{-z}. \quad (\text{C2})$$

Likewise  $c_\Delta^K(0)$  given by Eq. (4.11) is most easily obtained via definition (4.6) of  $v$ . Then  $H_2(r) \rightarrow C_2(r)$  with  $C_2(r)$  given by Eq. (4.4), and we find

$$v = v(-\xi) = -24\xi \left( K_y \frac{1+z}{z^2} + K_y^2 \frac{1}{2z} \right) = -24\xi \left( \frac{(1+z)e^{-z}}{3\kappa} + \frac{z^3 e^{-2z}}{18\kappa^2} \right). \quad (\text{C3})$$

Thus with Eqs. (3.8), (4.11), (C2), and (C3)

$$\frac{c_\Delta^K(0)}{R_K} = \frac{\pi\kappa 2\kappa v(-\xi)}{6\xi} = -\frac{4\pi}{9} [2(1+z)^2 + z^3] e^{-2z}, \quad (\text{C4})$$

$$z \frac{\partial}{\partial z} \left( \frac{c_\Delta(0)}{R_K} \right) = \frac{4\pi}{9} z^2 (4+z+2z^2) e^{-2z}. \quad (\text{C5})$$

With expression (C2) for  $\kappa$  inserted in Eq. (4.25) and then compared with expression (C5), one finds that the last two terms of integral (C1) cancels. Then expression (C4) is inserted in its first term to obtain

$$f = -\frac{\hbar\omega_0}{9\rho} \int_0^\infty R_K^2 [2(1+z)^2 + z^3] e^{-2z} dK \quad (\text{C6})$$

which is the low density Casimir free energy (2.6) (with  $R = 1$ ).

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