Beware of density dependent pair potentials

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Abstract. Density (or state) dependent pair potentials arise naturally from coarse-graining procedures in many areas of condensed matter science. However, correctly using them to calculate physical properties of interest is subtle and cannot be uncoupled from the route by which they were derived. Furthermore, there is usually no unique way to coarse-grain to an effective pair potential. Even for simple systems like liquid Argon, the pair potential that correctly reproduces the pair structure will not generate the right virial pressure. Ignoring these issues in naive applications of density dependent pair potentials can lead to an apparent dependence of thermodynamic properties on the ensemble within which they are calculated, as well as other inconsistencies. These concepts are illustrated by several pedagogical examples, including: effective pair potentials for systems with many-body interactions, and the mapping of charged (Debye-Hückel) and uncharged (Asakura-Oosawa) two-component systems onto effective one-component ones.

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1. Introduction

No known materials exist in nature whose behaviour can be completely captured by pair potentials alone. Even a noble gas like Argon has a finite contribution from three-body Axilrod-Teller triple-dipole interactions\(^1\). Thus, the pair-potentials used to describe condensed matter systems always arise from coarse-graining procedures, where a subset of the degrees of freedom of the full (quantum) statistical mechanical system are integrated out. In the aforementioned example, integrating the three-body interactions over angular coordinates results in effective parameters for the Lennard Jones (LJ) potential, which will depend on state. In metallic systems, integrating out the free electrons leads to a configuration independent volume term and pair potentials that depend on the global density\(^2\). Alternate coarse-graining procedures for metals such as the embedded atom method\(^3, 4\), effective medium theory\(^5\), Finnis-Sinclair potentials\(^6\) or glue potentials\(^7\) result in a local density dependence.

Coarse-graining methods are crucial to deriving tractable statistical mechanical treatments of soft-matters systems, where a large number of different length and time-scales may coexist. An increasingly popular coarse-graining technique consists of deriving effective potentials and exploiting their analogy to well studied simple atomic or molecular systems to calculate phase behaviour and correlations\(^8, 9, 10\). Again, these effective interactions are often reduced to an approximate pairwise description with parameters that depend on state.

Direct inversion from experimental structure factors are another way to derive the parameters for effective pairwise potentials\(^11, 12\). These almost always show
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a dependence on state, especially for the case of soft-matter systems. This is not surprising, of course, since one can easily imagine that the interactions between two effective particles depends on the overall density. For example, changing the concentration of a micellar solution may affect the internal structure of the micelles, which in turn leads to a density dependence of the effective pair interaction between the particles.

That an effective pair potential derived in one context doesn’t always perform well in another is well known, and usually categorised as a problem of transferability. For example, if the parameters of an effective pair potential depend on density (but the explicit density dependence is not known), then a parameterisation of the potential at \( \rho_1 \) is not the same as the one needed at a different density \( \rho_2 \) – the potential at \( \rho_1 \) is not transferable to the state point at \( \rho_2 \).

What I will endeavour to show in the present paper is that there are deeper problems associated with the use of effective pair potentials, even when the problem of transferability appears to be solved. The particular example studied is pair potentials that depend on the global density \( \rho \) as \( v(r; \rho) \). The focus is partially pedagogical. For that reason rather simple models are treated, with a special emphasis on the liquid phase. While many of these results have already appeared in one form or another in the literature, they are worth repeating.

The paper is organised as follows: Section 2 describes the apparent inconsistencies that arise between the virial and compressibility routes to thermodynamics for a simple density dependent pair potential \( v(r; \rho) \). Section 3 discusses the effective pair potentials that result from integrating out three and higher order many-body interactions. The effective pair potential that correctly describes the excess internal energy is shown to be different from the one that correctly describes the pair structure. These points are illustrated with a specific application from polymer solutions. In section 4 the McMillan-Mayer\[13\] tracing out procedure is analysed for an exactly solvable lattice version of the Asakura-Oosawa\[14\] model. While this procedure maps onto a useful effective one-component picture in the semi-grand ensemble, integrating out the smaller particles in a canonical ensemble does not lead to an effective Hamiltonian decomposable as a sum over independent interactions. For charged systems the canonical ensemble is the natural choice to integrate out microscopic co and counterions. Again, apparent ambiguities arise when the density dependent Debye-Hückel potential is used to derive thermodynamics. Finally, conclusions from these different model calculations are summarised in section 5.

2. General thermodynamic inconsistencies from a naive application of density dependent pair potentials

As a first rather general example, consider a homogeneous fluid in a volume \( V \), whose \( N \) particles interact with a spherically symmetric pair potential \( v(r; \rho) \), which depends on the global density \( \rho = N/V \). There are no volume, one-body, or many-body terms. No further assumptions as to the origin of the density dependence are made. Two established ways to calculate the equation of state (EOS) \( Z \) and other thermodynamic properties from the correlation functions are\[15\]:

\[ \text{‡ Effective potentials could also depend on other state variables like temperature } T, \text{ but here I mainly focus on density dependence} \]
(i) the compressibility route:

\[ Z_c = \frac{\beta P}{\rho} = \int_0^\rho \frac{\partial \beta P(\rho')}{\partial \rho'} \, d\rho' = \int_0^\rho \left[ 1 - \rho' \hat{c}(k = 0; \rho') \right] \frac{d\rho'}{\rho}, \]

where \( \hat{c}(k = 0; \rho') \) is the zero-wavelength component of the Fourier Transform (FT) of the direct correlation function \( c(r), \beta = 1/k_B T, \) and \( P \) is the pressure. This relationship follows from simple properties of the correlation functions and their connections to thermodynamics in the grand canonical ensemble – it is therefore independent of the particular form of the interactions between the particles, which need not be pairwise additive\[13\].

(ii) the virial route:

\[ Z^\rho_{\text{vir}} = \frac{\beta P}{\rho} = 1 - \frac{2}{3} \beta \pi \rho \int_0^\infty r^2 \left\{ r \frac{\partial v(r; \rho)}{\partial r} - 3 \rho \frac{\partial v(r; \rho)}{\partial \rho} \right\} g(r) \, dr, \]

where \( g(r) \) is the radial distribution function. The standard way to derive the virial equation is directly through the canonical partition function

\[ Q(N, V, T) = \frac{\Lambda^{-3N}}{N!} \int d\mathbf{r}^N \exp \left\{ -\beta \sum_{i<j} v(r_{ij}; \rho) \right\}, \]

where \( \Lambda \) is the usual thermal de Broglie wavelength. The volume derivative in

\[ \beta P = \left( \frac{\partial \log Q(N, V, T)}{\partial V} \right)_{N,T} \]

also acts directly on the pair potential, which brings in the extra \( \partial v(r; \rho)/\partial \rho \) term in the virial equation \[2\], a result first pointed out in 1969 by Ascarelli and Harrison\[16\] in the context of density dependent pair potentials used for modelling liquid metals. This particular form of the virial equation is only valid for pair potentials, but the derivation of generalisations for systems with three-body terms is straightforward.

So far so good: both the compressibility equation (which doesn’t change from the density independent case) and the virial equation (which does) appear to be derived for the case of a density dependent pair potential. Nevertheless, this apparent rigour deceives, since it is trivial to find density dependent pair potentials where the two routes generate different thermodynamics. Consider, for example, a special class of density dependent pair potentials with

\[ v(r; \rho) = \epsilon(\rho) v^0(r). \]

Two possible \( \epsilon(\rho) \) are shown in Fig. 1. The compressibility equation \[1\] results in a different \( Z \) at \( \rho = \rho^* \) for potentials (a) and (b), since the effects of all densities below \( \rho^* \) are relevant. In contrast, the virial equation \[2\] cannot distinguish between the two potentials at \( \rho = \rho^* \) because it only includes a local density dependence. Of course it is not surprising that the two routes to thermodynamics disagree, since one was derived in the canonical ensemble, which only samples a single global density, while the other was derived in the grand-canonical ensemble, which samples all densities.

However, the origin of the discrepancy lies deeper than that. One might think that the virial equation is less reliable, since it only treats the density dependence as a local derivative. But, as the following example will show, the two routes disagree even for a simple linear density dependence; even worse, the density dependence correction of Ascarelli and Harrison\[16\] corrects in the wrong direction – it makes the discrepancy between the two routes worse.
Consider a fluid interacting via the simple Gaussian potential

\[ v(r; \rho) = \epsilon(\rho) \exp[-r^2] \]  

which could be viewed as a model for interactions between polymer coils [17, 18]. This potential falls into the class of mean field fluids [19, 20, 21, 10], for which the simple random phase approximation (RPA) \( c(r; \rho) \approx v(r; \rho) \) is very accurate and even becomes asymptotically exact in the limit of small \( \epsilon(\rho) \) or large \( \rho \). For integrable density-independent potentials \( v(r) \), the compressibility route leads to an EOS of the mean-field (\( Z_{MF} \)) form

\[ Z_{RPA}^c = Z_{MF} = 1 + \frac{1}{2} \beta \hat{v}(k = 0), \]  

where \( \hat{v}(k) \) is the FT of the potential. For the same integrable density independent potentials, the virial route (2) reduces to

\[ Z_{0 \text{vir}}^c = Z_{MF} - \frac{2}{3} \beta \pi \rho \int_0^\infty r^2 \left\{ r \frac{\partial v(r; \rho)}{\partial r} \right\} h(r) dr, \]  

where \( h(r) = g(r) - 1 \). In the limit of small \( \hat{v}(k = 0) \) or high densities, the two routes to \( Z \) approach each other [19]; the RPA closure approximation is nearly self-consistent.

For the density dependent \( v(r; \rho) \) given by Eq. (6), the compressibility equation (1) takes on a simple form:

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The virial route without density-dependent corrections, i.e. Eq. (3), results in

\[ Z_{0 \text{vir}}^c \approx Z_{MF} = 1 + \pi^{3/2} \left( \frac{1}{2} \epsilon_0 \rho + \frac{1}{3} \epsilon_1 \rho^2 \right) \]  

for the limit of small \( \hat{v}(k = 0) \) or large \( \rho \). Within the RPA the corrections to Eq. (11) from the second term in Eq. (6) can be analytically calculated for Gaussian potentials [19] and explicitly shown to be small for the limit being considered.
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\[ \beta v(r; \rho) = (1 + 0.1 \rho) \exp(-r^2) \]

\[ Z^{RPA}_{c} \]

\[ Z^{RPA}_{\rho} \]

\[ Z^{vir}_{0} \]

\[ Z^{vir} \]

Figure 2. Comparison of three routes to thermodynamics for an effective potential \( \beta v(r; \rho) = (1 + 0.1 \rho) \exp(-r^2) \). \( Z^{RPA}_{c} \) is given by Eq. (10), \( Z^{RPA}_{\rho} \) comes from an analytical RPA solution to the virial equation (9), and \( Z^{vir}_{0} \) from an analytical RPA solution to the simpler virial equation (9). The density-dependent correction to the virial equation increases the disagreement between \( Z_{c} \) and \( Z^{vir}_{0} \). Inset: In contrast to the density-dependent case, the RPA virial and compressibility routes to \( Z \) for \( v(r) = 2 \exp(-r^2) \) agree within the accuracy of the graph, demonstrating the near self-consistency of the closure for such potentials.

At this level, the two routes clearly don’t agree. If \( \epsilon_1 > 0 \) then \( Z^{0}_{vir} > Z_{c} \), while if \( \epsilon_1 < 0 \) then \( Z^{0}_{vir} < Z_{c} \). But, one might argue, the discrepancy should stem from ignoring the density derivative term in the virial equation (9). Instead, the opposite is true. Adding the density derivative correction results in

\[ Z^{\rho}_{vir} = Z^{0}_{vir} + 2 \pi \rho^2 \int r^2 g(r) \epsilon_1 \exp(-r^2) dr. \]  (12)

Since \( g(r) \geq 0 \), \( \epsilon_1 > 0 \) implies that \( Z^{\rho}_{vir} > Z^{0}_{vir} > Z_{c} \), and \( \epsilon_1 < 0 \) implies that \( Z^{\rho}_{vir} < Z^{0}_{vir} < Z_{c} \). In other words, the full virial equation (9), derived explicitly from the canonical ensemble with a density dependent potential, is even worse than virial expressions (11) or (1) which ignore the density derivative terms. These points are illustrated in Fig. 2 for a particular example of the potential (9).

The problem clearly lies deeper than the fact that the virial equation only contains a local density derivative, since, for the example potential (9), this should be sufficient to describe all the density dependence. The next sections provide a partial answer to this apparent conundrum by explicitly deriving density dependent potentials, and showing that they should really be viewed as mathematical constructs whose physical interpretation cannot be separated from the way in which they were derived.

3. Example 1: effective pair potentials from many-body interactions

This section demonstrates both in general and with an explicit example that there is no unique way to represent averages over many-body interactions as averages over a

\[ \frac{\partial \epsilon(\rho)}{\partial \rho} > 1 \] and vice versa.
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single pair potential that depends on the global density $\rho$. Although this has already been pointed out several times in the literature\[23, 24, 25, 26\], mainly in the context of noble gasses, it is worth partially repeating because it often seems forgotten.

3.1. Effective density dependent pair potentials from three-body potentials

Consider a homogeneous one component fluid system interacting with a density independent pair potential $w^{(2)}(r_i, r_j)$ and triplet potential $w^{(3)}(r_i, r_j, r_k)$. The Hamiltonian can be written as:

$$H = K + \sum_{i<j} w^{(2)}(r_i, r_j) + \sum_{i<j<k} w^{(3)}(r_i, r_j, r_k)$$  \hspace{1cm} (13)

with $K$ the kinetic energy operator. By using this Hamiltonian in a standard canonical partition function, the following exact expression can be derived for the excess internal energy $U$:

$$U(N, V, T) = \frac{1}{2} \rho^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 g_{12} w_{12} + \frac{1}{6} \rho^3 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 g_{123} w_{123}$$  \hspace{1cm} (14)

where $w_{12} = w^{(2)}(r_1, r_2)$, $w_{123} = w^{(3)}(r_1, r_2, r_3)$. $g_{12} = g^{(2)}(r_{12})$ and $g_{123} = g^{(3)}(r_{12}, r_{13}, r_{23})$ are the homogeneous pair and triplet radial distribution functions respectively, and $r_{ij}$ is the distance between particle $i$ and particle $j$.

Three-body interactions are often cumbersome to use; an effective pair-potential which reproduces the properties of the full system would be much more convenient. A popular method to achieve this consists of calculating the energy of the system governed by the original many-body Hamiltonian through an accurate method (like Eq. (14), and then finding an effective pair potential $v^{eff}_U(r_{ij}; \rho)$ that reproduces the same energy at the same state-point. For the system at hand, this can be done explicitly\[23, 24, 26\] by writing Eq. (14) as

$$U(N, V, T) = \frac{1}{2} \rho^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 g_{12} w_{12} + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 g_{123} v^{eff}_U(r_{12}; \rho),$$  \hspace{1cm} (15)

which defines the effective pair potential

$$v^{eff}_U(r_{ij}; \rho) = w_{12}(r_{ij}) + \delta v_U(r_{ij}; \rho)$$  \hspace{1cm} (16)

where

$$\delta v_U(r_{ij}; \rho) = \frac{1}{3} \rho \int d\mathbf{r}_{13} g_{13} g_{23} G_{123} w_{123}$$  \hspace{1cm} (17)

is the (additive) density dependent correction to the bare pair potential $w_{12}(r)$. Here $G_{123}$ is defined as the correction to the Kirkwood superposition approximation[27] for the triplet radial distribution function:

$$g_{123} = g_{12} g_{13} g_{23} G_{123}.$$  \hspace{1cm} (18)

In contrast to the virial equation (2) of the previous section, re-deriving the two-body energy equation for a general $v(r; \rho)$ within the standard canonical ensemble route[15] does not result in extra density dependent terms. In other words, within the canonical ensemble, an effective density dependent pair interaction can be constructed that correctly captures – by averages over pair correlations alone – the internal energy $U(N, V, T)$ of a system with two and three-body interactions. However, $v^{eff}_U(r; \rho)$ is not sufficient for a complete pairwise description. The three body interaction $w_{123}$ also modifies $g_{12}$, and although $v^{eff}_U(r; \rho)$ generates a different $g_{12}$ than would be found by
using only \( w_{12} \), the pair correlations are not those of the original system, as will be shown below.

A very useful theorem that facilitates the study of pair correlations states that for a given homogeneous many-body system at a global density \( \rho \), there exists a bijective one to one mapping between a unique pair potential \( v_{\text{eff}}^g(r; \rho) \) and the \( g^{(2)}(r) \) at that density. While the explicit analytical construction of \( v_{\text{eff}}^g(r; \rho) \) is not as straightforward as that of its energy analogue \( v_{\text{eff}}^U(r; \rho) \), an expansion to lowest order in density and \( w_{123} \) can be derived:

\[
v_{\text{eff}}^g(r_{12}; \rho) \approx w_{12}(r_{12}) + \delta v_{\rho}(r_{12}; \rho) = w_{12}(r_{12}) + \rho \int d\mathbf{r}_3 \{1 - \exp(-w_{123})\} g_{13} g_{23}.
\]  

(19)

Comparing the density-dependent corrections to \( v_{\text{eff}}^g(r; \rho) \) and \( v_{\text{eff}}^U(r; \rho) \) in the limit of small \( \rho \) and weak \( w_{123} \) leads to:

\[
\frac{\delta v_{\text{eff}}^U(r; \rho)}{\delta v_{\rho}(r; \rho)} = \frac{1}{3} + O(w_{123}^2; \rho^2).
\]  

(20)

To lowest order, the two density dependent corrections differ by a factor of three!

The unique one-to-one correspondence between \( g^{(2)}(r) \) and \( v_{\text{eff}}^g(r; \rho) \) therefore implies that \( v_{\text{eff}}^g(r; \rho) \) cannot reproduce the correct pair correlations for use in Eq. (15). This proves that the pair potential derived from the energy equation for a many-body system cannot completely and self-consistently capture the excess energy within a pairwise description; \( v_{\text{eff}}^g(r; \rho) \) is also needed to generate the correct \( g^{(2)}(r) \). On the other hand, because the compressibility equation (1) is independent of the underlying interactions, \( v_{\text{eff}}^g(r; \rho) \) is sufficient to derive the true compressibility, and from it other thermodynamic quantities of interest, within a purely pairwise description. But the price to pay for coarse-graining a many-body system to an effective two-body system in this way is that the thermodynamics can only be calculated along one specific route. Neither \( v_{\text{eff}}^g(r; \rho) \) nor \( v_{\text{eff}}^U(r; \rho) \) have a well defined physical meaning independent of the way in which they were derived. The arguments of this subsection are not new, as the following quote, made over 30 years ago in exactly the same context, demonstrates:

"We record our opinion that the use of density-dependent effective pair potentials can be misleading unless it is recognised that these are mathematical constructs to be used in specified equations rather than physical quantities."

3.2. A worked example: polymers as soft colloids

The concepts of the previous section can be made more concrete by examining a recent coarse-graining of polymers as soft colloids. This system has the advantage that many-body correlations and interactions can be accurately calculated from computer simulations, allowing detailed comparisons of the coarse-grained system with the original many-body system.

The first step in the coarse-graining procedure is to choose an effective coordinate for the polymers, which we take to be the centre of mass (CM). The next step is to integrate out the monomeric degrees of freedom to derive an effective interaction between the polymer CM. Following the discussion in reference [11], the Helmholtz free energy of this system is

\[ A = \int d\mathbf{r}_{123} \{1 - \exp(-w_{123})\} g_{13} g_{23}. \]

(29)

Note that this pair potential cannot simultaneously represent the correct three-body correlations. See e.g. ref. [32] for a detailed example and discussion of this point.
energy $F$ of a set of $N$ polymers of length $L$ in a volume $V$, with their CM distributed according to the set of coordinates $\{r_i\}$, can be written as the following expansion:

$$F(N,V;\{r_i\}) = F^{(0)}(N,V) + \sum_{i<j}^N w^{(2)}(r_i,r_j) + \sum_{i<j<k}^N w^{(3)}(r_i,r_j,r_k) + \ldots \quad (21)$$

\[ \ldots + \sum_{i<j<k}^N w^{(N)}(r_i,r_j \ldots r_N) \]

In the scaling limit, each term in the series is independent of $L$ as long as the $n$-tuple CM coordinates $\{r_1, r_2 \ldots r_n\}$ are expressed in units of $R_g$, the radius of gyration at zero density. This coarse-grained free-energy contains an implicit statistical average over all the monomeric degrees of freedom for a fixed set of CM coordinates $\{r_i\}$.

$F^{(0)}(N,V)$ is the zero-body volume term, related to the internal free energy of a single polymer; translational symmetry implies that there is no explicit one-body term. The pair and higher body terms are defined in the standard way: the $\delta v_n$ to the effective pair potential, $g^{\text{eff}}(r; \rho)$ which exactly reproduces $g(r)$. Explicit examples of $g^{\text{eff}}(r; \rho)$ are shown in Fig. 3, taken from ref. [32], where further details can be found.

The relative importance of each term decreases for increasing $n$, so that in principle the many-body expansion (21) is expected to converge.[32]

The free energy $F(N,V)$ of the underlying polymer system follows from a final trace over all CM coordinates

$$F(N,V) = -\log \sum_{\{r_i\}} \exp \left[-F(N,V;\{r_i\})\right] \quad (22)$$

so that Eq. (22) can be viewed as an expansion of the effective interaction between the CM in terms of (entropic) many-body interactions, in a close analogy to expansion of the energy of atomic or molecular systems in many-body interactions.[33]

But in practise following this path is extremely cumbersome, because the number of coordinates and concomitant complexity of the interactions $w^{(n)}$ grows rapidly with increasing order $n$. To circumvent this problem one could simply truncate the expansion (21) at the pair level, but this would completely ignore the many-body interactions. Instead, we recently proposed[14][15][32] a coarse-graining method which takes the many-body interactions into account in an average way. First, at a given $\rho$, the $g(r)$ between the CM of a polymer was generated by computer simulations. Next, for each density, an Ornstein-Zernike integral equation approach was used to invert the $g(r)$ and generate the unique[28] effective pair potential $v^{\text{eff}}_g(r; \rho)$ which exactly reproduces $g(r)$. Explicit examples of $v^{\text{eff}}_g(r; \rho)$ are shown in Fig. 3 for different densities $\rho/\rho^\ast$, where $\rho^\ast = 3/(4\pi R_g^3)$ denotes the crossover from the so-called “dilute” to the “semi-dilute” regimes.[34]. For $\rho \to 0$, $v^{\text{eff}}_g(r; \rho) \to w^{(2)}(r)$ while the difference $\delta v_g(r; \rho) = v^{\text{eff}}_g(r; \rho) - w^{(2)}(r)$ grows with increasing density.

For the polymer system, the expansion (19) for the density dependent correction to the effective pair potential, $\delta v_g(r; \rho)$, can be explicitly calculated.[32]. The results, plotted in Fig. 3, show that despite the existence of higher order interactions $w^{(n)}$ with $n > 3$ this weak $w^{(3)}$ form performs remarkably well, demonstrating that for a polymer solution, the three-body interaction is the dominant cause of the density dependence in $v^{\text{eff}}_g(r; \rho)$ at least for $\rho/\rho^\ast \leq 1$. 

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Figure 3. Effective potentials $w^{(n)}(r)$ between the CM of $L = 500$ self-avoiding walk polymer coils. The coordinate $r$ denotes the pair distance for $n = 2$, the length of an equilateral triangle for $n = 3$ and the length of a tetrahedron for $n = 4$. For $n = 5$ only the interaction at full overlap was calculated. (taken from Ref. [32])

Figure 4. The effective polymer pair potentials $v^{eff}(r; \rho)$, derived at different densities $\rho/\rho^*$ from an Ornstein-Zernike inversion of the CM pair distribution functions $g(r)$ of $L = 500$ self-avoiding walk polymer coils. (taken from Ref. [32])
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Figure 5. Explicit simulations of Eq. (19) show that the three-body interaction \( w^{(3)}(r_i, r_j, r_k) \) is the dominant cause of the density dependence of \( v_g^{eff}(r; \rho) = w^{(2)}(r) + \delta v_g(r; \rho) \) at lower densities. (taken from ref. [32])

Since \( v_g^{eff}(r; \rho) \) was explicitly constructed to reproduce the correct pair correlations, it follows that the true thermodynamics of the full many-body system should be reproduced by using this potential in the compressibility equation (1). The results shown in Fig. (6) confirm this: full polymer simulations of the EOS \( Z \) for \( L = 500 \) and \( L = 2000 \) self avoiding walk polymers on a cubic lattice compare well with the EOS \( Z_\text{c} \) calculated with the appropriate \( v_g^{eff}(r; \rho) \). The small residual differences at large \( \rho \) are most likely due to numerical difficulties in performing accurate inversions at these high densities [35].

We now have a concrete example where the explicit construction of \( v_g^{eff}(r; \rho) \) leads to the full thermodynamics of a many-body system within a purely pairwise description. But what happens when this density dependent pair potential is used within the virial equation (2)? Fig. 6 shows that the virial equation without the explicit density derivative is accurately approximated by the mean-field form \( Z_\text{vir}^0 \approx Z_{\text{MF}} = 1 + \rho \hat{v}(k = 0; \rho) \). Just as was found for positive \( \epsilon_1 \) in section 2, \( Z_\text{vir}^0 \) overestimates the true \( Z \), and adding the density-dependent correction (not shown) results in a significantly larger overestimate.

These results provide a partial explanation for the thermodynamic inconsistencies found in section 2. If \( v(r; \rho) \) is equivalent to \( v_g^{eff}(r; \rho) \) then only the compressibility equation has an unambiguous physical interpretation. On the other hand, one can also follow a route similar to that used to derive \( v_g^{eff}(r; \rho) \) to obtain a \( v_\text{vir}^{eff}(r; \rho) \) which will reproduce the true pressure of an underlying many-body system through the virial equation [24, 26, 36]. This potential will not equal \( v_g^{eff}(r; \rho) \), and so won’t generate the correct pair correlations needed in Eqs. (2) or (3). For an underlying many-body system, no single pairwise density dependent pair potential \( v(r; \rho) \) exists which can, through either the full density dependent [2] or the density-independent [3] forms of the virial equation, yield the true thermodynamics.

Nevertheless, Fig. 6 shows that the relative overestimate found using \( v_g^{eff}(r; \rho) \) in the virial expression is less than the relative underestimate found when all many-body terms are ignored by only taking \( w^{(2)}(r) \) into account. Using \( v_g^{eff}(r; \rho) \) in the
Beware of density dependent pair potentials

Figure 6. Equation of state of a polymer solution calculated in several ways: Circular symbols are for direct simulations self avoiding walk polymers; the two $Z_c$ follow from Eq. (1); within the statistical errors of the method, they agree with the direct simulations of the full polymer system. $Z_{\text{vir}}^0$ was calculated by computer simulations with $v_{\text{eff}}(r; \rho)$, and agrees well with the simpler $Z_{MF}$. In contrast to $Z_c$, this is not a good estimate for the true EOS. Finally, when $Z_{MF}$ is calculated without any density dependence of the pair potential, i.e. with $w^{(2)}(r)$ only, it strongly underestimates the EOS.

simple virial expression \[Z_c \approx (\alpha/2)\rho^{3.3}\] is therefore a better approximation than either ignoring density dependence all together (as with $w^{(2)}(r)$), or using the full density dependent form \[Z_c \approx (\alpha/2)\rho^{3.3}\] of the virial equation. In fact for the dilute regime, $\rho/\rho^* \leq 1$, where the polymers as soft colloids coarse-graining technique is most useful, the absolute differences between the virial and compressibility routes to the EOS are quite small. Differences in the structure generated by the two effective potentials are also rather small. On the other hand, for the semi-dilute regime ($\rho/\rho^* > 1$), the polymer EOS scales as $Z \propto \rho^{1/(3\nu - 1)} \approx \rho^{1.3}$, where the Flory exponent $\nu \approx 0.59$. At these higher densities the RPA approximation is excellent, which suggests that the dominant density dependence of the FT of $v_{\text{eff}}(r; \rho)$ scales as $v_{\text{eff}}(0; \rho) \sim \alpha \rho^{1.3}$, with $\alpha$ a density independent constant. This implies that $Z_c \sim (\alpha/2.3)\rho^{1.3}$, while $Z_{\text{vir}}^0 \approx Z_{MF} \sim (\alpha/2)\rho^{1.3}$. Using $v_{g}^{eff}(r; \rho)$ in the virial equation at high densities results in the correct scaling exponent, but a prefactor which is about 15% too high. In contrast, ignoring the many-body terms altogether by using only $w^{(2)}(r)$ in either the virial or the compressibility equations, results in $Z \sim \rho$, which scales with the wrong exponent.

3.3. Lessons for coarse-graining many-body systems

The two previous subsections have shown that there is no unique way to represent the effects of many-body interactions in effective pair interactions. This has important implications for several techniques to derive such effective pair potentials. For example, if an ab-Initio or other higher level approach is used to generate the structure of a many-body system, then the effective pair potential that reproduces this structure will
not be the same as the pair potential that correctly describes the internal energy. When the many-body interactions are weak, these differences may not be that important, but when they are strong, they may be significant. However, as seen for the polymers as soft colloids approach, using \( v^{\text{eff}}(r; \rho) \) in the virial equation is still a better approximation than completely neglecting all many-body interactions. One might hope that the same is true for methods that derive effective pair potentials from internal energies or from structure.

In general, the stronger the many-body interactions, the more likely that extra care must be exercised when applying an effective pair potential derived by one route (i.e. structure) to extract other physical quantities (i.e. energy). This has implications for work done on systems with strong angular forces like water, where rather complicated effective pair-potentials have be constructed to mimic certain properties\[37\].

A more physically motivated way to average over many-body interactions may be to derive effective pair interactions with a local density dependence, since when the local instantaneous density of a liquid is higher than the global average, one expects the relative strength of the many-body interactions to be more important there, and vice versa for lower local densities. In fact, for a number of systems, one can show explicitly that a local density dependence is equivalent to many-body interactions\[33, 38\] (the same can be done for internal degrees of freedom\[38\]). Although this doesn’t imply that any many-body interaction can be consistently mapped onto a local density dependence, for those cases where it can be done, a completely self-consistent thermodynamics should exist based on these effective potentials.

Another obvious problem with a global density dependence arises when one tries to treat inhomogeneous systems. Even for Argon, the LJ pair potential generates a surface tension that differs by up to to 19% compared to calculations that include explicit three-body effects\[42\]. Again, a local density dependence would appear the more natural way to coarse-grain. Of course this opens up new problems, such as how exactly does one define the local density etc. . .

4. Example 2: effective one-component Hamiltonians for two-component systems

Effective state dependent potentials naturally arise from tracing out one component in a two-component mixture. For uncharged systems such procedures were first carefully formulated by McMillan and Mayer in their famous theory of solutions\[13\]. As they, and many other authors have stressed (see e.g. \[25, 43, 44\]), this works most naturally in an ensemble where the component to be traced out is treated grand-canonically. For charged systems this is no longer the case; instead, charge-neutrality makes the canonical ensemble the natural choice.

As the following pedagogical examples will illustrate, whereas tracing out procedures for uncharged systems are quite well understood, for charged systems the waters are still muddied.

\[\text{¶} \text{An interesting recent example for an NVT simulation can be found in }[40]. \text{ However, the original effective potential studied was of the } v^{\text{eff}}(r; \rho) \text{ form }[1], \text{ while in }[41] \text{ it is used in a virial equation like Eq. }[4]. \text{ The lack of thermodynamic self-consistency found by these authors stems in part from their use of a density dependent interaction without a careful analysis of its origin.} \]
4.1. Asakura Oosawa and related models

A popular model for polymer-colloid mixtures consists of treating the colloids as simple hard spheres (HS) of radius $R_c$ and the polymers as penetrable sphere (PS) whose interaction with the colloids is HS like, with a cross diameter $\sigma_{cp}$ of order $R_c + R_g$, but whose interaction with other the polymers is ideal gas like [14]. Here I introduce a very simple and exactly solvable lattice version of this Asakura Oosawa (AO) model, described in Fig. 7.

In the grand canonical ensemble the partition function for the mixture becomes

$$\Xi_{mix}(\mu_b, \mu_s, N) = \sum_{\{n_i\}} \sum_{\{m_i\}} \exp\left( \mu_b \sum_i n_i + \mu_s \sum_i m_i \right)$$

(23)

where $\mu_i$ denotes the chemical potential of each species, and the sums are over all possible configurations $\{n_i\}$ and $\{m_i\}$ of the big ("colloidal") and small ("polymeric") particles respectively. Since the model is athermal, one can set $\beta = 1$; in addition, the de Broglie wavelength is set to $\Lambda = 1$ which simplifies notation throughout this section.

For a given configuration of the big particles $\{n_i\}$, there will be $M(\{n_i\})$ links left for the small particles. Their partition function can then be calculated

$$\Xi_{small}(\{n_i\}) = \sum_{l=0}^{M} \frac{M! z_s^l}{l!} = \exp[z_s M(\{n_i\})]$$

(24)

where the fugacity $z_s = \exp[\beta \mu_s]$. For a fixed configuration $\{n_i\}$ of big particles, the
number of free links is:

$$M(\{n_i\}) = 2N - 4 \sum_i n_i + \sum_{<i,j>} n_i n_j$$  \hspace{1cm} (25)$$
since there are two links for each site, each big particle excludes 4 links, but when

two big particles touch, they only exclude 7 links, because one is doubly excluded, as

illustrated by the crosses in Fig. 7. This increase in the effective volume available (and concomitant entropy) for the small particles when two big ones touch is the origin of the osmotic depletion effect\[14]. A large enough fugacity of the small particles can induce an entropy driven phase-separation of the big particles.

With the explicit form (25) for the available “free volume” $M(\{n_i\})$, the full

partition function (23) simplifies to

$$\Xi_{mix}(\mu_b, \mu_s, N) = \exp \left[2z_sN \sum_{\{n_i\}} \exp \left[(\beta \mu_b - 4z_s) \sum_i n_i + z_s \sum_{<i,j>} n_i n_j \right]\right].$$ \hspace{1cm} (26)$$

This illustrates the essence of the McMillan-Mayer tracing out procedure: the sums

over states in the partition function of the original two-component system are rewritten

as a single sum over the states of an effective one-component system. There is no need

to invoke any Born-Oppenheimer type time-scale separation arguments; the procedure

might even be viewed as simply a mathematical trick. One could just as well trace

out the big particles. But the particular advantage of tracing out the small particles is

that the effective one-component system is simpler to treat, since it can be mapped

onto a binary lattice gas model with an effective chemical potential $\mu_{eff}^b = \mu_b - 4z_s$

and an effective Hamiltonian that, in turn, is decomposable as a pairwise sum over

nearest neighbours with an interaction strength $\beta \epsilon_{eff} = -z_s$. By mapping onto an

Ising spin system in 2-D, this model, with its entropically driven phase-separation transition, can be exactly solved, as shown previously for a closely related model of non-additive hard squares\[45]. Mathematically these models are a special cases of the more general decorated Ising model introduced by Widom\[46].

Keeping both species grand-canonical facilitates the mapping to an Ising model, but it is just as easy to integrate out the small particles in a semi-grand ensemble, i.e.

fixing $N_b, z_s, N$, resulting in an effective partition function of the form:

$$Z_{mix}(N_b, z_s, N) = \exp \left[z_s(2N - 4N_b) \right] \sum_{\{n_i\}'} \exp \left[z_s \sum_{<i,j>} n_i n_j \right].$$ \hspace{1cm} (27)$$

where $\{n_i\}'$ denotes all possible ways of arranging $N_b$ particles on a lattice of $N$ sites. Again, as long as $z_s$ is fixed, $Z_{mix}$ can be interpreted as an effective one-component system, interacting with an effective Hamiltonian of the form

$$\beta H_{eff}(N_b, z_s, N; \{n_i\}) = H_{bb} - z_s 2N + z_s 4N_b - z_s \sum_{<i,j>} n_i n_j \hspace{1cm} (28)$$

with a configuration independent “volume term”, and a pairwise decomposable pair interaction. $H_{bb}$ is the bare hard-core big-big interaction. All the standard statistical mechanics for such one-component systems can now be brought to bear to calculate correlations and phase-behaviour. The volume term contributes to thermodynamic quantities, but not to the phase-behaviour[44, 1].
The tracing out procedure can also be done in the canonical ensemble, keeping both \( N_b \) and \( N_s \) fixed:

\[
Z_{mix}(N_b, N_s, N) = \sum_{\{n_i\}'} (M(\{n_i\}))^{N_s} = \sum_{\{n_i\}'} \exp \left[ N_s \log \left( 2N - 4N_b + \sum_{<ij>} n_i n_j \right) \right]
\]

But now the effective one-component system is no longer equivalent to a system with a pair-decomposable effective Hamiltonian; at best it can be rewritten as:

\[
H^{\text{eff}}(N_b, N_s, N; \{n_i\}) = H_{bb} - N_s \log [2N - 4N_b] - N_s \log \left[ 1 + \frac{1}{2N - 4N_b} \sum_{ij} n_i n_j \right]
\]

In the limit of only two big particles the logarithms can be expanded and pair term in the Hamiltonian reduces to the same form as found in the same limit for the grand-canonical tracing out procedure. But for a larger number of big particles this ceases to be true; the Hamiltonian can no longer be written as a sum over independent many-body interactions of the form of Eqs. (13) or (21). The effect on \( H^{\text{eff}}(N_b, N_s, N; \{n_i\}) \) of changing the number of pairs in a configuration \( \{n_i\} \) by one depends on the configuration of all other pairs in the system. The McMillan-Mayer mathematical tracing out procedure does not lead to such a useful simplification in the canonical ensemble as it does in the semi-grand ensemble.

Similar manipulations can be performed for off-lattice two-component systems such as the original AO model\cite{14}. Integrating out the \( N_p \) PS polymeric particles for a fixed configuration \( \{r_i\} \) of \( N_c \) colloidal HS results in effective Hamiltonians of the form:

\[
H^{\text{eff}}(N_c, z_p, V; \{r_i\}) = H_{cc} + \Omega(N_c, z_p, V; \{r_i\}) \quad (31)
\]

\[
H^{\text{eff}}(N_c, N_p, V; \{r_i\}) = H_{cc} + F(N_c, N_p, V; \{r_i\}) \quad (32)
\]

for the semi grand and canonical ensembles respectively. \( H_{cc} \) is the bare colloid Hamiltonian. \( \Omega(N_c, z_p, V; \{r_i\}) \) is the grand-potential and \( F(N_c, N_p, V; \{r_i\}) \) is the Helmholtz free energy of an inhomogeneous system of PS particles in the external field of the colloids. The free energy form of these effective Hamiltonians holds for a general two-component system\cite{4}. Integrating over all possible configurations \( \{r_i\} \) of the colloidal particles leads to the full two-component partition function. For the AO model these Hamiltonians take a particularly simple form since

\[
\Omega(N_c, z_p, V; \{r_i\}) = -z_p V^{\text{free}}(N_c, V; \{r_i\}) \quad (33)
\]

is the grand potential of an ideal gas at in the accessible free volume \( V^{\text{free}}(N_c, V; \{r_i\}) \) and similarly

\[
F(N_c, N_p, V; \{r_i\}) = N_p \log [N_p] - N_p - N_p \log [V^{\text{free}}(N_c, V; \{r_i\})] . \quad (34)
\]

is the Helmholtz free energy of an ideal gas of \( N_p \) particles in the accessible free volume.

The calculation of \( V^{\text{free}}(N_c, V; \{r_i\}) \), the direct analogue of \( M(\{n_i\}) \) in the AO lattice models, simplifies dramatically if the size-ratio \( R_p/R_c \leq 0.1547 \). There are then no triplet or higher order overlaps of the exclusion zones, and the accessible free volume can be written as

\[
V^{\text{free}}(N_c, V; \{r_i\}) = V - N_c V_1 + \sum_{i<j} V_2(r_{ij}) \quad (35)
\]
where \( V_1 = \frac{2}{3} \pi (\sigma_{cp})^3 \) is the volume excluded by each colloidal particle, and \( V_2(r) \) has the standard AO form \([14]\), depending only on the relative separation \( r \) of two particles. (Note the correspondence with Eq. (24) for the lattice model, where \( V = 2N, V_1 = 4 \) and the sum over \( V_2(r) \) is replaced by a nearest neighbour lattice sum). The effective Hamiltonians of Eqs. (31) and (32) simplify to

\[
H^\text{eff}(N_c, z_p, V; \{r_i\}) = H_{cc} - z_p V + z_p N_c V_1 - z_p \sum_{i<j} V_2(r)
\]

(36)

\[
H^\text{eff}(N_c, N_p, V; \{r_i\}) = H_{cc} + N_p \log \left( \frac{N_p}{V - N_c V_1} \right) - N_p
- N_p \log \left[ 1 + \frac{1}{V - N_c V_1} \sum_{i<j} z_p V_2(r) \right].
\]

(37)

Just as was found for the lattice model, the canonical tracing out procedure leads to a Hamiltonian that cannot be written as a sum over independent interactions of the form of Eqs. (13) or (21), and the standard AO form \([14]\), depending only on the relative separation \( r \) and the sum over \( \rho_c \) of two particles. For larger size-ratios, the mapping results in three-body and higher order interactions, leading to similar problems to those discussed in section \([14]\) when one tries to derive an effective pair potential. Also, interactions between the small particles will lead to effective three-body and higher terms.

† For larger size-ratios, the mapping results in three-body and higher order interactions, leading to similar problems to those discussed in section \([14]\) when one tries to derive an effective pair potential.

‡ The small differences between the volume terms in the lattice and off-lattice versions of the AO model stem from kinetic energy terms that are ignored in the former case.
Now suppose one were working in the canonical ensemble, and naively used the Asakura-Oosawa depletion potential \( v^{eff}_p(r; \rho_p) \), as has sometimes been done in the literature. Then \( z_p = z_p(\rho_c, \rho_p) \) would no longer be an external parameter but would instead depend on the state of the system. For example, for small size-ratios a good approximation is \( z_p \approx \rho_p/(1 - \rho_c V_1) \). One might be tempted to define an effective one-component thermodynamics by fixing \( \rho_p \), and treating it as an external parameter, as might be natural in an experiment. The potential then takes on the \( \rho_c \) dependent form \( v^{eff}_p(r; \rho_c; \rho_p) \). If this potential is taken as given, without enquiring as to its origins, as was done in section 3, then the compressibility and virial equations take forms similar to Eqs. (1) and (2) respectively, since \( v^{eff}_p \) depends on \( \rho_c \). One might expect that the ensuing thermodynamics would again be that of the osmotic system, but now neither the derived virial nor the derived compressibility equation is correct.

For the present case of a fixed \( \rho_p \), the compressibility equation (1) using \( v_p(r; \rho_p, \rho_c) \) does not result in the correct osmotic pressure because \( z_p \) varies when \( \rho_c \) is changed. On the other hand, using \( v^{eff}_p(r; \rho_c; \rho_p) \) in the simpler virial equation (39), i.e. one without a density derivative, does generate the correct osmotic EOS, as follows from the following arguments: The thermodynamic properties are independent of ensemble, so, for a given state point \((N_c, N_p, V)\), the osmotic pressure is the same as in the semi-grand ensemble at a state point \((N_c, z_p, N)\) such that \( N_p > z_p N_c V = N_p \). There the potential \( v^{eff}_p(r; \rho_p, \rho_c) = v^{eff}_p(r; z_p) \) generates the correct pair correlations \( g_{cc}(r) \), and also the correct virial pressure \( \Pi(N_c, N_p, V) \) through Eq. (39). But the apparent relevance of this osmotic virial equation within the canonical ensemble is deceptive – it only follows because it can be derived in the semi-grand ensemble, and used at a state point where \( v^{eff}_p(r; \rho_c, \rho_p) = v^{eff}_p(r; z_p) \).

Of course the lack of consistency between virial and compressibility routes should not be surprising, since a careful tracing out procedure demonstrates that the effective Hamiltonian \( (27) \) for the canonical ensemble cannot be decomposed into a sum over independent pair potentials. Therefore, using the Asakura-Oosawa pair potential in this ensemble is not rigorously justified, except for instances where parallels with the semi-grand ensemble can be made\( \uparrow \).

In summary then: for a fixed \( z_p \), a completely self-consistent one-component thermodynamics can be derived in the semi-grand ensemble for an AO system. But within the canonical ensemble, a McMillan-Mayer style tracing out procedure leads to an effective Hamiltonian that cannot easily be written as a sum over pair and higher order interaction terms; the ensuing one-component system does not have a simple interpretation as an effective liquid. Moreover, if the AO depletion potential is naively applied in the canonical ensemble for fixed \( \rho_p \), then the density-dependence of the pair potential again leads to an apparent lack of consistency between different routes to osmotic thermodynamics. In contrast to the case studied in section 3, where the effective density dependent potential \( v^{eff}_p(r; \rho) \) that arises from tracing out three-body interactions generates the correct thermodynamics only through the compressibility equation, here only the virial equation (39) should be used.

\( \uparrow \) At this point I should point out that in the limit \( N_c = 2 \), both the canonical and the grand-canonical ensembles do result in the same pair potential, as can be seen by expanding the log in Eq. (14). A similar conclusion holds for higher order interactions, should they be relevant. However, I stress that great care must be used when these low density effective interactions are applied at finite colloid densities in the canonical ensemble.
4.2. Debye–Hückel model

The effective interactions and resulting phase-behaviour of charge-stabilised colloidal suspensions have been the subject of much recent debate\[48, 8\]. In contrast to uncharged mixtures, global charge-neutrality implies that the canonical ensemble is the natural choice in which to integrate out the co and counter ions, to arrive at an effective one-component colloidal picture. And this explains in part why the problem is so difficult, since, as was shown in the previous subsection, tracing out one component in the canonical ensemble does not necessarily lead to an obvious description in terms of independent (many-body) interactions. In addition, direct computer simulations of the full mixture are greatly complicated by the long-range nature of the Coulomb interactions and the large length scale differences between a typical colloidal particle, and the co- and counter-ions.

Rather than attempting yet another tracing out procedure, this section has a much more modest goal, namely to illustrate pitfalls that arise from a naive application of a very simple textbook density dependent potential of the Debye–Hückel screened Yukawa form

\[
\beta v_{DH}(r; \rho) = \frac{Z^2}{r} \exp \left[ -\kappa(\rho) r \right].
\]  

(40)

Here \( Z \) is the charge of the colloidal particle, and \( \kappa(\rho) = \sqrt{\frac{4\pi Z \rho}{\epsilon}} \) is the screening parameter in the absence of salt. The Bjerrum length \( \lambda_B = \beta e^2 / \epsilon \), with \( e \) the elemental charge and \( \epsilon \) the dielectric constant, has been set to 1, to simplify the notation. Since \( \kappa \) depends on the overall density (through charge neutrality), it should come as no surprise that a simple application of the compressibility equation (1) and the virial equation (2) do not generate the same thermodynamics. Since Eq. (40) is an integrable potential,

\[
\beta \hat{v}(k = 0; \rho) = \frac{4\pi Z^2}{\kappa^2} = \frac{Z}{\rho},
\]  

(41)

its thermodynamic behaviour resembles that of a mean field fluid\[10\] for large \( \rho \) or small effective \( Z \), where the RPA closure should be quite accurate. Thus the two routes lead to:

\[
Z^{RPA}_c = 1 + Z,
\]  

(42)

which can be interpreted as the ideal EOS of the colloids and \( Z \) counterions, and

\[
Z^{vir} = (1 + \frac{1}{2} Z) - \frac{2}{3} \beta \pi \rho \int r^2 \left[ h(r)(\frac{\partial v_{DH}(r)}{\partial r}) - g(r)3\rho \frac{\partial v_{DH}(r)}{\partial \rho} \right].
\]  

(43)

Even the leading term in the virial equation differs from the compressibility equation. Since both the \( r \) and \( \rho \) derivatives of \( v_{DH}(r; \rho) \) are always negative, the second two terms of \( Z^{vir} \) both reduce its value w.r.t. the leading \( Z^{MF} = (1+\frac{1}{2}Z) \) term\[10\], increasing the difference between the two routes even further. The present discrepancy originates not in the lack of consistency of the closure, but rather in the naive application of a density dependent pair potential. A more careful analysis of the underlying two-component colloid + counterion system shows that volume terms must also be taken into account\[48\], but these don’t bring the two routes any closer together. The only

\[\parallel\] At least in the regime where the RPA is a reasonable approximation. Note that the virial equation can be exactly solved in the RPA approximation\[22\].
way to know which (if any) of the two routes is the more reliable would be to derive them from a careful analysis of the full tracing out procedure.

The arguments above may have repercussions for the modelling of liquid metals by effective density-dependent pair potentials. There, the Ascarelli-Harrison form of the virial equation (4) has often been applied, but as other examples in this paper show, it is not yet clear whether this equation is reliable. In fact, a recent careful derivation of an effective one-component virial equation within within a two-component electron ion picture by Chihara et al. [49] does not include an explicit density derivative.

Finally, it appears that effective potentials in charged systems will always be density dependent due to charge-neutrality. But this same charge neutrality implies that a two component system can be viewed effectively as a one-component one. For example, all the partial structure factors have the same \( k \to 0 \) limit, up to trivial prefactors, i.e. they are not independent. The density dependence in charged systems most likely has a different character from that found in uncharged systems.

5. Conclusions

The overall conclusion of this paper is simply that

- **an effective density dependent pair potential** \( v(r; \rho) \) **cannot be properly interpreted without reference to the coarse-graining procedure by which it was derived.**

This was shown by a number of explicit examples. The only systems where an effective pair potential could be rigorously interpreted as part of an effective Hamiltonian were the AO model for \( R_g/R_c \leq 0.1547 \) and its lattice analogue. Other potentials like \( v_{\text{eff}}^s(r; \rho) \) cannot be formally interpreted as part of an effective Hamiltonian. Instead, they should be viewed as mathematical devices to calculate desired properties from a particular equation [23, 24, 25, 26].

Some of the more detailed points are repeated below:

- A pair potential that depends on global density, \( v(r; \rho) \), does not lead to the same thermodynamics in the canonical and grand-canonical ensembles.
- The status of the Ascarelli-Harrison [16] form of the virial equation (4), with an added \( \partial v(r; \rho) \partial \rho \) term, is suspect. For uncharged systems and many-body systems, counter examples where it does not apply and even makes thermodynamic inconsistencies worse, can easily be constructed. Whether it is valid for liquid metals or other charged systems remains to be proved.
- There is no unique way to represent the effect of many-body interactions as density dependent pair interactions [23, 24, 25, 26]. The potential that correctly reproduces the structure, \( v_{\text{eff}}^s(r; \rho) \), will not generate the right internal energy when used in the energy equation etc... At best, one can pick a \( v_{\text{eff}}^s(r; \rho) \) that performs well for the particular physical properties one is interested in. For example, the parameters commonly used in the LJ potential to model Argon can be viewed as a compromise between those that correctly reproduce the energy, the virial pressure, and the structure [24].

\footnote{One example where Eq. (4) appears to be better than forms without the density derivative can be inferred from the discussion of the Debye-Hückel model by Belloni [8]. By adding the explicit volume term to his application of the Debye-Hückel potential in Eq. (4), the virial pressure closely resembles an approximate form derived from a two-component picture.}
Beware of density dependent pair potentials

- The previous statement implies a link between problems with the *transferability* of an effective pair potential, and problems with its *representability*. For example, if many-body interactions generate a large relative density dependence in $v^{eff}(r; \rho)$, then the potential derived by a given route at $\rho_1$ will differ significantly from the one derived at $\rho_2$ (transferability problems). This large density dependence also implies important differences between $v_{U}^{eff}(r; \rho)$ and $v_{g}^{eff}(r; \rho)$ (representability problems).

- A McMillan-Mayer type tracing out procedure for a two-component system in the canonical ensemble does not lead to an effective one-component Hamiltonian that be written as a sum of independent interactions.

- The Debye-Hückel potential, like all such density dependent pair potentials, leads to thermodynamic inconsistencies when it is naively used in an effective one-component picture. At present it is not yet clear what the correct route to thermodynamics is.

- Obvious problems arise when potentials like $v(r; \rho)$ are used in inhomogeneous systems. There it would make more sense to coarse-grain to potentials that depend on a measure of the local density. In some cases, this can be shown to be equivalent to a many-body interaction approach.

I finish with the question: when do these results matter? The picture is not as bleak as I might have painted it in the discussions above. Indeed, in the case of Argon, the differences between $v_{g}^{eff}(r; \rho)$, and $v_{U}^{eff}(r; \rho)$ are not so large, so that a single compromise effective pair potentials works admirably well for the liquid phase. In addition, many examples can be found for soft-matter systems where ignoring the many-body forces altogether, – simply using $w^{(2)}(r)$ in the expansion of an $H^{eff}$ – works quite well. This is true for many systems described by depletion potentials,[50, 51] or for the effective interactions derived for star-polymer[52] or dendrimers.[53]. And in other cases, such as the polymers as soft colloids example of section 3, using $v_{g}^{eff}(r; \rho)$ in the simple virial equation may still be a better approximation than ignoring many-body effects altogether. Nevertheless, the particular coarse-graining procedure used to derive $v^{eff}(r; \rho)$ must always be kept in mind – the naive consumer of effective pair potentials should beware.

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An effective potential $v_{eff}^{vir}(r;\rho)$ can be defined that generates the same pressure as the full three-body virial equation when used in the standard two-body virial equation without a density dependent contribution (see e.g.\cite{26} for an example, where $\delta v^{vir}(r;\rho) = 3\delta v^{U}(r;\rho)$). But since this effective potential is density dependent, one might also use the density dependent form of the virial equation, which would generate a different effective potential.

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