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Radiative corrections to van der Waals interaction in fluids

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Abstract

The van der Waals interaction energy is derived for a homogenous fluid of polarizable particles. Low-temperature corrections to the van der Waals interaction energy are computed numerically for three cases: Dilute media with radiative interactions, arbitrarily dense media without radiative interactions, and arbitrarily dense media with radiative interactions. The validity of the model used to calculate the corrections at arbitrary densities is argued for, by comparison with the results for low densities.

Sammendrag

Van der Waals-kraften utledes for et homogent fluid med polariserbare partikler. Korreksjoner til van der Waals-kraften ved lav temperatur beregnes numerisk for tre tilfeller: Medier med lav tetthet og strålingsvekselvirkning, medier med vilkårig tetthet men uten strålingsvekselvirkning, samt medier med vilkårig tetthet og strålingsvekselvirkning. Gyldigheten til modellen brukt for å beregne korreksjonene ved vilkårige tettheter argumenteres for, ved sammenligning med resultatene for lave tettheter.

Preface

This thesis marks the end of my studies at the five year master programme of applied physics at NTNU, and was carried out in two parts in the period August 2011 to June 2012. I would like to thank my supervisor, Johan Skule Høye, for patiently providing me with excellent advice, and always being available to give said advice.

Contents

Preface	3
1 Introduction	5
1.1 Units and conventions	5
1.2 The van der Waals interaction energy	6
2 Radiative interactions, dilute media	8
2.1 Altered interaction energy	8
2.2 Calculation of free energy per interaction	9
2.3 Calculation of free energy per particle	11
3 Arbitrary densities, instantaneous dipole interaction	15
3.1 The Ornstein-Zernike equation	15
3.2 Calculation of the free energy per particle	17
4 Arbitrary densities, radiative correction	22
4.1 New Ornstein-Zernike equation	22
4.2 Calculation of the free energy per particle	22
4.3 Proper expression for free energy	27
4.4 Calculation of the free energy	29
5 Conclusion	39
A Full expression for final term	40
References	43

1 Introduction

To study the chemical properties of fluids, knowing the free energy contained in the fluids is useful. This quantity lets us know the amount of work that can be done by the fluid when interacting with external elements, and thus helps predict whether a reaction will be spontaneous, and lets us know if a specific arrangement is stable or will degenerate.

A commonly considered situation is a homogenous fluid of polarizable particles. In this situation, the particles will act as dipoles, and interact with each other through dipole interaction. Usually, the approach to this problem would be to assume that the fluid is dilute, and that the dominating interaction between the particles is the instantaneous dipole interaction. Taking this approach leads to the well known van der Waals interaction energy.

In this thesis, we will examine corrections to this approach, in the cases where we can no longer assume a dilute fluid, as well as the case where we no longer neglect radiative contributions to the interaction energy.

Considering radiative contributions implies that our problem becomes dynamic, which normally would mean that a method using the canonical distributions of statistical mechanics would fail. We shall apply a method that will allow us to bypass this problem, giving accurate results for the Casimir energy per particle in the fluid.

In the case of arbitrary, homogenous, densities, we will be making use of the Ornstein-Zernike equation under the conditions of the mean spherical approach. This will give us a set of equations to be used for determining the free energy of the particles numerically. In the case where radiative interactions are neglected, we will show analytically that our result indeed corresponds to the van der Waals energy as density approaches zero.

In the case where radiative interactions are taken into account, we will produce computations for a lower order correction, while giving a full expression in the appendix.

In all cases, explicit computations will be made numerically, and compared to the van der Waals interaction energy.

This thesis builds on work done for the autumn project of the author, which is important to the understanding of the work done in the thesis. Sections from that project will be quoted and expanded upon without offering a citation.

1.1 Units and conventions

To simplify graphing, good quantities are needed. Most importantly, we want the graphed quantities to be dimensionless. For the most part, this is achieved by normalizing results. For instance, distance from the center of a particle, r is normalized by the hard-sphere radius of the particle, R ,

$$r \rightarrow r^* = r/R. \quad (1)$$

This implies that distance becomes a unitless quantity, necessarily transforming also other quantities. I shall attempt to clarify how key equations are transformed when going from a such normalized description, to a non-normalized view.

Perhaps most importantly, this thesis will use gaussian units (transforming from SI-units to gaussian units is a matter of writing $4\pi\epsilon_0 = 1$). This is done to keep it consistent with the majority of the cited works. When works that do not use gaussian units are cited, care will be taken to make note of any difference.

1.2 The van der Waals interaction energy

Let us first begin by calculating the van der Waals interaction energy at low density. We shall do this by using a statistical mechanical approach, which will then be altered as we move on to the more involved problems. The van der Waals interaction energy is found by considering electric dipole interaction between molecules with a net charge of zero. The dipole moments are assumed to be induced by an external electric field, and have a polarizability which fluctuates thermally. These harmonic fluctuations result in a distribution function for the dipole moment of each molecule which, assuming a static polarizability α , is equal to

$$\rho(s) = \exp\left(-\frac{\beta s^2}{2\alpha}\right) \quad (2)$$

where $\beta = 1/k_B T$.

Assuming perfect dipoles, the interaction energy of two dipoles separated by a displacement \mathbf{r} can be shown to be [1]

$$V(\mathbf{r}) = \frac{1}{r^3} [\mathbf{s}_1 \cdot \mathbf{s}_2 - 3(\mathbf{s}_1 \cdot \hat{\mathbf{r}})(\mathbf{s}_2 \cdot \hat{\mathbf{r}})] \quad (3)$$

where \mathbf{s}_i is the dipole moment of particle i , and where the hats are used to denote a unit vector.

The partition function is found by considering a system describing the possible configurations of two molecules, perturbing the configuration with the dipole interaction energy [2]

$$Z = \int d^3s_1 d^3s_2 \rho(s_1) \rho(s_2) \exp(-\beta V(\mathbf{r})), \quad (4)$$

yielding a free energy per interaction

$$F = -\frac{3\alpha^2}{\beta r^6}, \quad (5)$$

the van der Waals interaction. We note that this is linear in temperature, and is expected to disappear as $T \rightarrow 0$. If we were not to normalize r according to the hard-sphere radius, this equation should still be of the same form. In accordance with this, we see that when normalizing the radius we also normalize the polarizability,

$$\alpha \rightarrow \alpha^* = \alpha/R^3. \quad (6)$$

The energy calculated here assumes that we have a dilute medium, and that the dipole interaction happens instantaneously, that is, that there is no radiative term. Obviously, this assumption has the advantage of being computationally easy. What is more, it seems like a robust assumption - results obtained from calculations using it seem to fit well with experimental results. Regardless, investigating the deviation this approach yields from a

more thorough approach is of interest. To do this, we will calculate energy, first keeping radiative interactions, secondly dropping radiative interactions but using arbitrarily high (but physical) densities, and finally using arbitrarily high densities as well as a radiative term. All the computations will be made at $T \rightarrow 0$.

2 Radiative interactions, dilute media

In this section, we shall calculate the radiative correction to the van der Waals interaction defined in the preceding section. We begin by finding a new expression for the interaction energy, later stating the change made to the partition function and the resulting free energy.

2.1 Altered interaction energy

Wanting to find the radiative correction, we first need to find the interaction energy. This is done by considering Maxwell's equations, as in [3]:

$$\begin{aligned}\nabla \times \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad \nabla(\mathbf{E} + 4\pi\mathbf{P}) = 0, \\ \nabla \times \mathbf{B} &= \frac{1}{c} \frac{\partial}{\partial t}(\mathbf{E} + 4\pi\mathbf{P}), \quad \nabla\mathbf{B} = 0\end{aligned}\quad (7)$$

We make the ansatz

$$\begin{aligned}\mathbf{E} = \mathbf{E}(\mathbf{r}, t) &= \mathbf{E}'(\mathbf{r})e^{i\omega't + \delta t} = \mathbf{E}'(\mathbf{r})e^{i\omega t} \\ \mathbf{P} = \mathbf{P}(\mathbf{r})e^{i\omega t}, \quad \mathbf{B} &= \mathbf{B}'(\mathbf{r})e^{i\omega t}\end{aligned}\quad (8)$$

where ω has an infinitesimal imaginary part, to ensure that as $t \rightarrow -\infty \Rightarrow \mathbf{E}(\mathbf{r}, t) \rightarrow 0$, meaning that we only consider time-retarded solutions. Using this ansatz, we can eliminate \mathbf{B} , yielding

$$\nabla \times (\nabla \times \mathbf{E}') = -\left(\frac{\omega}{c}\right)^2 (\mathbf{E}' + 4\pi\mathbf{P}'), \quad \nabla(\mathbf{E}' + 4\pi\mathbf{P}') = 0 \quad (9)$$

By Fourier transform, this becomes

$$k^2[\tilde{\mathbf{E}} - \hat{k}(k\tilde{\mathbf{E}})] = \left(\frac{\omega}{c}\right)^2 (\tilde{\mathbf{E}} + 4\pi\tilde{\mathbf{P}}), \quad \hat{k}(\tilde{\mathbf{E}} + 4\pi\tilde{\mathbf{P}}) = 0 \quad (10)$$

Leading to an expression for the fourier transform of the induced electric field,

$$\tilde{\mathbf{E}} = -\frac{4\pi}{3} \frac{k^2}{k^2 - \omega^2/c^2} [3\hat{k}(\hat{k}\tilde{\mathbf{P}}) - \tilde{\mathbf{P}}] + \frac{4\pi}{3} \left(\frac{2\omega^2/c^2}{k^2 - \omega^2/c^2} - 1 \right) \tilde{\mathbf{P}}. \quad (11)$$

Approximating the molecules of the fluid as point dipoles, we have $\mathbf{P}'(\mathbf{r}_1) = \mathbf{s}_1\delta(\mathbf{r}_1)$, implying that $\tilde{\mathbf{P}} = \mathbf{s}_1$. From this, the fourier transformed interaction energy becomes

$$\begin{aligned}\tilde{V}(12) &= -s_1s_2\tilde{\psi}(12), \\ \tilde{\psi}(12) &= \tilde{\psi}_D(k)\tilde{D}(12) + \tilde{\psi}_\Delta(k)\tilde{\Delta}(12), \\ \tilde{\psi}_D(k) &= -\frac{4\pi}{3} \frac{k^2}{k^2 - \omega^2/c^2}, \quad \tilde{\psi}_\Delta(k) = \frac{4\pi}{3} \left(\frac{2\omega^2/c^2}{k^2 - \omega^2/c^2} - 1 \right), \\ \tilde{D}(12) &= 3(\hat{k}\hat{s}_1)(\hat{k}\hat{s}_2) - \hat{s}_1\hat{s}_2, \quad \tilde{\Delta}(12) = \hat{s}_1\hat{s}_2,\end{aligned}\quad (12)$$

Inverting the transform, we end up with

$$\begin{aligned}\psi_D(r) &= \frac{e^{i\omega r}}{r^3} \left[1 + i\frac{\omega r}{c} - \frac{1}{3} \left(\frac{\omega r}{c} \right)^2 \right] \\ \psi_\Delta(r) &= \frac{2}{3} \left(\frac{\omega}{c} \right)^2 \frac{e^{i\omega r}}{r} - \frac{4\pi}{3} \delta(r)\end{aligned}\quad (13)$$

2.2 Calculation of free energy per interaction

Following [2], we now replace equation (2), with

$$\rho(\{S_q\}) = C \exp \left\{ - \sum_{p=0}^{N-1} \left[\frac{1}{2} \frac{\sigma}{\eta} (s_{p+1} - s_p)^2 + \frac{\eta}{2\alpha} s_p^2 \right] \right\} \quad (14)$$

with $\sigma = M/(\hbar e)^2$, M being the nucleus mass and e being its charge, and where N is the number of particles and $\eta = \beta/N$.

We should note that we are no longer using classical methods, as this distribution stems from the propagator solution to the Schrödinger equation for a harmonically oscillating dipole, with $i\hbar\beta$ being interpreted as imaginary time. The reason for doing this is our desire to consider the radiative interactions by means of statistical mechanics. Normally, this would be problematic, as the radiative interactions represent a dynamic problem, which we cannot handle by means of statistical mechanics. However, in obtaining this distribution, we interpret our particles no longer as point-particles, but as polymer rings forming closed loops of length β . Thus, imaginary time is interpreted not as a temporal, but as a spatial dimension. In this way, we find that we can still apply the tools of statistical mechanics to the problem.

What is more, it is only this part that needs to be calculated using quantum mechanics. Once we use this distribution, the remaining elements of the problem can be viewed classically. So, by using this distribution, we have gone from a dynamic interaction between two point-particles, to a static interaction between all the elements on two polymers.

This distribution, combined with the new interaction energy, leads to a different partition function, and by introducing $\tau = \frac{i\omega r}{c} = \frac{|K|r}{\hbar c}$ and $K = 2\pi n/\beta$, $n \in \mathbb{Z}$, this will lead to an expression for the free energy per interaction

$$\beta F = -\frac{3}{2r^6} \sum_{n=-\infty}^{\infty} e^{-2\tau} \left[2\left(1 + \tau + \frac{1}{3}\tau^2\right)^2 + \left(\frac{2}{3}\tau^2\right)^2 \right] \alpha_K^2 \quad (15)$$

where

$$\alpha_K = \frac{\alpha}{\alpha\sigma K^2 + 1} = \frac{1}{\sigma(K^2 + (\hbar\omega_0)^2)}, \quad (16)$$

is the effective polarization and ω_0 can be viewed as the eigenfrequency of the oscillator, $\omega_0^2 = (\alpha\sigma\hbar^2)^{-1}$. Considering the limit $T \rightarrow 0$, we have $\sum \rightarrow 2(\beta\hbar c/2\pi r) \int_0^\infty d\tau$, yielding

$$F = -\frac{3\hbar c}{2\pi r^7} \int_0^\infty d\tau e^{-2\tau} \frac{[2(1 + \tau + \frac{1}{3}\tau^2)^2 + (\frac{2}{3}\tau^2)^2]}{\sigma^2(\frac{(\hbar c)^2\tau^2}{r^2} + (\hbar\omega_0)^2)^2} \quad (17)$$

which can be rewritten as

$$F = -\frac{3}{2(\hbar c)^3\pi r^3} \int_0^\infty d\tau e^{-2\tau} \frac{[2(1 + \tau + \frac{1}{3}\tau^2)^2 + (\frac{2}{3}\tau^2)^2]}{\sigma^2(\tau^2 + (\frac{\omega_0 r}{c})^2)^2} \quad (18)$$

or as

$$F = -\frac{3}{2\pi r^6} \int_0^\infty dK e^{-2\frac{Kr}{\hbar c}} \frac{[2(1 + \frac{Kr}{\hbar c} + \frac{1}{3}(\frac{Kr}{\hbar c})^2)^2 + (\frac{2}{3}(\frac{Kr}{\hbar c})^2)^2]}{\sigma^2(K^2 + (\hbar\omega_0)^2)^2}. \quad (19)$$

The energy obtained as a function of the distance between the two molecules is described in figure 1. From this figure it is apparent that the largest contributions to the free energy happen if the particles are close to each other.

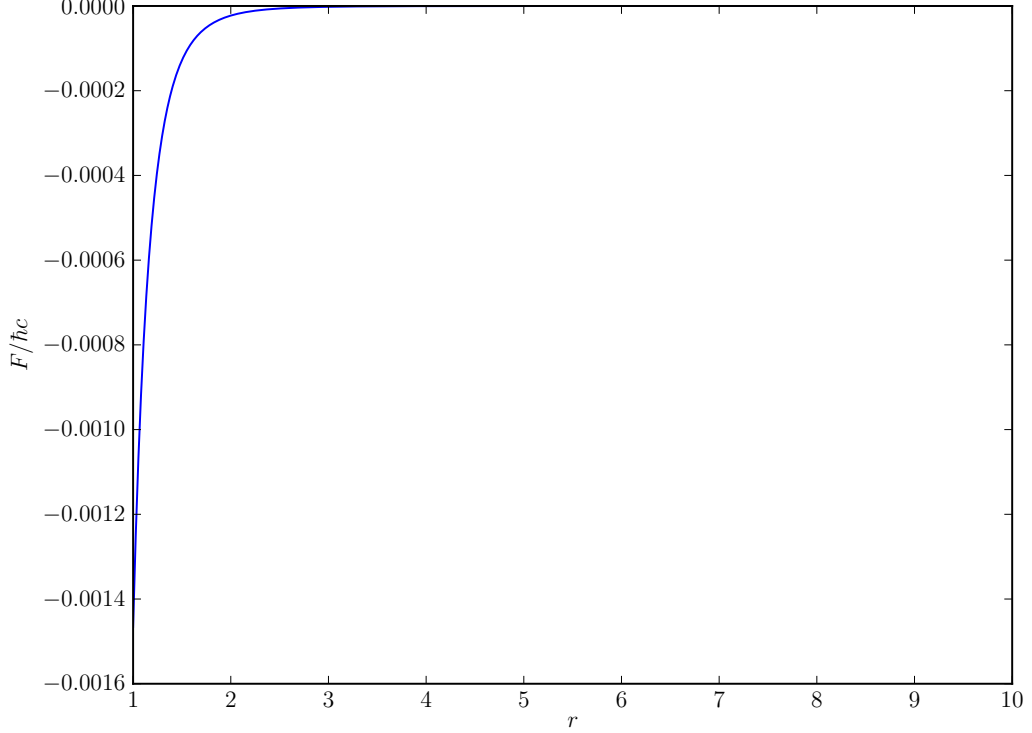


Figure 1: Free energy per particle to particle interaction, calculated as a function of the distance, r between the two molecules

We can consider this result further, by checking how quickly the energy diminishes. To better understand our result, we shall consider the two asymptotic cases of letting $\omega_0 \rightarrow 0$ and $\omega_0 \rightarrow \infty$, respectively:

If $\frac{\omega_0 r}{c} \ll 1$, we get, using equation (19)

$$F = -\frac{3}{2\pi r^6} \alpha^2 \int_0^\infty dK \frac{2}{\sigma^2 (K^2 + (\hbar\omega)^2)^2} \quad (20)$$

yielding $F = -\frac{3}{4r^6} \alpha^2 \hbar\omega_0$. If we set ω_0 to 0, we obtain the expected result of equation (5), so we see that letting $\omega_0 \rightarrow 0$ gives us the expected result for the van der Waals interaction. In this van der Waals limit, the radiative term does not contribute to the energy.

If we let $\frac{\omega_0 r}{c} \rightarrow \infty$, we get, using equation (18)

$$F = -\frac{3\hbar c}{2\pi\sigma^2(\hbar\omega_0)^4 r^7} \alpha^2 \int_0^\infty d\tau [2(1 + \tau + \frac{1}{3}\tau^2)^2 + (\frac{2}{3}\tau^2)^2] \quad (21)$$

yielding $F = -\frac{23\hbar c \alpha^2}{4\pi r^7}$. This limit is purely radiative, and independent of ω_0 , implying that letting ω_0 grow large will lead to a constant expression.

2.3 Calculation of free energy per particle

We now consider the total free energy per particle in the fluid, f , using the equation

$$f = \frac{1}{2} \int dV \rho(\vec{r}) F(\vec{r}) \quad (22)$$

where $\rho(\vec{r})$ denotes the particle density, and in this case is set to be constant, $\rho(\vec{r}) = \rho$. We note that a density would have dimensions of inverse volume, so we normalize as before, $\rho \rightarrow \rho^* = \rho R^3$. The factor 1/2 is obtained by noting that the energy contained in each interaction is shared between two particles. Noting that there is no angular dependency in F , we recall that assuming hard spheres, $F = 0$ for $r < 1$.

$$f = 2\pi\rho \int_1^\infty dr \left(-\frac{3}{2\beta r^4} \sum_{n=-\infty}^\infty e^{-2\tau} [2(1 + \tau + \frac{1}{3}\tau^2)^2 + (\frac{2}{3}\tau^2)^2] \alpha_K^2 \right) \quad (23)$$

Swapping order of summation and integration, and using that $\tau = \frac{|K|r}{\hbar c}$, we are able to calculate the integral analytically, applying that

$$\int_\tau^\infty d\tau' \frac{e^{-2\tau'}}{\tau'^n} = \frac{e^{-2\tau}}{2\tau^n} - \int_\tau^\infty d\tau' \frac{n}{2} \frac{e^{-2\tau'}}{\tau'^{n+1}} \quad (24)$$

we find

$$f = -\frac{\pi\rho}{\beta} \sum_{n=-\infty}^\infty e^{-2\tau} [\tau^3 + 2\tau^2 + 4\tau + 2] \alpha_K^2 \quad (25)$$

with τ having a slightly altered form after r was integrated out, $\tau = \frac{|K|}{\hbar c}$. We again consider the limiting case as $T \rightarrow 0$; implying that

$$f = -\rho\alpha^2\hbar c \int_0^\infty d\tau e^{-2\tau} \frac{[\tau^3 + 2\tau^2 + 4\tau + 2]}{\sigma^2((\tau\hbar c)^2 + (\hbar\omega_0)^2)^2} \quad (26)$$

Introducing the dimensionless quantity $\lambda = 2\pi\frac{c}{\omega_0 R}$ and inserting for $\sigma = (\alpha(\hbar\omega_0)^2)^{-1}$ we then get

$$f = -\rho\alpha^2\hbar c \frac{(2\pi)^4}{\lambda^4} \int_0^\infty d\tau e^{-2\tau} \frac{[\tau^3 + 2\tau^2 + 4\tau + 2]}{(\tau^2 + (2\pi/\lambda)^2)^2} \quad (27)$$

This expression is a complete expression for the Casimir energy at low densities. When going to arbitrary densities, this will be a useful reference value, and we label it $f_{Cas}(\rho = 0)$. Here, $\rho = 0$ should not be understood as an argument of the function, but rather as shorthand, informing us that we are using an expression assuming low densities.

We once more consider two asymptotic limits, both of which can be calculated analytically. These will then be compared to the asymptotics that were previously found, such as to verify our calculations. Then, the free energy per particle is calculated numerically.

Considering the limit as $\lambda \rightarrow \infty$, we only consider lowest-order terms in τ , and have

$$f = -\rho\alpha^2\hbar c \frac{2\pi}{\lambda^4} \int_0^\infty d\tau \frac{2}{(\tau^2 + (2\pi/\lambda)^2)^2}. \quad (28)$$

This can be evaluated using trigonometric substitution, yielding $f = -2\rho\pi^2\alpha^2\hbar c/2\lambda$, complying with what was found in equation (20). This value is useful for comparison to other results, as it is non-zero if we do not put restraints

on ω_0 , meaning that we can compare it to other results from the quantum mechanical distribution function and maintain a sensible result. We write

$$f_{vdW}(\rho = 0) = -2\rho\pi^2\alpha^2\hbar c/2\lambda. \quad (29)$$

again, with $\rho = 0$ implying that the expression has been derived in the low-density limit, and not that we set ρ equal to zero.

Moving on, we notice that we can expand to second order in τ , resulting in the equation

$$f = -\rho\alpha^2\hbar c \frac{(2\pi)^4}{\lambda^4} \int_0^\infty d\tau \frac{2 - 2\tau^2}{(\tau^2 + (2\pi/\lambda)^2)^2} \quad (30)$$

yielding $f = -\pi\rho\alpha^2\hbar c \left(\frac{2\pi}{\lambda} - \left(\frac{2\pi}{\lambda}\right)^3\right)/2$. This is the lowest order radiative correction to the van der Waals interaction. In fact, trying to expand to higher orders does not seem to be possible, as higher order terms in τ would result in a divergent integral. Regardless, the integral converges when the full expression is used, as the exponential term in this case will be dominating.

Considering the limit as $\lambda \rightarrow 0$, we obtain

$$f = -\rho\alpha^2\hbar c \int_0^\infty d\tau e^{-2\tau} [\tau^3 + 2\tau^2 + 4\tau + 2] \quad (31)$$

yielding $f = -23\hbar c\rho\alpha^2/8$, complying with the results obtained from (21). This expression is fully radiative; being in this limit means that the contribution from an instantaneous dipole interaction would be zero. We denote this limit f_{Rad} .

In figure 2, we illustrate how the energy calculated from equation (27) varies between the radiative regime and the van der Waals regime. We notice that the transistive region between the two occurs in the area between $\lambda \sim 10^{-1}$, and $\lambda \sim 10^1$. Incidentally, in this area the first order correction to the van der Waals energy would start failing completely, as the corrective term would cancel out the van der Waals-term when $2\pi/\lambda = 1$. When going to higher densities, we will have problems describing this regime. We will thus limit ourselves to consider the regime where $\lambda \geq 10$ henceforth.

In figure 3, the energy is plotted as a function of λ . It can be seen that the energy goes to zero as $\lambda \rightarrow \infty$, as was expected, whereas $\lambda \rightarrow 0$ yields a very steep decline to a constant and negative value for f .

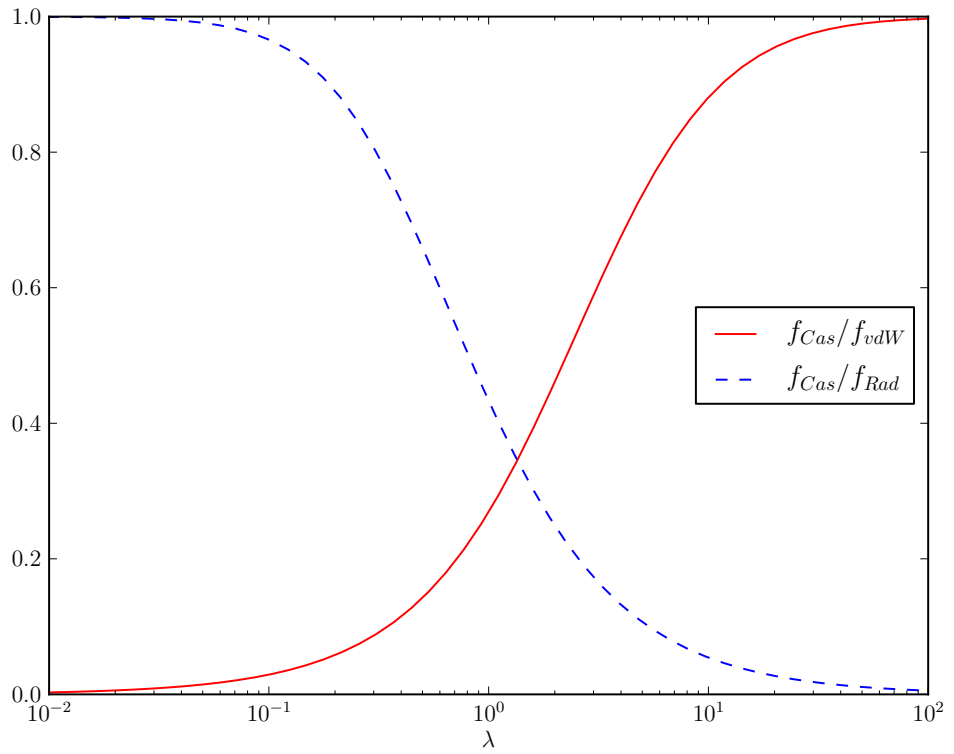


Figure 2: The energy calculated from (27), normalized by the energy in the purely radiative limit, and the van der Waals limit, respectively. In the area $10^{-1} \leq \lambda \leq 10^1$ the free energy is dominated by neither radiative or instantaneous interactions.

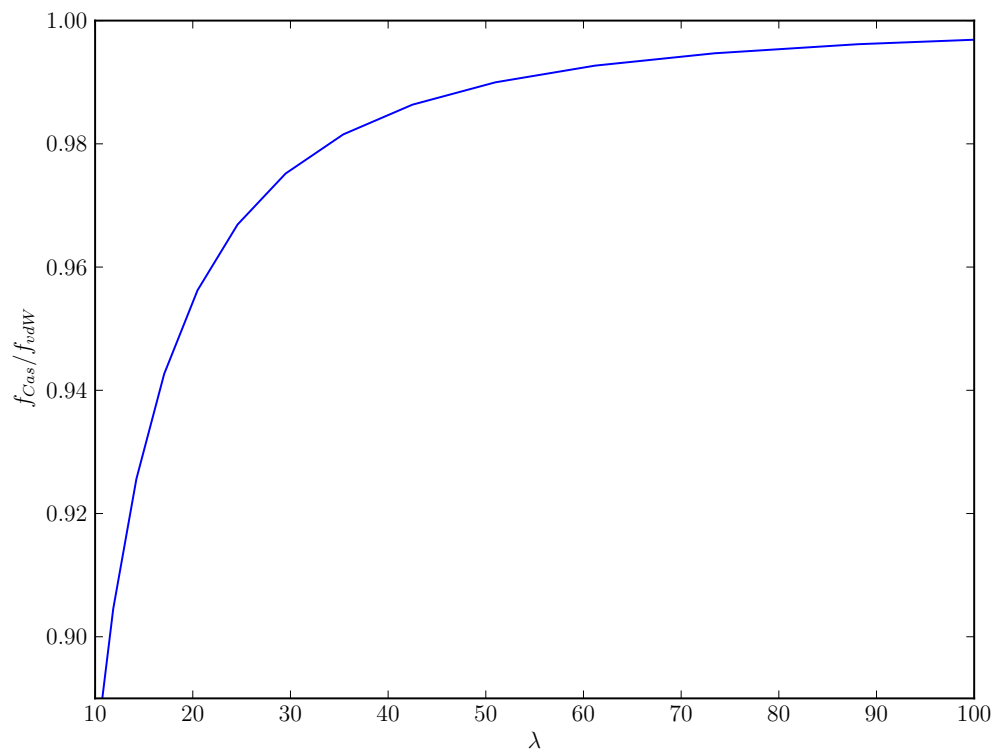


Figure 3: Free casimir energy at low density, normalized by the van der Waals interaction energy at low density, as a function of λ . As λ increases, the energy approaches the van der Waals level. As λ decreases, however, the radiative terms provide a significant correction.

3 Arbitrary densities, instantaneous dipole interaction

Rather than considering the dilute limit, we can consider a model for arbitrary, but constant particle densities. First, we shall consider the static dipole interaction. We begin by introducing the Ornstein-Zernike equation, then state results needed to make our computation. We briefly discuss errors made in our numerical computation due to using a cutoff, but show that this should lead to a negligible error. Explicit calculations are then made, showing how the correction changes with density and polarizability of the fluid.

3.1 The Ornstein-Zernike equation

As the fluid is no longer assumed to be dilute, we can not assume that the interactions between two particles are unaffected by other particles. We thus need to alter our model. We shall make use of the Ornstein-Zernike (OZ) equation,

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{13})c(r_{23})d\vec{r}_3 \quad (32)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$. Here $h(r)$ is defined as the total correlation function, $h(r) = g(r) - 1$, where $g(r)$ is the normalized pair distribution function, while $c(r)$ is defined the direct correlation function. By using this relationship, we will be able to consider multi-particle interactions, as can be seen by considering the second term on the left hand side, which clearly couples interactions between two particles to the interactions between other particles.

In this project, we use the mean spherical approach, in which we make the approximation

$$c(r) = -\beta V(r). \quad (33)$$

The OZ-equation for dipole interactions has been solved by Wertheim, and we shall make use of his solution in order to better understand the subsequent results, giving a heuristic description of the alterations that will be made to his results. In [5], a system of dipoles with common dipole moment $|s| = m$ is considered. This system differs from our system, in that the dipole moments are not assumed to be fluctuating harmonically. The solutions to the problem are given by

$$\begin{aligned} h(12) &= h_0(r) + s_1 s_2 (h_D(r)D(12) + h_\Delta(r)\Delta(12)) \\ c(12) &= c_0(r) + s_1 s_2 (c_D(r)D(12) + c_\Delta(r)\Delta(12)). \end{aligned} \quad (34)$$

Where we have used s_1 and s_2 in order to ease the understanding of later changes. Making fourier transforms, we introduce the variables c_1 , c_2 , h_1 and h_2 , with

$$\begin{aligned} c_1(r) &= (3\kappa)^{-1} [\hat{c}_D(r) + \frac{1}{2}\hat{c}_\Delta(r)], \\ c_2(r) &= (3\kappa)^{-1} [\hat{c}_D(r) - \hat{c}_\Delta(r)], \end{aligned} \quad (35)$$

and where a similar expression is valid for h_1 and h_2 . In these expressions, we have introduced κ , defined by

$$\kappa = \int_1^\infty dr r^{-1} h_\Delta(r) \quad (36)$$

The problem is through this reduced to decoupled equations;

$$\begin{aligned} h_1(r) - c_1(r) &= 2\kappa\rho(h_1 * c_1) \\ h_2(r) - c_2(r) &= -\kappa\rho(h_2 * c_2), \end{aligned} \quad (37)$$

where the $*$ refers to the convolution between the two functions. The boundary conditions are

$$\begin{aligned} c_1(r) = c_2 &= 0, \quad r > R \\ h_1 = h_2 &= -1, \quad r < R. \end{aligned} \quad (38)$$

Equation (32) has now been reduced to two hard-sphere OZ-equations, the solutions for which are the same as those for the hard-sphere Percus-Yevick equation

$$c_1 = c_s(r, 2\kappa\rho), \quad h_1 = h_s(r, 2\kappa\rho) \quad (39)$$

$$c_2 = c_s(r, -\kappa\rho), \quad h_2 = h_s(r, -\kappa\rho) \quad (40)$$

of interest here is the $c_s(r, \rho)$, as c_1 and c_2 give an expression for c_Δ , which will be used later in the expression for the free energy of the fluid. In [7] a solution is shown to be of the form

$$c_s(r, \rho) = -(1 - \eta)^{-4}[(1 + 2\eta)^2 - 6\eta(1 + \frac{1}{2}\eta)^2 r + \eta(1 + 2\eta)^2 \frac{1}{2}r^3]. \quad (41)$$

Here, $\eta = \frac{\pi}{6}\rho R^3$, and we see that by inserting for the values in equation (40), and defining $\xi = \kappa\frac{\pi}{6}\rho R^3$ we obtain

$$\begin{aligned} c_1 &= -(1 - 2\xi)^{-4}[(1 + 4\xi)^2 - 12\xi(1 + \xi)^2 r + 2\xi(1 + 4\xi)^2 \frac{1}{2}r^3] \\ c_2 &= -(1 + \xi)^{-4}[(1 - 2\xi)^2 + 6\xi(1 - \frac{1}{2}\xi)^2 r - \xi(1 - 2\xi)^2 \frac{1}{2}r^3]. \end{aligned} \quad (42)$$

In order to follow [4], we shall make two changes to the model that was solved by Wertheim. First, we introduce a harmonically fluctuating potential for the dipole moments, as was done for our calculations of the van der Waals interaction energy in the introduction. By making this change, we can no longer say that $s_1 s_2 = m^2$, and must instead consider the average value; $\langle s^2 \rangle$. This leads to a slightly different solution, similar to Wertheim's in form, but where the density is replaced by an effective density, which will be a function of a version of α which itself is modified due to the manyparticle interactions. We can denote this effective density R , safe in the knowledge that it will not be confused for the hard-sphere radius, as we are about to replace it with an effective effective density.

This change is due to our second alteration, in which we return to the quantum mechanical partition function, for which we saw in the low-density case that α became replaced by α_K . Making this alteration here leads to a similar change, and thus we replace R with R_K , which will be defined in short order.

Having done this, we end up with a set of useful relations [4]:

$$c_\Delta^K(0) = -2\kappa[q_1 - q_2] = -16\xi, \quad (43)$$

$$\frac{1}{3}(q_1 - q_2) = \frac{4\pi}{9}R_K \quad (44)$$

$$q_i = \frac{(1 + 2\xi_i)^2}{(1 - \xi_i)^4} \quad (45)$$

$$\xi_1 = 2\xi, \quad \xi_2 = -\xi \quad (46)$$

$$\xi = \frac{\pi}{6} \kappa R_K \quad (47)$$

$$R_K = \frac{3\rho}{\sigma K^2 + 1/\alpha + c_\Delta^K(0)} \quad (48)$$

with R_K now acting as an effective density for each mode K , where each mode K , in turn, is treated as having an effective polarizability α_K .

3.2 Calculation of the free energy per particle

Using equation (76) of [4], the full internal energy per molecule is set to be

$$\beta u = 3 \sum_K \frac{\sigma \hbar^2 \omega_0^2 + c_\Delta^K(0)}{\sigma(K^2 + \hbar^2 \omega_0^2) + c_\Delta^K(0)}. \quad (49)$$

Being interested in the free energy due to interactions, we subtract from equation (49) the zero-density energy;

$$3 \sum_K \frac{\sigma \hbar^2 \omega_0^2}{\sigma(K^2 + \hbar^2 \omega_0^2)} \quad (50)$$

thus obtaining the internal energy obtained from interaction,

$$\beta u_{int} = 3 \sum_K \frac{\sigma K^2 c_\Delta^K(0)}{(\sigma(K^2 + \hbar^2 \omega_0^2) + c_\Delta^K(0))\sigma(K^2 + \hbar^2 \omega_0^2)} \quad (51)$$

At zero temperature, the internal energy should be equal to the free energy. Thus, at low densities and at zero temperature, this result should correspond to that of equation (28). Going to low densities, equation (44) becomes (observing that low densities imply low values for ξ)

$$24\xi = \frac{4\pi\rho}{\sigma(K^2 + \hbar^2 \omega_0^2)}. \quad (52)$$

Inserting for equation (43), we thus have

$$\beta u_{int} = \sum_K \frac{-8R^{-3}\pi\rho\sigma K^2}{(\sigma(K^2 + \hbar^2 \omega_0^2))^3} \quad (53)$$

Letting $T \rightarrow 0$, we now get

$$f = -\frac{8\rho\alpha^2}{R^3} \int_0^\infty dK \frac{K^2/(\hbar\omega_0)^2}{(K^2/(\hbar\omega_0)^2 + 1)^3} = -\frac{8\rho\alpha^2\hbar\omega_0}{R^3} \int_0^\infty dK \frac{K^2}{(K^2 + 1)^3} \quad (54)$$

resulting in $f = -\pi\rho\alpha^2\hbar\omega/2R^3$, the same as the result from equation (28). To see that these two equations are indeed equivalent, we add and subtract 1 in the numerator of the fraction, yielding

$$f = -\frac{8\rho\alpha^2\hbar\omega_0}{R^3} \int_0^\infty dK \left(\frac{1}{(K^2 + 1)^2} - \frac{1}{(K^2 + 1)^3} \right). \quad (55)$$

We then do a partial integration,

$$\int_0^\infty \frac{dK}{(K^2 + 1)^2} = \frac{K}{(K^2 + 1)^2} + 4 \int_0^\infty dK \left(\frac{1}{(K^2 + 1)^2} - \frac{1}{(K^2 + 1)^3} \right) \quad (56)$$

implying that $\int_0^\infty \frac{dK}{(K^2+1)^3} = \frac{3}{4} \int_0^\infty \frac{dK}{(K^2+1)^2}$, resulting in

$$f = -\frac{2\rho\alpha^2\hbar\omega_0}{R^3} \int_0^\infty \frac{dK}{(K^2+1)^2}, \quad (57)$$

identical to equation (28).

No longer considering the dilute limit, equation (51) must be calculated numerically. We proceed, by dividing the integral into a sum over small increments of K , and using equation (44) to calculate a value for ξ for each K numerically, by use of Newton's method. To be able to make this numerical calculation, it is necessary for ξ to be an injective function of K^2 , in the region where K^2 goes from 0 to ∞ . By letting $\rho \rightarrow 0$, and noting that $0 < \xi < 1/2$ [5], we see that a strict upper limit for α/R^3 is $1/8$.

Since we are approximating an integral to ∞ with a sum, a cutoff for K must be made. From equation (57), we know that the integrand goes as $1/K^4$ for low densities. Further, as K increases, the effective density R_K decreases, so this relationship should hold also for higher densities for a high enough K . Using that $0 < \xi < 1/2$, we can replace ξ with $1/2$; this will lead to an upper bound for the integrand, so we have shown that the integrand will go as $1/K^2$ - decreasing rapidly. Keeping this in mind, the summation is made to $K = 50$. Figure 4 shows the contributions made by the various K -modes to the total f . From this, it seems apparent that a summation to $K = 50$ is more than sufficient. Figures 5 and 6 plot f compared with the low-density approximation, f_0 . We see that even when ρ and α are chosen to be very high, the correction is only approximately 5%, and that it decreases linearly with ρ , and linearly with α for sufficiently small α .

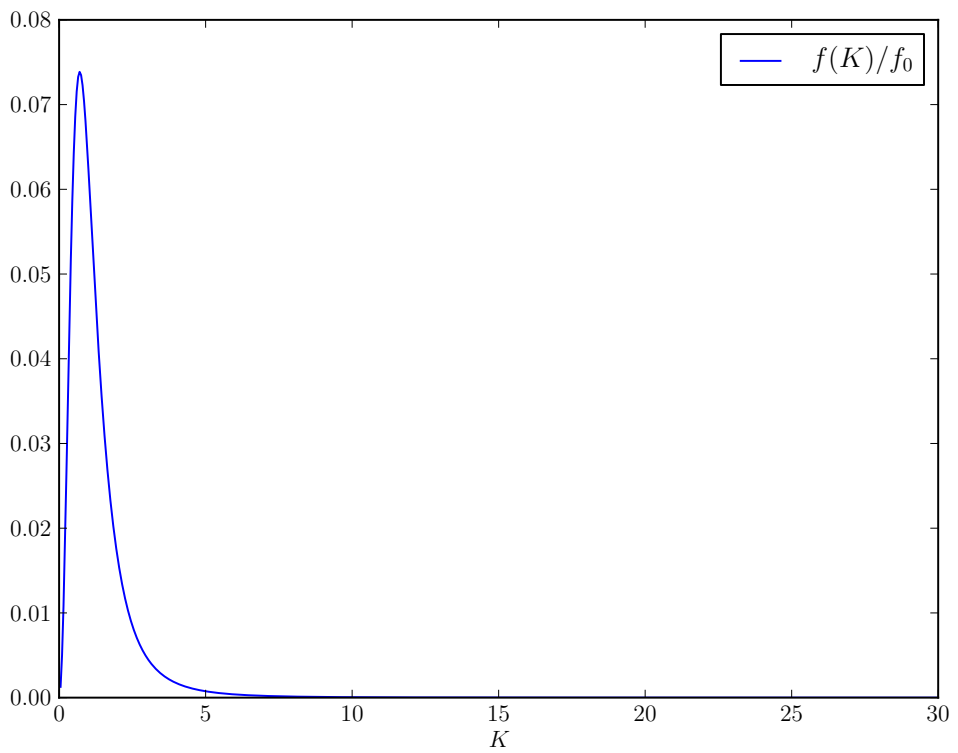


Figure 4: Contributions to the total free energy per particle as a function of K for static dipole interactions, arbitrary density for $\rho = 3/\pi$, $\alpha = 1/8$

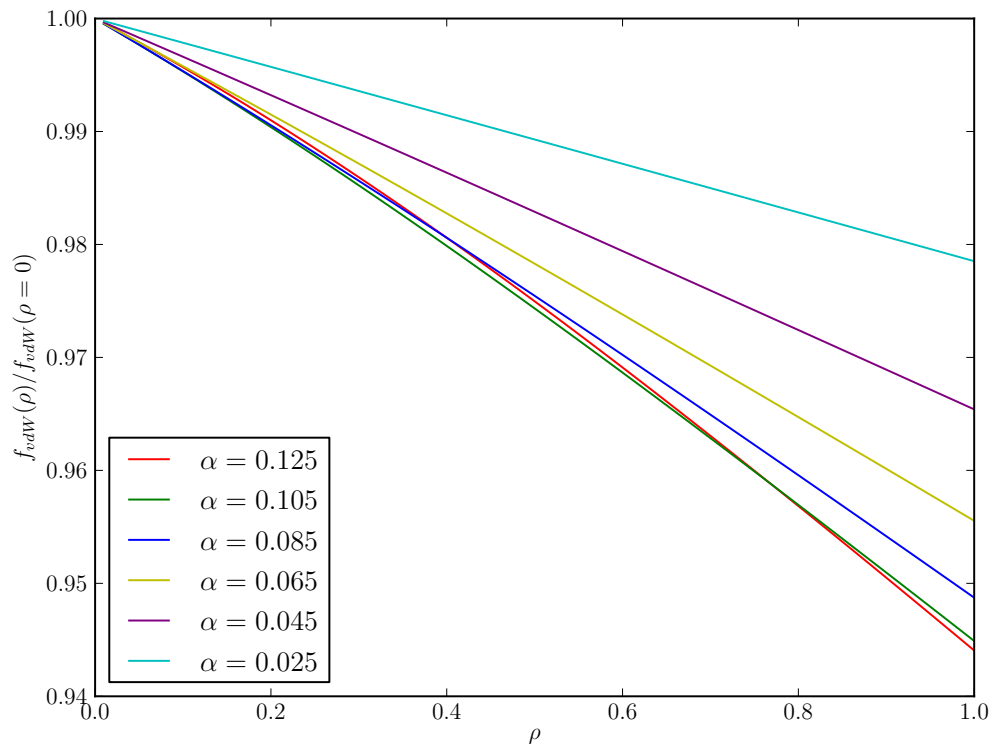


Figure 5: Comparison of van der Waals energy calculated for arbitrary density compared to the result obtained when assuming low density, as a function of density, ρ . Note that for higher values of α , the lines seem to be entangled, a result which makes sense when viewing figure 6.

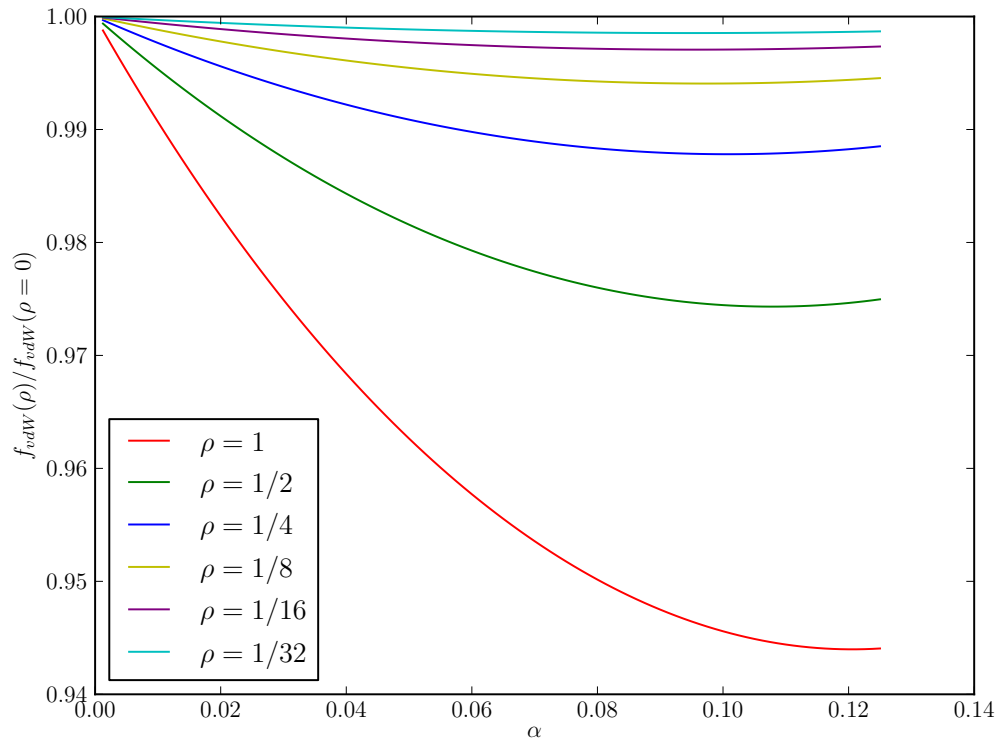


Figure 6: Comparison of van der Waals energy calculated for arbitrary density compared to the result obtained when assuming low density, as a function of polarizability α . The difference between the two results increases steadily until a point of inflection, when it flattens out and ultimately decreases slightly.

4 Arbitrary densities, radiative correction

The next step of interest is to take into account radiative terms, as was done in section 2. This implies changing the interaction potential, to that defined by equations (12) and (13). Following Høye and Stell, we shall only consider the lowest order radiative correction, implying that λ be chosen very large. To illustrate some pitfalls, we shall first use a naive approach, showing that it does not in fact lead to a correct solution, before finally introducing corrections to the approach.

4.1 New Ornstein-Zernike equation

In [3], Høye and Stell once more reduce the problem to equation (37). This time, however, the boundary conditions are

$$\begin{aligned} c_1 &= 0, \quad r > R \\ c_2 &= (1/3\kappa)\left(\frac{KR}{\hbar c}\right)^2(e^{-Kr/\hbar c}/r), \quad r > R \\ h_1 &= h_2 = -1, \quad r < R \end{aligned} \tag{58}$$

While the equation for c_1 remains a hard-sphere equation, the equation for c_2 is now a one-Yukawa problem. This is solved generally by Waisman in [8]. In [6] Høye and Stell expand further upon it, and give calculations for the case when $\lambda \rightarrow \infty$. We should be able to use this result to obtain a lowest order radiative correction, which should correspond to equation (30) when $\rho \rightarrow 0$.

4.2 Calculation of the free energy per particle

Introducing radiative terms, as in [3], and assuming that $\lambda \gg 1$ equation (44) instead becomes

$$\frac{1}{3}(q_1 - a_2) = 0, \tag{59}$$

while (43) becomes

$$c_{\Delta}^K(0) = -2\kappa[q_1 - (a_2 + v_2)] = 2\kappa v_2 \tag{60}$$

where a_2 is defined by equation (2.1) of [6], while $\frac{v_2}{K_y}$ is defined by equation (2.43) of the same.

First, we wish to eliminate the κ of equation (60), as was done in section 3. This is done by comparing equation (1.1.c) of [6] with equation (38) of [3]. Now, the z 's are identified with the ω s, while the K_y s are chosen by z -parametrization, so that $K_y = K_{y0}z^2$. Comparing equations (9) to (11) of [3] with equation (15), we have $z = \frac{|K|R}{\hbar c} = \frac{2\pi|K|}{\hbar\omega_0\lambda}$. As $z \rightarrow 0$, the van der Waals result should be obtained. Consequently, we have

$$K_y = \frac{z^2 e^{-z}}{3\kappa}. \tag{61}$$

From equations (2.22), (2.34), (2.35), (2.39), (2.42) and (2.43) in [6], we have

$$A(x) = (1-x)^2 a(x); \quad p(x) = \frac{(1+2x)^2}{(1-x)^2} \tag{62}$$

$$U_0(x) = \frac{6x}{K_y} \left(\frac{z+2}{z}\right)^2 (K_y - \sigma_y v(x))^2 \tag{63}$$

$$\sigma_y = \frac{1}{2z} \left[\frac{z-2}{z+2} + \exp(-z) \right] \quad (64)$$

$$A(x) - p(x) = - \left[1 - \frac{\frac{1}{4}z^2}{(\sqrt{p(x)} + \frac{1}{2}z)^2} \right] U_0(x) \quad (65)$$

$$\frac{U_1}{U_0} = 2 - \sqrt{p(x)} - \frac{\frac{1}{4}z^2}{\sqrt{p(x)} + \frac{1}{2}z} \quad (66)$$

and

$$\frac{v(x)}{K_y} = \frac{[(4+2z)(U_1/U_0) - (4+2z-z^2)]2z}{2[(z-2) + (z+2)e^{-z}](U_1/U_0) - [(z^2+2z-4) + (4+2z-z^2)e^{-z}]}. \quad (67)$$

Inserting for equations (59) and (60) as well as defining

$$(1-x)^2 g(x) = z^2 e^{-z} \left(\frac{z+2}{z} \right)^2 \left[1 - \frac{\frac{1}{4}z^2}{(\sqrt{p(x)} + \frac{1}{2}z)^2} \right] \left(1 - \sigma \frac{v(x)}{K_y} \right)^2, \quad (68)$$

we now obtain

$$\frac{1}{3}(q_1 - q_2^0) = \frac{\pi}{9} R_K g(-\xi) \quad (69)$$

and

$$c_{\Delta}^K(0) = \frac{2}{3} z^2 e^{-z} \frac{v(-\xi)}{K_y}. \quad (70)$$

We are interested in the behavior of $c_{\Delta}^K(0)$ when taking the radiative correction into account, as this can tell us something about how the radiative term affects the free energy-contributions from larger K s. Expecting the deviation to increase with increasing values of ρ and α , we make the comparison at $\alpha = 1/8$, $\rho = 3/\pi$. Further, λ is chosen to be relatively large, $\lambda = 100$. As illustrated in figure 7, $c_{\Delta}^K(0) > 0.9c_{\Delta}^K(0)^0$, $K < 5$. Apparent from figure 4, this is where the main contribution to the free energy is found in the static case.

Naively, we can now proceed as in section 3, using equation (51), to calculate free energy at zero temperature numerically. It turns out, however, that our approach fails to yield the expected results when the density and polarizability approach zero. This is illustrated in figures 8 and 9. In the following sections, we shall discuss and amend this flaw.

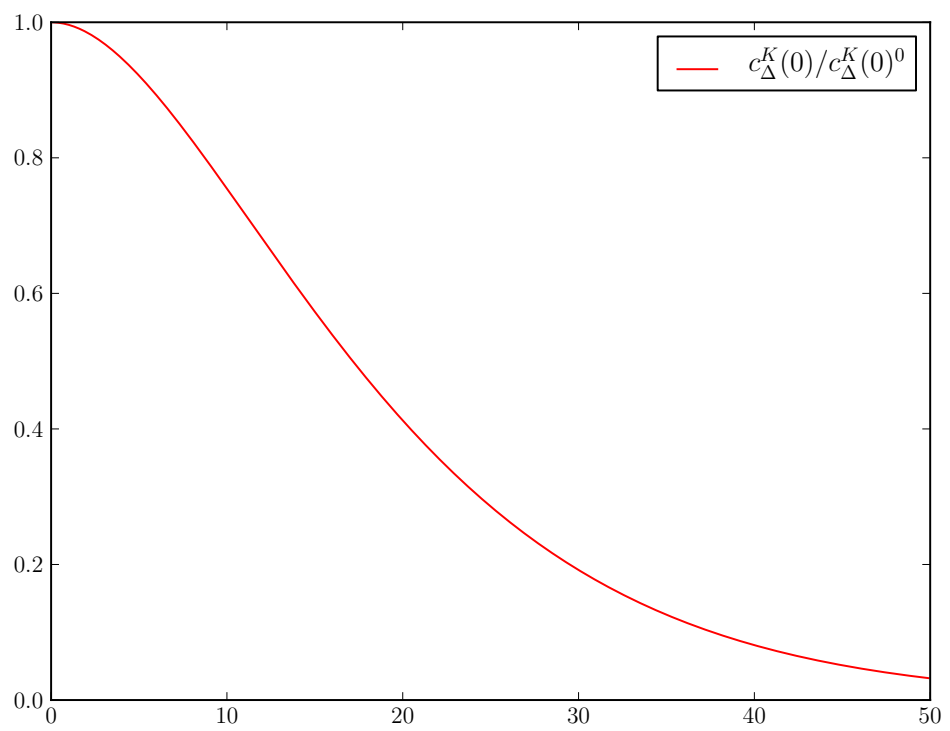


Figure 7: $c_{\Delta}^K(0)/c_{\Delta}^K(0)^0$ for $\rho = 3/\pi$, $\alpha = 1/8$, $\lambda = 100$

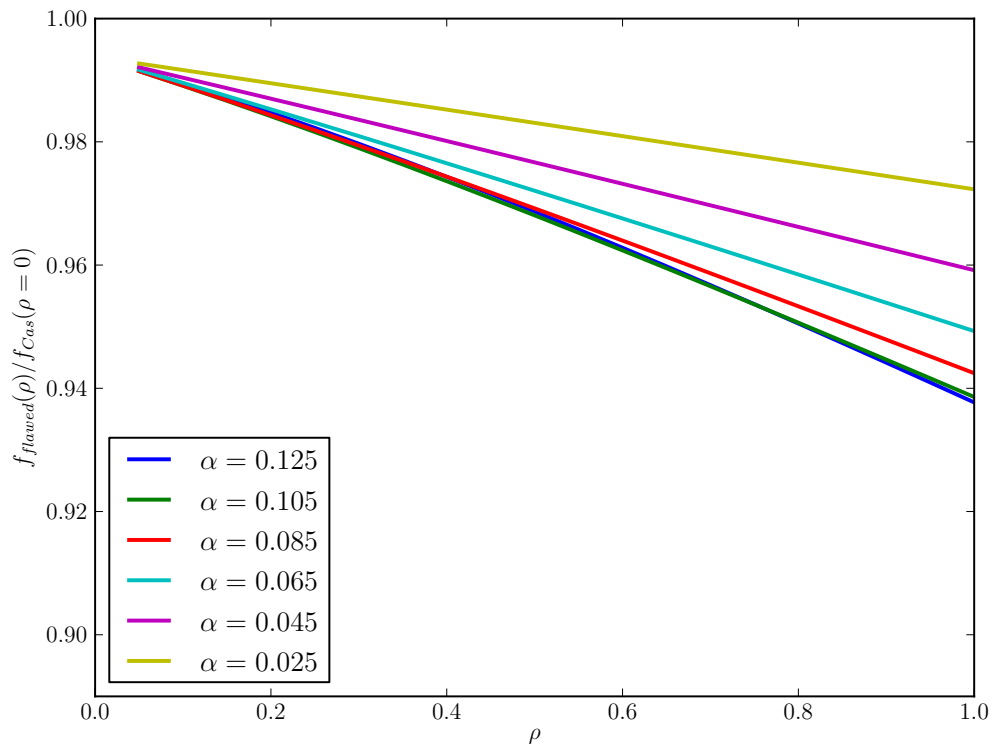


Figure 8: Calculation of Casimir energy for arbitrary densities, normalized by the known expression for Casimir energy at low density, as a function of the density, ρ . As ρ approaches zero, the result converges, but not to the expected value of 1. $\lambda = 100$.

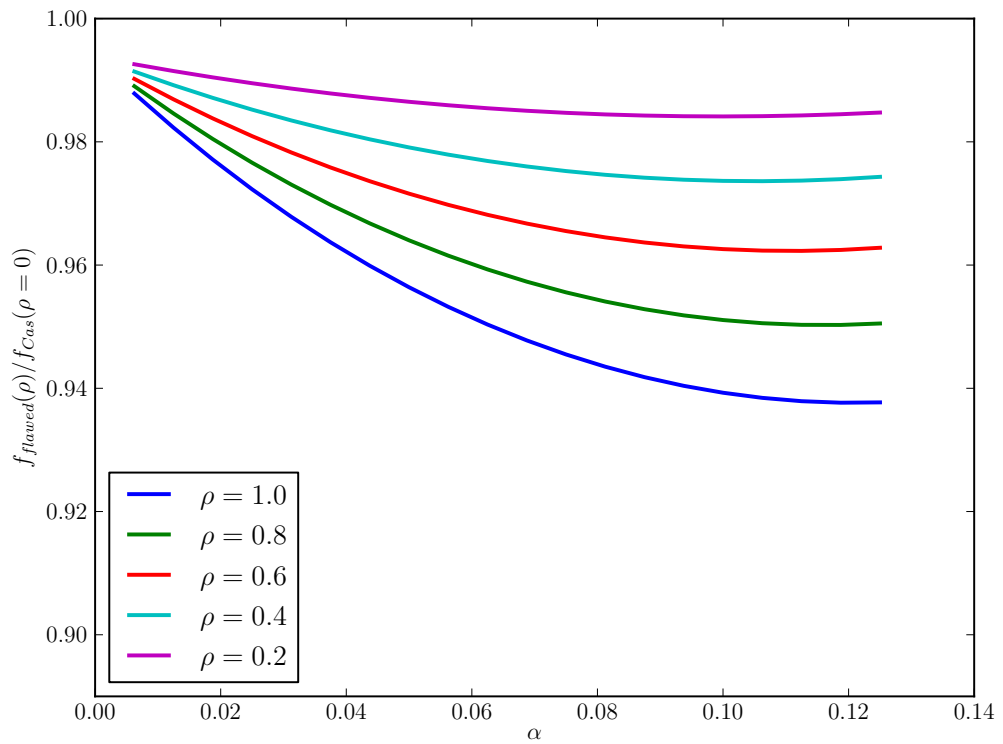


Figure 9: Calculation of Casimir energy for arbitrary densities, normalized by the known expression for Casimir energy at low density. When α approaches zero, the result converges, but not to the expected value of 1. $\lambda = 100$.

4.3 Proper expression for free energy

The primary reason for the discrepancy lies in the derivation of the expression for internal energy. We shall now do this derivation explicitly so as to highlight why we get a deviation.

Starting with equation (68) of the same article, we have

$$-\beta\rho f = \frac{3}{2}\rho \sum_K \ln\left(\frac{\sigma R_K}{3\rho\eta^2}\right) - \frac{1}{2} \frac{1}{(2\pi)^3} \sum_K \int d\mathbf{k} [\ln(1 - R_K \tilde{c}_1^K(\mathbf{k})) + 2\ln(1 - R_K \tilde{c}_2^K(\mathbf{k}))] + I_0 \quad (71)$$

From basic statistical mechanics[9], we have that the internal energy of a particle, u is related to the free energy of the particle by the relation

$$u = \frac{\partial}{\partial\beta}(\beta f) \quad (72)$$

We thus have

$$\begin{aligned} \beta\rho u &= \beta \frac{\partial}{\partial\beta}(\beta\rho f) \\ &= -\frac{3}{2}\rho \sum_K \beta \frac{\partial}{\partial\beta} \ln\left(\frac{\sigma R_K}{r\rho\eta^2}\right) \end{aligned} \quad (73a)$$

$$- \frac{1}{2} \frac{1}{(2\pi)^3} \sum_K \int d\mathbf{k} \beta \frac{\partial}{\partial\beta} [\ln(1 - R_K \tilde{c}_1^K(\mathbf{k})) + 2\ln(1 - R_K \tilde{c}_2^K(\mathbf{k}))] \quad (73b)$$

Because $\beta = N\eta$ and $K = 2\pi n/\beta$, we have that $\beta \frac{\partial}{\partial\beta} = \eta \frac{\partial}{\partial\eta} = -K \frac{\partial}{\partial K}$. Equation (73a) now becomes

$$-\frac{3}{2}\rho \sum_K \left[-K \frac{\partial}{\partial K} \ln(\sigma R_K) - \eta \frac{\partial}{\partial\eta} \ln(3\rho\eta^2) \right] = -\frac{3}{2}\rho \sum_K \left[\frac{-K}{R_K} \frac{\partial}{\partial K} R_K - 2 \right] \quad (74)$$

Inserting for the derivative of R_K ,

$$\frac{\partial}{\partial K} R_K = \frac{\partial}{\partial K} \frac{3\rho}{\sigma K^2 + 1/\alpha + c_\Delta^K(0)} = -\frac{R_K^2}{3\rho} (2\sigma K + \frac{\partial}{\partial K} c_\Delta^K(0)) \quad (75)$$

we find that equation (73a) gives the contribution to $\beta\rho u$

$$\sum_K \left[3\rho - \sigma K^2 R_K - \frac{1}{2} R_K K \frac{\partial}{\partial K} c_\Delta^K(0) \right] \quad (76)$$

We now consider the contributions from equation (73b). We have (changing $\beta \frac{\partial}{\partial\beta}$ to $-K \frac{\partial}{\partial K}$, and canceling the negative sign)

$$\begin{aligned} & \frac{1}{2} \frac{1}{(2\pi)^3} \sum_K \int d\mathbf{k} K \frac{\partial}{\partial K} [\ln(1 - R_K \tilde{c}_1^K(\mathbf{k})) + 2\ln(1 - R_K \tilde{c}_2^K(\mathbf{k}))] \\ &= \frac{1}{2} \frac{1}{(2\pi)^3} \sum_K \int d\mathbf{k} \left\{ \frac{1}{1 - R_K \tilde{c}_1^K(\mathbf{k})} \left[K \frac{\partial}{\partial K} (R_K \tilde{c}_1^K(\mathbf{k})) \right] \right. \\ & \left. + 2 \frac{1}{1 - R_K \tilde{c}_2^K(\mathbf{k})} \left[K \frac{\partial}{\partial K} (R_K \tilde{c}_2^K(\mathbf{k})) \right] \right\} \end{aligned} \quad (77)$$

which we rewrite, using $\tilde{h}_i^K(\mathbf{k}) = \frac{\tilde{c}_i^K(\mathbf{k})}{1 - R_K \tilde{c}_i^K(\mathbf{k})}$ as

$$\sum_K \frac{1}{2} \frac{1}{(2\pi)^3} \int d\mathbf{k} \left\{ \tilde{h}_1^K(\mathbf{k}) K \frac{\partial}{\partial K} R_K + 2\tilde{h}_2^K(\mathbf{k}) K \frac{\partial}{\partial K} R_K \right. \quad (78a)$$

$$\left. + R_K^2 \tilde{h}_1^K(\mathbf{k}) \frac{\partial}{\partial K} \tilde{c}_1^K(\mathbf{k}) + 2R_K^2 \tilde{h}_2^K(\mathbf{k}) \frac{\partial}{\partial K} \tilde{c}_2^K(\mathbf{k}) \right. \quad (78b)$$

$$\left. + R_K K \frac{\partial}{\partial K} (\tilde{c}_1^K(\mathbf{k}) + 2\tilde{c}_2^K(\mathbf{k})) \right\} \quad (78c)$$

where the last two equations are obtained by rewriting

$$\frac{R_K}{1 - R_K \tilde{c}_i^K(\mathbf{k})} = \frac{R_K}{1 - R_K \tilde{c}_i^K(\mathbf{k})} + R_K - R_K = \frac{R_K^2 \tilde{c}_i^K(\mathbf{k})}{1 - R_K \tilde{c}_i^K(\mathbf{k})} + R_K \quad (79)$$

Using that $\tilde{h}_1^K(\mathbf{k}) + 2\tilde{h}_2^K(\mathbf{k}) = \tilde{h}_\Delta^K(\mathbf{k})$, we rewrite equation (78a)

$$\sum_K \frac{1}{2} \frac{1}{(2\pi)^3} K \frac{\partial}{\partial K} R_K \int d\mathbf{k} \tilde{h}_\Delta^K(\mathbf{k}). \quad (80)$$

This integral we can write as

$$\sum_K \frac{1}{2} \frac{1}{(2\pi)^3} K \frac{\partial}{\partial K} R_K \int d\mathbf{k} \tilde{h}_\Delta^K(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{0}} = \sum_K \frac{1}{2} K \frac{\partial}{\partial K} R_K h_\Delta^K(\mathbf{r} = 0) = 0 \quad (81)$$

so we see that equation (78a) vanishes. We next consider equation (78c). Similar as the previous part, we note that $\tilde{c}_1^K(\mathbf{k}) + 2\tilde{c}_2^K(\mathbf{k}) = \tilde{c}_\Delta^K(\mathbf{k})$, yielding

$$\frac{1}{2} \sum_K \frac{1}{(2\pi)^3} \int d\mathbf{k} R_K K \frac{\partial}{\partial K} \tilde{c}_\Delta^K(\mathbf{k}) = \frac{1}{2} \sum_K R_K K \frac{\partial}{\partial K} \tilde{c}_\Delta^K(0) \quad (82)$$

which cancels out the last part of equation (76). Finally, we turn to equation (78b). We write it into two parts

$$\frac{1}{2} \sum_K R_K^2 \frac{1}{(2\pi)^3} \left\{ \int d\mathbf{k} \tilde{h}_1^K(\mathbf{k}) K \frac{\partial}{\partial K} \tilde{c}_1^K(\mathbf{k}) + 2 \int d\mathbf{k} \tilde{h}_2^K(\mathbf{k}) K \frac{\partial}{\partial K} \tilde{c}_2^K(\mathbf{k}) \right\} \quad (83)$$

Let us first consider the first part. We fourier transform, yielding

$$\begin{aligned} & \frac{1}{2} \sum_K R_K^2 \frac{1}{(2\pi)^3} \int d\mathbf{k} \tilde{h}_1^K(\mathbf{k}) K \frac{\partial}{\partial K} \tilde{c}_1^K(\mathbf{k}) \\ &= \frac{1}{2} \sum_K R_K^2 \frac{1}{(2\pi)^3} \int d\mathbf{k} \int d\mathbf{r}_1 \int d\mathbf{r}_2 h_1^K(\mathbf{r}_1) K \frac{\partial}{\partial K} c_1^K(\mathbf{r}_2) e^{i\mathbf{k}(\mathbf{r}_1 + \mathbf{r}_2)} \\ &= \frac{1}{2} \sum_K R_K^2 \int d\mathbf{r} h_1^K(\mathbf{r}) K \frac{\partial}{\partial K} c_1^K(\mathbf{r}) \end{aligned} \quad (84)$$

where in the last step we have used $\int d\mathbf{k} e^{-i\mathbf{k}(\mathbf{r}_1 + \mathbf{r}_2)} = (2\pi)^3 \delta_{\mathbf{r}_1, -\mathbf{r}_2}$ and the fact that $c(\mathbf{r})$ is isotropic, $c(-\mathbf{r}) = c(\mathbf{r})$. Now, we note that $h_1^K(\mathbf{r}) = 2\kappa H_1^K(\mathbf{r}) = 2\kappa(G_1^K(\mathbf{r}) - 1)$, meaning that we can rewrite this equation as

$$\kappa \sum_K R_K^2 \int d\mathbf{r} \left\{ G_1^K(\mathbf{r}) K \frac{\partial}{\partial K} c_1^K(\mathbf{r}) - K \frac{\partial}{\partial K} c_1^K(\mathbf{r}) \right\} \quad (85)$$

Now, for a hard sphere, we have that $c(r) = 0, r > 1$, while $G(\mathbf{r}) = 0, r < 1$, so the first part is zero. For the second part, we again write this as a fourier transform around $\mathbf{k} = 0$, yielding

$$-\frac{\kappa}{(2\pi)^3} \sum_K R_K^2 K \frac{\partial}{\partial K} \tilde{c}_1^K(0) \quad (86)$$

we return to the second part of equation (83). We follow the same steps as for the first part, using $h_2(r) = -\kappa H_2(\mathbf{r}) = \kappa(1 - G_2(\mathbf{r}))$, ending up at

$$\frac{\kappa}{(2\pi)^3} \sum_K R_K^2 K \frac{\partial}{\partial K} \tilde{c}_2^K(0) - \kappa \sum_K R_K^2 \int d\mathbf{r} G_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) \quad (87)$$

This time, the second term does not cancel out; as we are no longer considering a hardsphere solution, but rather a Yukawa potential. Finally, we use the relation $\tilde{c}_1^K(0) - \tilde{c}_2^K(0) = \tilde{c}_D^K(0) = 0$, ending up with

$$-\kappa \sum_K R_K^2 \int d\mathbf{r} G_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) \quad (88)$$

Combining equations (73a) and (73b) thus gives us the expression

$$\beta\rho u = \sum_K \left[3\rho - \sigma K^2 R_K - \kappa R_K^2 \int d\mathbf{r} G_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) \right] \quad (89)$$

so we see that we have a correction term compared to the expression we had for static interactions. We can evaluate the correction term a bit further. First, we note that $G_2^K(\mathbf{r}) = 0, r < 1$. Further, introducing $z = |K|/\hbar c$ we have that $c_2^K(\mathbf{r}) = \frac{1}{3} z^2 \frac{e^{-zr}}{r}, r > 1$. So, we get for the correction term

$$\sum_K \left[-\kappa R_K^2 \int_1^\infty d\mathbf{r}(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) - \kappa R_K^2 \int_1^\infty d\mathbf{r} H_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) \right] \quad (90)$$

The first part of this we can easily evaluate by moving $K \frac{\partial}{\partial K} = z \frac{\partial}{\partial z}$ outside of the integral, integrating out and differentiating we obtain

$$-\frac{4\pi}{3} R_K^2 \kappa z^2 e^{-z}. \quad (91)$$

The second part is more involved. However, for low densities, we have that $H(\mathbf{r}) = C(\mathbf{r})$, so we can write, using $c_2^K(\mathbf{r}) = -\kappa C_2^K(\mathbf{r})$

$$-\kappa R_K^2 \int_1^\infty d\mathbf{r} H_2^K(\mathbf{r}) z \frac{\partial}{\partial z} c_2^K(\mathbf{r}) = R_K^2 \int_1^\infty d\mathbf{r} c_2^K(\mathbf{r}) z \frac{\partial}{\partial z} c_2^K(\mathbf{r}) \quad (92)$$

which, again, easily evaluates to $\frac{\pi}{3} R_K^2 (z^3 - \frac{2}{3} z^4) e^{-2z}$. Therefore, going to low densities, we expect the energy to be given by the expression

$$\beta\rho u = \sum_K \left[3\rho - \sigma K^2 R_K - \frac{4\pi}{3} R_K^2 \kappa z^2 e^{-z} + \frac{\pi}{3} R_K^2 (z^3 - \frac{2}{3} z^4) e^{-2z} \right] \quad (93)$$

4.4 Calculation of the free energy

Having obtained an expression for the internal, and thus free, energy, we are faced with the same problem as in the previous problem. We have to calculate an integral in which one function is non-linearly dependant on the variable of integration. Specifically, we need to know how R_K and κ vary with K . We first subtract the zero-density energy, which is the same as it was in the case of instantaneous dipole-interactions. We are left with

$$\beta u_{int} = \sum_K \left[3 \frac{\sigma K^2 c_\Delta^K(0)}{(\sigma(K^2 + \hbar^2 \omega_0^2) + c_\Delta^K(0)) \sigma(K^2 + \hbar^2 \omega_0^2)} + \frac{9\rho}{(\sigma(K^2 + \hbar^2 \omega_0^2) + c_\Delta^K(0))^2} \left(\frac{4\pi}{3} \kappa z^2 e^{-z} + \frac{\pi}{3} (z^3 - \frac{2}{3} z^4) e^{-2z} \right) \right] \quad (94)$$

As before, when $T \rightarrow 0$, this becomes an integral over K , which we then cut off at a reasonable point. In this case, $K = 50$ is chosen, for the same reasons as in the non-radiative case.

Still, however, our method does not result in a value that correctly converges towards the van der Waals result as $\lambda \rightarrow \infty$. The reason lies in the derivation of an expression for $c_{\Delta}^K(0)$ that was done in section 4.2. In deriving this expression, we assumed that λ was very high. As such, we were able to use the linearized equations (2.39)-(2.42) in [6]. It turns out, however, that doing this will result in deviations to our final expression that are higher than what was first expected.¹ Clearly, then, we need to use full expressions when determining the values needed.

This creates some complications. Recall, that under the assumption that the linearized equations could be used, we needed to determine only one equation in order to determine a single variable (ξ) for each K . This was because the use of linearized equations allowed us to express U_0 and A directly as functions of ξ (cf. equations (62)-(70)). Now, however, we no longer have a simple relationship between these variables and ξ . Instead, we shall have to solve for ξ and one of the other variables simultaneously (or, as has been done, in repeated succession).

The relevant equations to use are equations (2.22), (2.24), (2.26), (2.31), (2.35),(2.36), (2.37) and (2.38) of [6]. Specifically:

$$A(x) = (1-x)^2 a; \quad p(x) = \frac{(1+2x)^2}{(1-x)^2} \quad (95)$$

where, as before, the x will in the final expression be replaced with $-\xi$.

$$\Gamma = (2 - \sqrt{p})U_0 - U_1 \quad (96)$$

$$2\sqrt{p}\Gamma = (U_0 + A - p)(U_0 + A) + \frac{1}{4}z^2(p - A) \quad (97)$$

which let us express U_1 in terms of U_0 ,

$$U_0 + A - p = \frac{1}{2}[-p - z\sqrt{A} + \sqrt{p^2 + 2pz\sqrt{A} + z^2p}], \quad (98)$$

letting us express U_0 as a function of ξ and a_2 ,

$$\sigma_y = \frac{1}{2z} \left[\frac{z-2}{z+2} + \exp(-z) \right]; \quad \tau_y = \frac{1}{2z} \left[\frac{z^2 + 2z - 4}{4 + 2z - z^2} + \exp(-z) \right] \quad (99)$$

$$y = \frac{4 + 2z - z^2}{2(2+z)} \frac{U_0}{U_1} \quad (100)$$

$$v = K_y \frac{1-y}{\sigma_y - \tau_y y} \quad (101)$$

which we shall rewrite into v/K_y , a size which figured prominently in the linear approach, and which is still of high significance. Finally, we have

$$K_y = \frac{z^2}{6x(z+2)^2} \left[\frac{\sigma_y - \tau_y y}{(\sigma_y - \tau_y)y} \right]^2 U_0, \quad (102)$$

¹Curiously, it seems that this approach would yield correct results if we were to remove the last term of equation (93) and compare the resulting energy with what we would find if we removed the τ^3 term in the integrand of equation (27)

which gives us an equation to be solved so as to determine a value for a_2 . Let us first rewrite this last equation, using that $K_y = \frac{z^2}{3\kappa} e^{-z}$. We obtain

$$\frac{2x}{\kappa} - \frac{e^z}{(z+2)^2} \left[\frac{\sigma_y - \tau_y y}{(\sigma_y - \tau_y) y} \right]^2 U_0 = 0, \quad (103)$$

indeed necessitating an expression for κ , which is found by inverting the second to last expression of equation (37) of [4],

$$\kappa = \frac{6\xi}{\pi R_K}. \quad (104)$$

As before, R_K is given as

$$R_K = \frac{3\rho}{\sigma K^2 + 1/\alpha + c_\Delta^K(o)} \quad (105)$$

where care should be taken not to confuse σ with σ_y . Further, $c_\Delta^K(0)$ is still given by the expression

$$c_\Delta^K(0) = \frac{2}{3} z^2 e^{-z} \frac{v(-\xi)}{K_y}. \quad (106)$$

Here, however, the similarity ends, as we cannot express $\frac{v}{K_y}$ in the same explicit manner as was done previously. Instead, we use equation (101) to express $\frac{v}{K_y}$ in terms of y , which itself is determined by U_0 (itself being a function of a_2). Clearly, then, equation (103) is expressible solely in terms of a_2 and ξ , but it cannot be reduced any further. Fortunately, we still have equation (59) to use, giving us our second equation to solve for two variables.

Similarly to the previous sections, we will use Newton's method to find our solutions. However, the fact that we are solving for two codependent variables complicates matters. First, we will want a good initial guess for the values of a_2 and ξ . This is obtained by solving the linearized problem, which we expect to be close to the true value. After this is done, we hold the value obtained for ξ fixed, and solve equation (103) to obtain a new value for a_2 . This value is then plugged into equation (59), which we solve to obtain a new value for ξ . This process is then repeated until we have obtained what we deem to be a sufficient precision on ξ and a_2 .

Obviously, this process is extremely slow. However, it does converge, and the value to which it converges is what is expected when considering the boundary conditions of $\rho \rightarrow 0$ and $\alpha \rightarrow 0$. Further, as the value of λ increases, the difference between the solution from the linear approximation and this full approach decreases, meaning that the relative difference in speed becomes somewhat smaller. This latter fact also allows us to make some alteration in our approach to cut down the speed needed further. The fact that the difference between the two solutions is a strictly decreasing function of λ implies that it also decreases as a function of K , provided that K is large enough. This means that for each K in our sum, we can determine if the difference between solutions is smaller than a chosen threshold value, beyond which we use the solution for the linearized problem.

Finally, we obtain the results for arbitrary density with radiative interactions. First, we should check that they do indeed converge to the Casimir result obtained in section 2 as $\rho \rightarrow 0$. As can be seen in figure 10, this

is indeed the case. Next, we would like to examine the dependence on ρ and α for low values of both the variables. It was thought that as ρ and α decreased, that $f(\rho)/f(\rho = 0)$ would simply be dependent on $\rho\alpha$. As figure 11 implies, this does not seem to be the case.

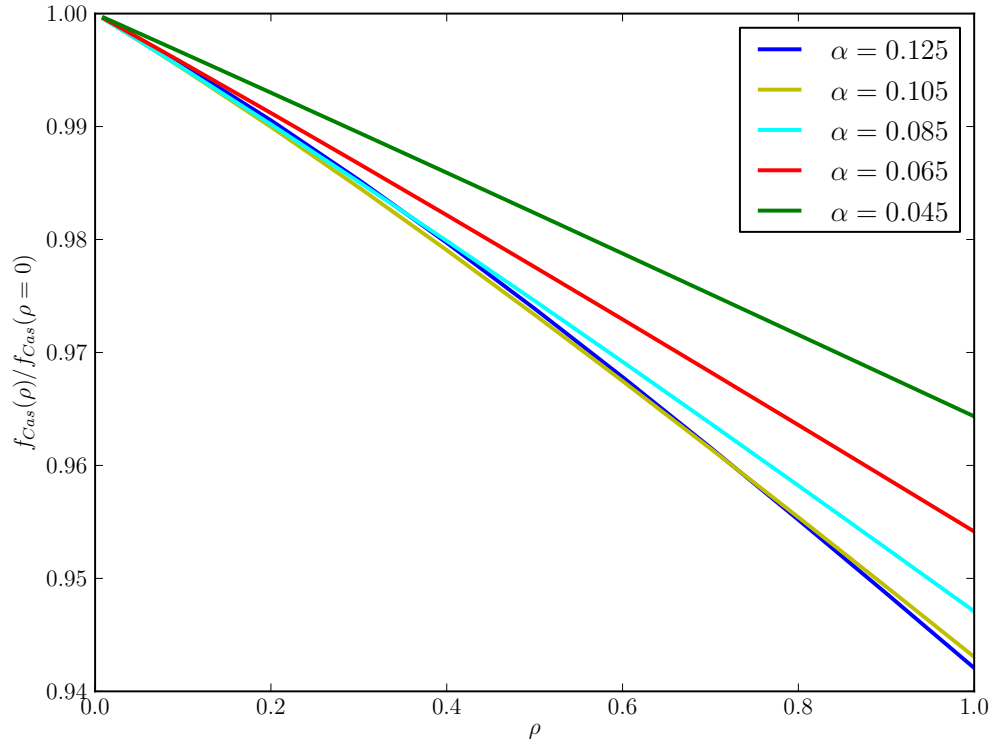


Figure 10: Comparison of Casimir energy calculated for arbitrary density ($f_{Cas}(\rho)$) versus Casimir energy calculated under the assumption that the density is zero ($f_{Cas}(\rho = 0)$). As the density decreases, the two energies approach each other. Notice how the two lower lines entangle each other as ρ varies; a behavior which is to be expected due to the behavior of the energy for high values of α . For this graph, we have chosen to use $\lambda = 20$. For different values of λ , the general behavior of the graph will be the same, although higher values of ρ will lead to slightly changed differences between the calculated energies.

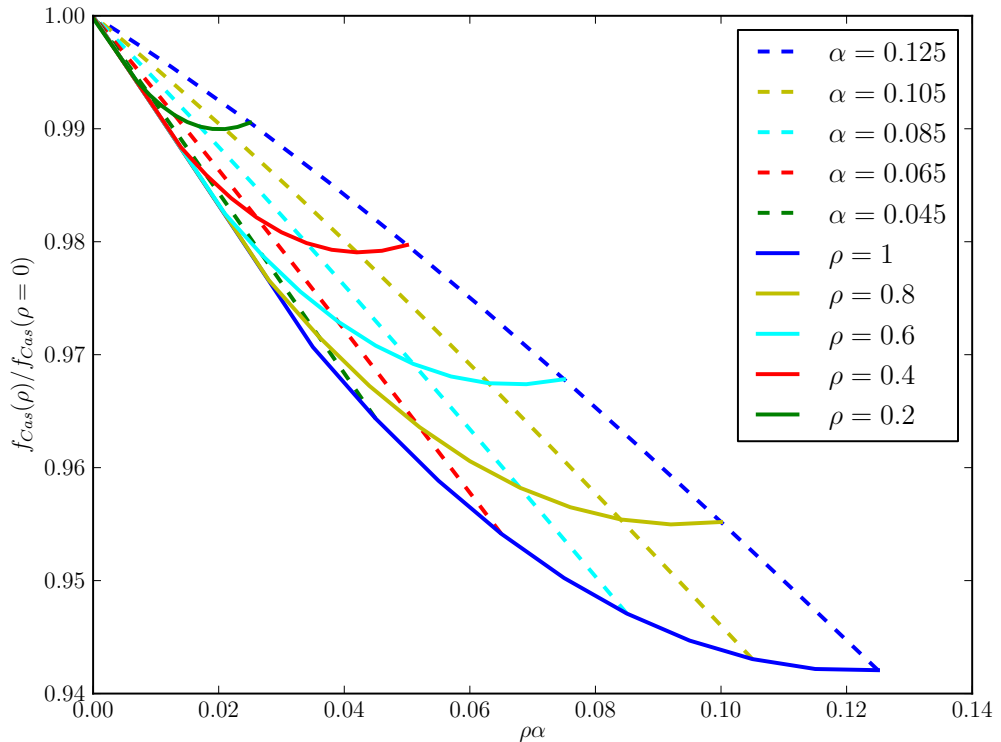


Figure 11: Comparison of Casimir energy calculated for arbitrary density ($f_{Cas}(\rho)$) versus Casimir energy calculated under the assumption that the density is zero ($f_{Cas}(\rho = 0)$). The dashed lines indicate that we have kept a fixed value of α , while varying ρ , whereas the full lines indicate the opposite relationship. Note how the full line always has its endpoint in the outermost dashed line, this obviously being due to said dashed line having α fixed at $1/8$. We expect the full lines to behave similarly for arbitrary values of ρ , that is to say that they should have a slight dip, before beginning an (almost linear) increase. Also note that the endpoint for the dip does not come for any fixed value of $\rho\alpha$. Finally, note that when the full lines start their increase, they increase at a far steeper rate than any of the dashed lines. All of these observations indicate that there is no value for $\rho\alpha$ small enough that the energy is predominantly $\rho\alpha$ -dependant, rather than some other function of ρ and α . For this graph, we have chosen to use $\lambda = 20$. For different values of λ , the general behavior of the graph will be the same, although higher values of ρ will lead to slightly changed differences between the calculated energies.

We now turn to the total correction to van der Waals interaction in dilute media, as illustrated by figures 12 and 13. As could be expected, the correction seems to behave similarly to that of section 3, albeit shifted by a value, which in the limiting case of $\rho \rightarrow 0$ should be, and is, equal to the correction obtained from the Casimir result calculated for dilute media in section 2. What is curious, however, is that this shift remains constant as a function of ρ and α . To simplify notation, we write

$$\Delta_f(\rho) = f_{Cas}(\rho) - f_{vdW}(\rho), \quad (107)$$

thus defining Δ_f as the difference between energy calculated when radiative interactions is and is not taken into account. Since we are primarily interested in the difference between low- and arbitrary density, we will suppress other arguments than ρ , even though we expect Δ_f not to be solely dependant on ρ . In figures 14 and 15 we see that for sufficiently large values of λ , Δ_f is independent of ρ and α . Examining this relation further, we can calculate $\Delta_f(\rho = 0)$ for various values of λ , by using the results from the first two sections. We can then plot this together with $\Delta_f(\rho)$ as calculated assuming arbitrary densities. As figure 16 shows, the two results are almost identical, with only an almost indiscernable difference as λ decreases to 10.

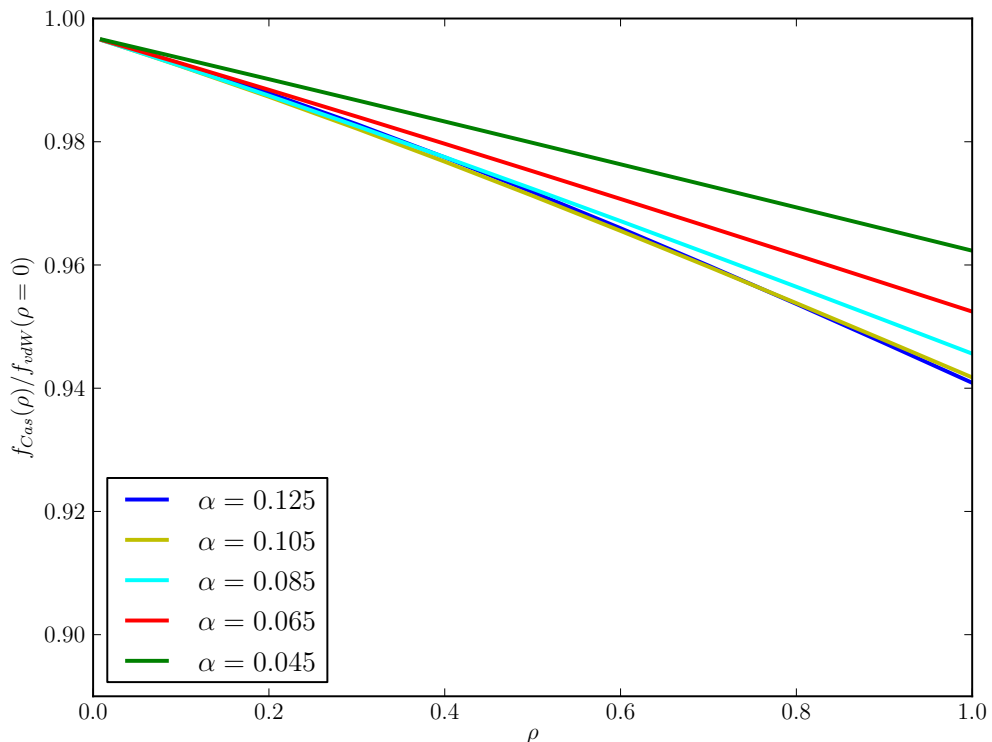


Figure 12: Comparison of Casimir energy at arbitrary densities ($f_{Cas}(\rho)$) versus van der Waals energy at zero density ($f_{vdW}(\rho = 0)$). As the density approaches zero, the ratio approaches the known ratio for Casimir energy at zero density versus van der Waals energy at zero density. In this figure, $\lambda = 100$, and we can see that the radiative correction is small compared to the corrections stemming from taking density into account.

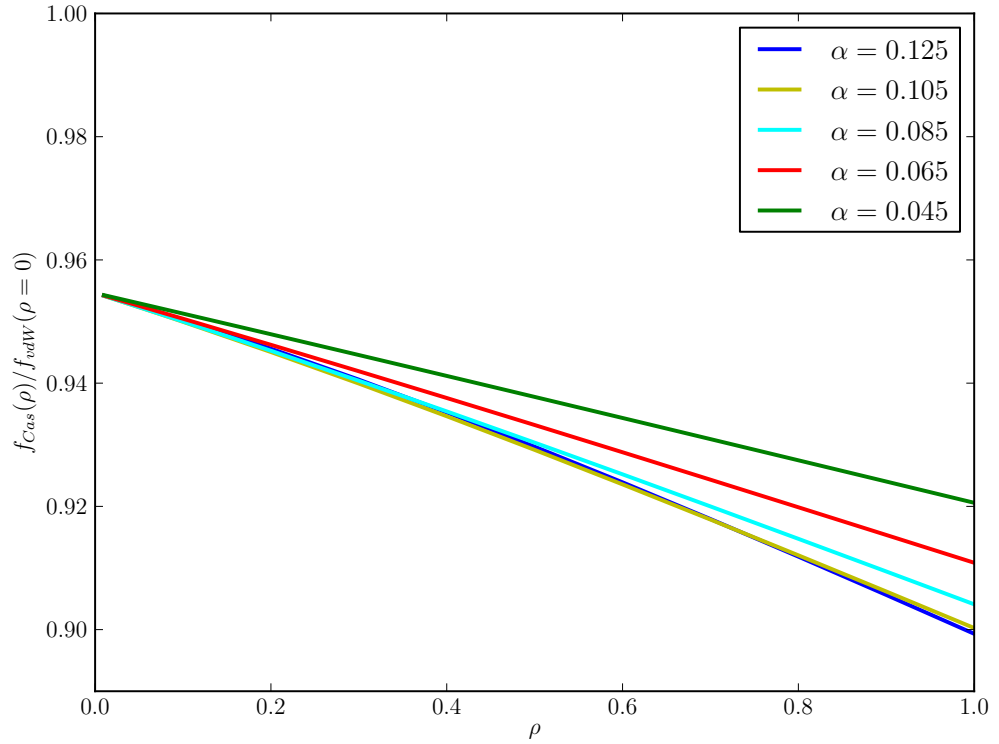


Figure 13: Comparison of Casimir energy at arbitrary densities ($f_{Cas}(\rho)$) versus van der Waals energy at zero density ($f_{vdW}(\rho = 0)$). As the density approaches zero, the ratio approaches the known ratio for Casimir energy at zero density versus van der Waals energy at zero density. In this figure, $\lambda = 20$, and we see that the correction that is due to including radiative terms is relatively high.

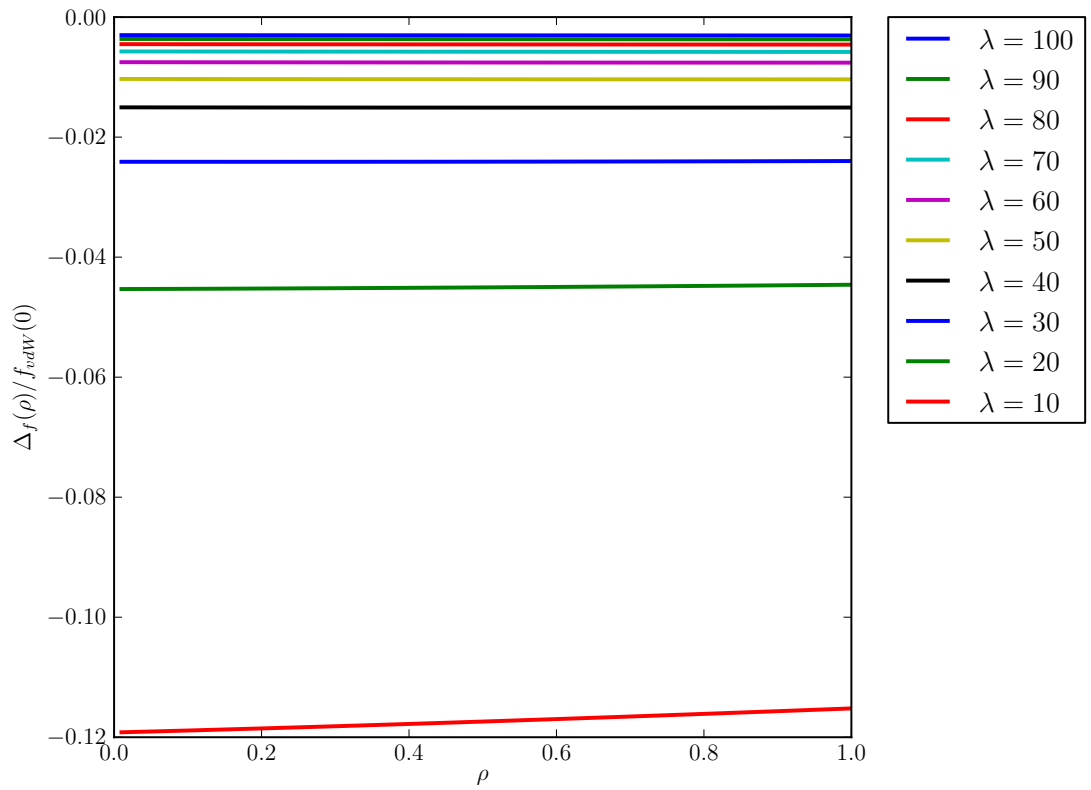


Figure 14: The difference between Casimir and van der Waals energy, Δ_f , calculated for arbitrary density is plotted as a function of ρ . To normalize our values, we have divided by $f_{vdW}(\rho = 0)$. Different stripes correspond to different values of λ . The difference remains constant as a function of ρ , except in the case where $\lambda = 10$, where there is a slight change as $\rho \rightarrow 0$. In this graph, $\alpha = 0.075$.

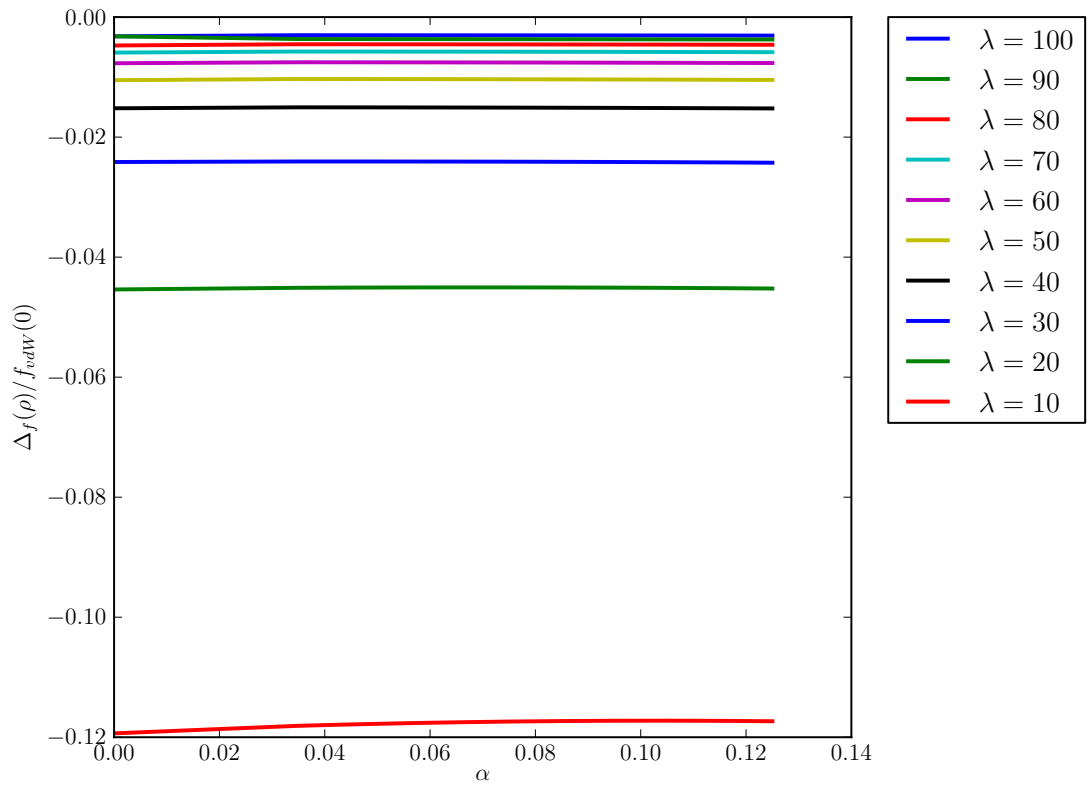


Figure 15: The difference between Casimir and van der Waals energy, Δ_f , calculated for arbitrary density is plotted as a function of α . To normalize our values, we have divided by $f_{vdW}(\rho = 0)$. Different stripes correspond to different values of λ . The difference remains constant as a function of α , except in the case where $\lambda = 10$, where there is a slight change as $\alpha \rightarrow 0$. In this graph, $\rho = 0.5$.

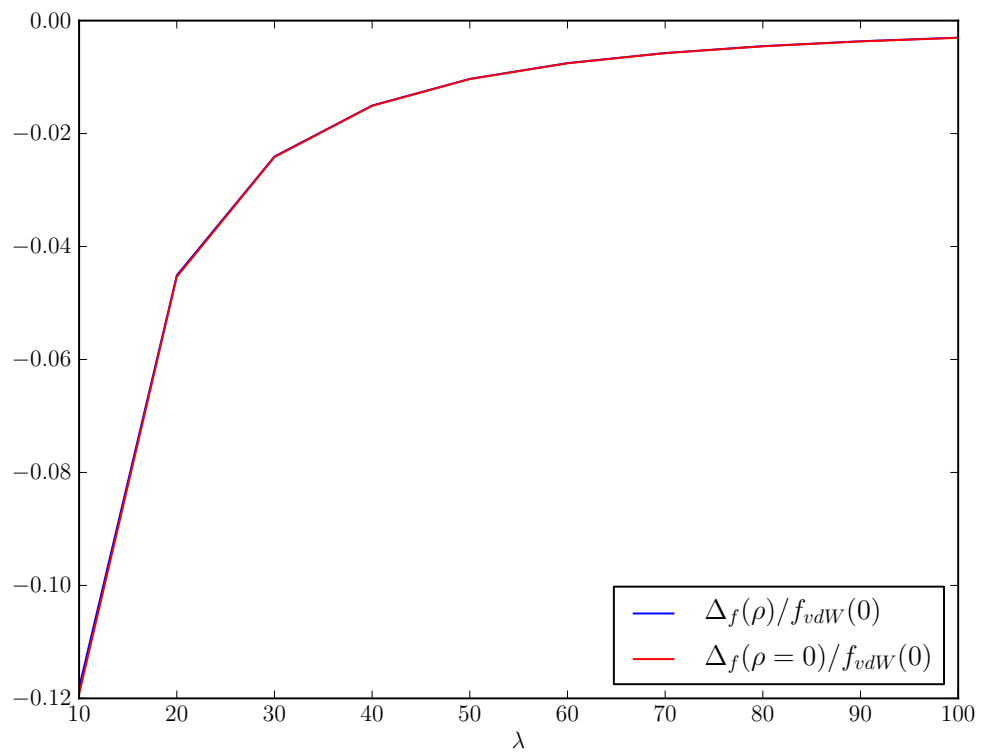


Figure 16: $\Delta_f(\rho)$ and $\Delta_f(\rho = 0)$ plotted as a function of λ in the same graph. The two values overlap completely for higher values of λ , with only a barely perceivable deviation as λ approaches a value of 10. For this computation, we have used $\rho = 0.5$ and $\alpha = 0.035$

5 Conclusion

Free energy in polarizable fluids has been calculated at low and arbitrary densities. Calculations have been made for radiative interactions, as well as non-radiative interactions. At low densities, we have shown that the lowest order correction to van der Waals-energy due to radiative interactions goes as $\frac{1}{\lambda^2}$, and that no higher order corrections can be made except for the full expression, which we have calculated numerically. We have demonstrated that the free energy in general becomes relatively smaller as λ increases.

For arbitrary densities, we have made use of the Ornstein-Zernike equation to calculate corrections that occur from multiparticle interactions. We shown analytically that our expression for the van der Waals interaction at arbitrary densities corresponds to that found for low densities as $\rho \rightarrow 0$. Numerically, we have demonstrated that the energy decreases slightly, as the density increases. We have shown that when the polarizability α changes, this too leads to a decrease in the energy - until an inflective point close to the maximal allowed value for α , after which the energy decrease stops, and for some values of ρ is even reverted.

Lastly, we have calculated the radiative corrections at arbitrary densities. We have demonstrated that for reasonable values of λ , the radiative correction is independent of density. For low values of λ , there is an indication that there will be a correction that is density- and polarizability dependent, but the calculations made have not been accurate enough for such low values of λ to make any decisive remarks.

A Full expression for final term

In this section, we shall compute the full expression for the free energy per particle. This shall be done using known expressions for the Laplace transform of the direct and total correlation functions. We start off with the expression we found in equation (89) for the internal energy per interaction:

$$\beta\rho u = \sum_K \left[3\rho - \sigma K^2 R_K - \kappa R_K^2 \int d\mathbf{r} G_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}) \right]. \quad (108)$$

The first two parts of the sum are well known, as they constitute the expression for the internal energy per interaction when considering instantaneous dipole interactions. The interesting part is the integral, which gives us the corrective term, and which we had previously approximated to lower order in equation (93). Thus, we aim to find an expression from

$$-\kappa R_K^2 \int d\mathbf{r} G_2^K(\mathbf{r}) K \frac{\partial}{\partial K} c_2^K(\mathbf{r}). \quad (109)$$

First, we should combine κ and $G_2^K(\mathbf{r})$ to obtain $g_2^K(\mathbf{r}) = -\kappa G_2^K(\mathbf{r})$. Next, we will make use of the fact that g and c are only radially dependant, as well as the identity $z \frac{\partial}{\partial z} = K \frac{\partial}{\partial K}$ to write our corrective term as

$$4\pi R_K^2 \int_0^\infty dr r^2 g_2^K(r) z \frac{\partial}{\partial z} c_2^K(r). \quad (110)$$

Further, we make use of

$$\begin{aligned} g_2^K(r) &= 0, \quad r < 1 \\ c_2^K(r) &= \frac{1}{3} z^2 \frac{e^{-zr}}{r} \end{aligned} \quad (111)$$

to write this equation as

$$\frac{4\pi}{3} R_K^2 \int_0^\infty dr r g(r) z \frac{\partial}{\partial z} (z^2 e^{-zr}), \quad (112)$$

which, taking the derivative, yields us

$$\frac{4\pi}{3} R_K^2 \int_0^\infty dr r g(r) e^{-zr} (2z^2 - rz^3). \quad (113)$$

We now turn to the appendix of [10], where the Laplace transform of the correlation functions (and thus, the pair distribution function) have been defined as

$$\begin{aligned} \hat{c}(s) &= \int_0^\infty dr r c(r) e^{-sr} \\ \hat{g}(s) &= \int_0^\infty dr r g(r) e^{-sr}. \end{aligned} \quad (114)$$

Using this, as well as the property of Laplace transforms that $\mathcal{L}(f(r)) = \hat{f}(s) \Rightarrow \mathcal{L}(rf(r)) = \hat{f}'(s)$ we can express equation (113) as

$$\lim_{s \rightarrow z} \frac{4\pi}{3} R_K^2 z^2 (2\hat{g}(s) - z^3 \hat{g}'(s)). \quad (115)$$

where the lim-notation has been used to clarify that $\hat{g}(s)$ still depends on z , implying that we should take the derivative with regards to s , and then let $s \rightarrow z$, rather than just differentiating with regards to z . Henceforth,

we will use $\hat{g}'(z)$ to signify this, and if the need arises we will write the other case as $\frac{\partial}{\partial z}\hat{g}(z)$.

Following the text of said appendix, we know that $\hat{g}(z)$ can be expressed in terms of v_2 , from the identity

$$v_2 = -24\xi K_y e^z \int_1^\infty dr e^{-zr} g_2(r) \quad (116)$$

(c.f. equation (2.4) in [6]), from which we obtain

$$\hat{g}(z) = -\frac{v_2}{K_y} \frac{e^{-z}}{24} \quad (117)$$

Obtaining $\hat{g}'(z)$ is more involved, for the aforementioned reasons. However, following the appendix of [10], we can make an expansion of the formal expression for $\hat{g}(s)$, eventually yielding

$$\hat{g}'(z) = \frac{\hat{g}(z)[\hat{c}_0(-z) - \hat{c}_0(z)]}{K_y e^z} \quad (118)$$

in which

$$\hat{c}_0(s) = \hat{c}(s) - K_y e^z \frac{1}{s+z} e^{-(s+z)}, \quad (119)$$

$$\begin{aligned} \hat{c}(s) = & -a_2 \frac{1}{s^2} [1 - (1+s)e^{-s}] - b_2 \frac{1}{s^3} [2 - (2+2s+s^2)e^{-s}] \\ & + \frac{1}{2}\xi a_2 \frac{1}{s^5} [24 - (24+24s+12s^2+4s^3+s^4)e^{-s}] \\ & - \frac{v_2}{z} \left[\frac{1}{s}(1-e^{-s}) - \frac{1}{z+s}(1-e^{-(s+z)}) \right] \\ & - \frac{v_2^2}{4K_y z^2 e^z} \left[\frac{1}{s-z}(1-e^{-(s-z)}) + \frac{1}{s+z}(1-e^{-(s+z)}) - 2\frac{1}{s}(1-e^{-s}) \right] \\ & + K_y e^z \frac{1}{s+z} e^{-(s+z)} \end{aligned} \quad (120)$$

and where $\hat{c}_0(\pm z) = \lim_{s \rightarrow \pm z} \hat{c}_0(s)$. In order to take this limit, we note that

$$\lim_{s \rightarrow z} \frac{1}{s-z} (1-e^{-(s-z)}) = \lim_{s \rightarrow -z} \frac{1}{s+z} (1-e^{-(s+z)}) = 1, \quad (121)$$

so finally we have

$$\begin{aligned} & \hat{c}_0(-z) - \hat{c}_0(z) \\ = & \frac{a_2}{z^2} [(1-z)e^z - (1+z)e^{-z}] \\ & + \frac{b_2}{z^3} [4 - (2-2z+z^2)e^z - (2+2z+z^2)e^{-z}] \\ & - \frac{1}{2}\xi a_2 \frac{1}{z^5} [48 - (24-24z+12z^2-4z^3+z^4)e^z - (24+24z+12z^2+4z^3+z^4)e^{-z}] \\ & + \frac{v_2}{z} \left[\frac{1}{z}(2-e^z-e^{-z}) + 1 + \frac{1}{2z}(1-e^{-2z}) \right] \\ & + \frac{v_2^2}{4K_y z^2 e^z} \left[\frac{1}{2z}(2-e^{2z}-e^{-2z}) - \frac{2}{z}(2-e^z-e^{-z}) \right]. \end{aligned} \quad (122)$$

Here, the ξ and a_2 will have to be computed numerically, as has been detailed previously, while v_2 can be expressed from equation (101) (keeping in mind that $v_2 = v(-\xi)$), and b_2 can be found using equations (2.7) and (2.10) of [6];

$$-6\xi b_2 = (1 + 8\xi - 2\xi^2)a_2 + u - 1, \quad (123)$$

$$u = 24\xi \left[v_2 \frac{1}{z} \left\{ \frac{1}{2} + \frac{1}{z^2} [(1+z)e^{-z} - 1] \right\} + \frac{v^2}{2K_y z^2 e^z} \left\{ \frac{\sinh z}{z} - \frac{\cosh z - 1}{z^2} - \frac{1}{2} \right\} - \frac{K_y(1+z)}{z^2} \right] \quad (124)$$

Here, care should be made not to confuse u with the internal energy, as used in the preceding sections. In this case, u is mostly related to the U_0 that was seen in the derivation of $\frac{v_2}{K_y}$.

In the end, we can combine these results with equation (115) to obtain the full radiative correction to the expression for free energy.

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