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2003 J. Phys.: Condens. Matter 15 S3467

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A manifesto for one-body terms: the simplest of all many-body interactions?

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Received 16 July 2003

Published 20 November 2003

Online at stacks.iop.org/JPhysCM/15/S3467

Abstract

It is argued that a particularly simple kind of many-body interaction can be developed by making the one-body or self-energy terms in the potential depend on a local environmental factor, such as the local density, in some way. Two examples of this are considered: a toy model for macroion suspensions, and an extension to the dissipative particle dynamics simulation method.

1. Introduction

Much work has been done on pair potentials which have an additional dependence on the local environment (e.g. on density) and can therefore be said to be many body in nature. An example is the use of screened Coulomb interactions for macroion suspensions, where the screening length depends on the ionic strength [1]. But possibly the simplest of all many-body interactions can be set up with the one-body or self-energy terms, normally treated as ignorable constants. Here I demonstrate this by considering two examples: a toy model density-functional theory (DFT) for macroion colloidal suspensions [2], and an extension to the dissipative particle dynamics (DPD) simulation method to allow for vapour–liquid equilibrium in a soft sphere fluid [3–5].

It is first useful to make some general comments. Consider a one-component system of N particles in a volume V with an arbitrary potential energy $U\{\mathbf{r}_i\}$, where \mathbf{r}_i labels the particle positions, and $i = 1, \dots, N$ labels the particles. Such a system may be isolated, or may be embedded in a solvent in which case U is the McMillan–Mayer potential energy depending on chemical potentials of solvent species [6, 7]. One can always expand this as

$$U\{\mathbf{r}_i\} = NU_1 + \sum_{i<j} U_2(r_{ij}) + \dots \quad (1)$$

where U_1 is the one-body term or self-energy per particle, U_2 is the pair potential (which I assume only depends on the magnitude of the separation, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$), and so on, by the following procedure. First consider an isolated particle. Since $U\{\mathbf{r}_i\}$ is completely generic, $U_1 = U\{\mathbf{r}_i\}$ for $N = 1$. Next consider an isolated pair of particles for which $U_2 = U\{\mathbf{r}_i\} - 2U_1$. Then consider isolated triplets, etc. By the very nature of this construction, U_1 , U_2 , etc do

not contain any density dependence. The one-body term is therefore a constant which can be thrown away (in McMillan–Mayer theory it may depend on the chemical potentials of the solvent species but these remain constant across coexisting phases).

Now introduce a density dependence in the terms in this expansion:

$$U\{\mathbf{r}_i\} = NU_1(\rho) + \sum_{i<j} U_2(\mathbf{r}_{ij}; \rho) + \dots \quad (2)$$

where $\rho = N/V$. Density-dependent pair potentials have been considered by a number of authors, but here I wish to focus on the density-dependent one-body term. This is no longer constant and cannot be thrown away since it has an arbitrary effect on the properties (since $NU_1 = V\rho U_1$ is proportional to the system volume, this term can also be called a volume term). One should recognize though that the ad hoc introduction of a density dependence in the terms in equation (1) is an arbitrary procedure not based on a formal expansion of $U\{\mathbf{r}_i\}$. One consequence of this is that great care must be taken to specify the nature of the density dependence in equation (2), as has been emphasized by Louis [8]. Here I assume that the dependence is on a *local density*, defined to be a measure of the number concentration of particles in the vicinity of the point of interest. Thus

$$\rho \rightarrow \rho_{\text{local}}(\mathbf{r}_i) = \sum_j w(\mathbf{r}_{ij}) \quad (3)$$

where $w(r)$ is a weighting function usually normalized to $\int d^3r w(r) = 1$. In this situation, the local densities that appear in the terms in equation (2) are determined once the positions of all the particles are known and as a consequence $U\{\mathbf{r}_i\}$ itself does *not* contain a density dependence. With this approach, there is no difficulty of interpretation of thermodynamic relations.

The density-dependent one-body term has non-trivial effects on the system properties and it is therefore of interest in considering models in which only this term is present. Specifically one can work with a local-density-dependent self-energy $u(\rho)$ such that the total potential energy is

$$U\{\mathbf{r}_i\} = \sum_i u_i, \quad u_i = u(\rho_i), \quad \rho_i = \sum_j w(\mathbf{r}_{ij}). \quad (4)$$

This construction is perhaps sufficiently novel that it might deserve a special name; for instance $u_i = u(\rho_i)$ could be termed a ‘mono-potential’.

The discussion above is specific to a one-component fluid, but the concepts generalize in an obvious way to multi-component fluids. I now give two examples where non-trivial behaviour follows purely from density-dependent self-energies.

2. Toy model for macroion suspensions

I consider a suspension of macroions of charge Z and diameter $\sigma = 2a$, in a supporting 1:1 electrolyte solution. This system, and its relevance to charge-stabilized colloidal suspensions, has attracted much interest recently [9–12]. Here I consider a very simple theory for the thermodynamics of the system, including *only* the self-energy of the macroions in the electrolyte solution. It is sufficiently simple that an obvious DFT can be constructed, but it still possesses interesting properties. A partial analysis of this model was presented a couple of years ago [2], and a more complete analysis is in preparation. The free energy per unit volume is

$$F/V = \rho_M k_B T (\log \rho_M - 1) + \rho_s k_B T (\log \rho_s - 1) + (Z\rho_M + \rho_s) k_B T (\log(Z\rho_M + \rho_s) - 1) + \rho_M u_M. \quad (5)$$

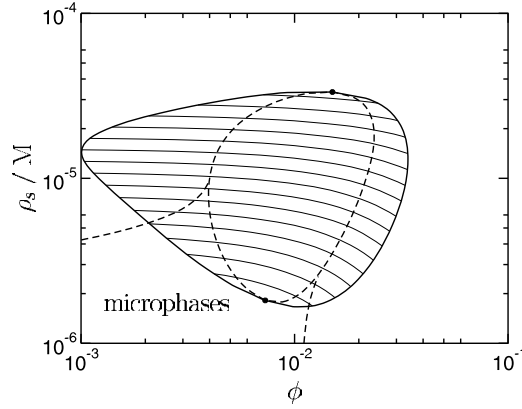


Figure 1. The phase behaviour of toy model free energy equations (5) and (6) for macroion suspensions at $Z = 10^3$ and $\sigma = 100$ nm, as a function of the macroion volume fraction ϕ and added salt concentration ρ_s . The dashed curves represent the boundaries where the macroion structure factor diverges at zero wavevector (interior spinodal curve) or at non-zero wavevector (outer dashed curve) [2]. Marked points are critical points, and tie lines are curved in this double-logarithmic plot.

The only non-ideal contribution arises from the macroion self-energy

$$u_M = \frac{Z^2 l_B k_B T}{2a(1 + \kappa a)}. \quad (6)$$

In equations (5) and (6), l_B is the Bjerrum length, k_B is Boltzmann's constant, T is temperature, and κ is the inverse Debye screening length due to the electrolyte solution. This is found from $\kappa^2 = 8\pi l_B \rho_I$ where $\rho_I = (\rho_+ + \rho_-)/2 = \rho_s + Z\rho_M/2$ is the ionic strength, ρ_{\pm} are the microion densities, ρ_s is the added salt concentration, and ρ_M is the macroion concentration. Interestingly, the self-energy coincides with that of a spherical capacitor, charged to $\pm Z$, with one plate at the macroion surface and the second a distance κ^{-1} away.

This model has a phase transition at low ionic strength which is similar to those of more sophisticated models [13, 14], and a typical phase diagram is shown in figure 1. The physics is that the self-energy causes the macroions to drift towards regions of higher ionic strength, which by charge neutrality are regions where the macroion concentration is already high; hence there is a natural tendency for clustering.

A severe criticism of the model is the linearization approximation used to calculate the self-energy in such a simple form. This means that the model can really only be called a 'toy model' and its relevance to charge-stabilized colloids is called into question. The linearization approximation can be improved, in which case the phase transition may or may not disappear completely [15–17].

The interest here, however, is that a simple DFT can be proposed which greatly advances the understanding of the phenomenology. I write

$$F = k_B T \int d^3 r \sum_{i=+,-,M} \rho_i(\mathbf{r}) \log[\rho_i(\mathbf{r}) - 1] + l_B k_B T \int d^3 r d^3 r' \frac{\rho_Q(\mathbf{r})\rho_Q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r \rho_M(\mathbf{r}) u_M(\mathbf{r}) \quad (7)$$

where the first term is the ideal solution entropy, the second term is a mean-field electrostatic term, and the last term is the macroion self-energy contribution constructed using a local

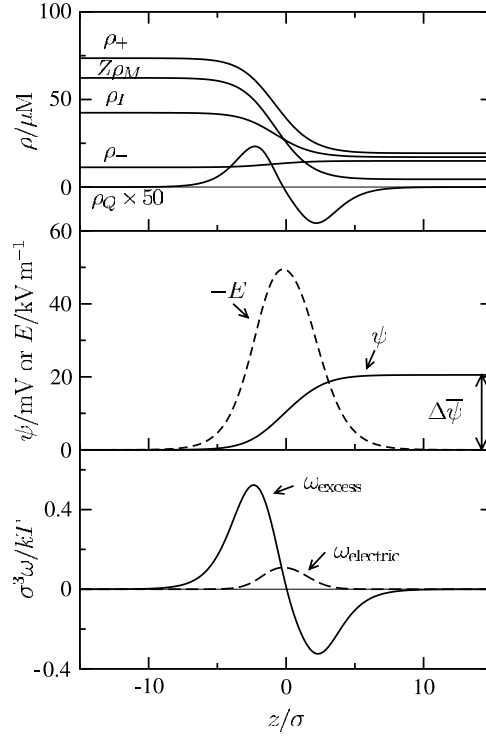


Figure 2. Density profiles for all species (top), the electric field and electrostatic potential (middle), and the excess grand potential together with electrostatic contribution (bottom), for a representative tie line near the upper critical point in figure 1.

ionic strength. In these, $\rho_Q(\mathbf{r}) = Z\rho_M(\mathbf{r}) + \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$ is the space charge density, $u_M(\mathbf{r}) = Z^2 l_B k_B T / 2a(1 + \kappa(\mathbf{r})a)$, a local Debye screening length is defined in terms of a smoothed local ionic strength, $[\kappa(\mathbf{r})]^2 = 8\pi l_B \bar{\rho}_I(\mathbf{r})$ with $\bar{\rho}_I(\mathbf{r}) = \int d^3r' w(|\mathbf{r} - \mathbf{r}'|) \rho_I(\mathbf{r}')$, $w(r)$ is a normalized weight function, and $\rho_I(\mathbf{r}) = [\rho_+(\mathbf{r}) + \rho_-(\mathbf{r})]/2$. It is easily shown that for a homogeneous system, this DFT reduces to the free energy in equations (5) and (6). Some kind of smoothing is essential to make the model well behaved; in this case I have arbitrarily chosen a simple weighting function $w(r) \propto \exp[-\alpha r^2/\sigma^2]$ with results for $\alpha = 1$ presented here.

One can calculate the structure factors predicted by this model rather easily by functional differentiation; this was done earlier [2]. For the simple choice of weighting function, the model makes the intriguing prediction that a peak at non-zero wavevector appears in the macroion structure factor at some state points. As indicated in figure 1, this peak diverges in the vicinity of the lower critical point signalling the appearance of microphase separation. (A knowledge of the actual macroion structure factor could be used to improve the choice of $w(r)$, as in conventional DFT.)

A second use of the DFT is to calculate interfacial profiles and surface tensions between coexisting phases. Since microphases interfere with the lower critical point in the present model, this can only be done in the vicinity of the upper critical point. More details will be presented elsewhere, but a representative example of the ion density profiles is shown in figure 2, together with electric fields and potentials, and the grand potential density. Note the appearance of a potential jump $\Delta\psi$ across the interface: this is the Donnan potential (sometimes

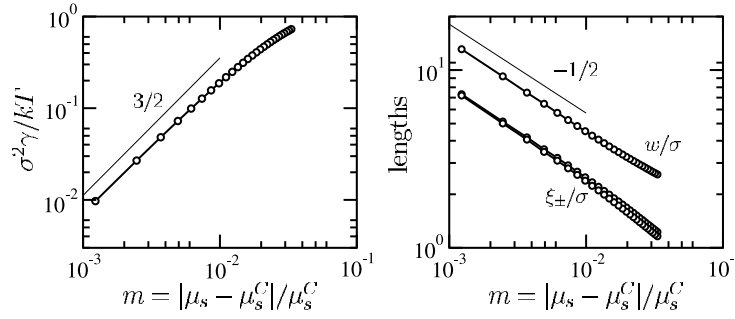


Figure 3. The scaling of the interfacial tension γ (left) and a measure of the interfacial width w and correlation lengths ξ_{\pm} (right), as a function of the scaled distance m from the upper critical point in terms of the added salt chemical potential μ_s .

known as the Galvani potential). The excess grand potential gives the surface tension which is typically of the order of $k_B T / \sigma^2$. The surface tension vanishes as one approaches the upper critical point, with a mean-field exponent, as shown in figure 3. The interfacial width, and correlation lengths determined from the decay of the profiles on either side of the interface, are also shown. They diverge with a mean-field exponent as one approaches the upper critical point.

For the present paper, note again that the only correlation term in the free energy is the self-energy of the macroions. Thus this model falls into the class discussed in the introduction. However, the features seen in this model such as phase separation, microphases, and a rich interfacial structure, are a consequence of the short range nature of the weighting function used to construct the local ionic strength competing with the long range Coulomb law. Thus we see that the nature and range of the weighting function are also important for determining the behaviour of the model. This will become even more apparent in the next example.

3. Many-body dissipative particle dynamics

A second example I shall discuss is a generalization of the DPD simulation method. The DPD method basically addresses a fluid of soft spheres with some kind of thermostat, and has found various applications in simulating complex fluids [18]. In the standard DPD, the soft spheres interact via soft pair potentials, but in the many-body generalization [3, 4], it is apparent that the potential energy is precisely of the form discussed in the introduction. Again more details are presented elsewhere [5]. The approach can be compared with similar work on smoothed particle applied mechanics [19] and smoothed DPD [20].

The ‘mono-potential’, if we wish to call it such, is

$$u_i = A\bar{\rho}_i + B\tilde{\rho}_i^2 \quad (8)$$

where there are *two* measures of the local density,

$$\bar{\rho}_i = \sum_j w(r_{ij}; r_c), \quad \tilde{\rho}_i = \sum_j w(r_{ij}; r_d), \quad (9)$$

constructed from a simple normalized weight function

$$w(r; R) = \frac{15}{2\pi R^3} (1 - r/R)^2 \quad (r < R) \quad (10)$$

with different ranges r_c and r_d . It is usual to take $r_c = 1$ to fix units of length and density, etc. If $r_d < 1$, $A < 0$ and $B > 0$, then the model exhibits phase coexistence between a liquid

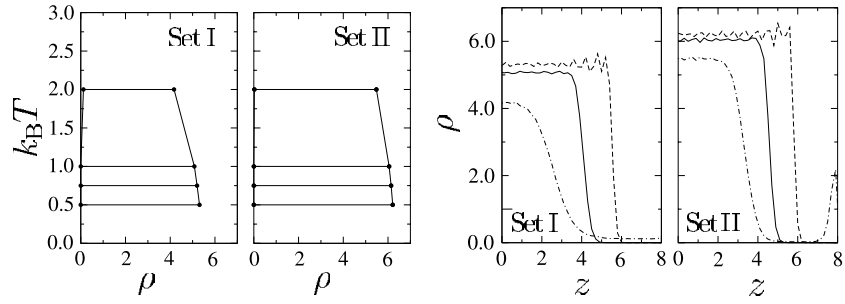


Figure 4. The phase diagram for many-body DPD (left two plots), and interfacial density profiles (right two plots) at $k_B T = 1$ (solid curve), $k_B T = 2$ (chain curve), and $k_B T = 0.5$ (dashed curve). Data for two different parameter sets are shown: $r_c = 1$, $r_d = 3/4$, $A = -4\pi/3$, and $B = 27\pi/64$ (set I) or $B = 135\pi/512$ (set II) [5].

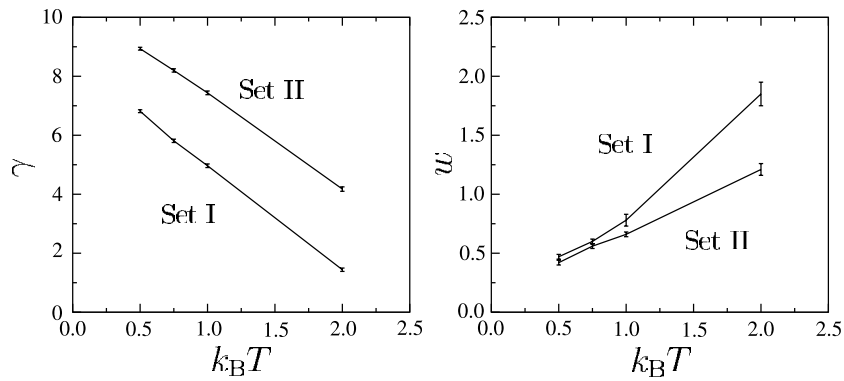


Figure 5. The surface tension γ (left) and a measure of the interface width w (right) for the two many-body DPD parameter sets of figure 4.

at a density $\rho \sim 5$ and a vapour phase of vanishingly small density. On the other hand, if $r_d > 1$, one may see microphase separation, although care has to be taken to make sure that the potential $U\{r_i\}$ is not ‘catastrophic’ the sense of Ruelle [8, 21].

The potential energy $U\{r_i\} = \sum_i u_i$ can be used directly in Monte Carlo simulations, or within the DPD framework via the forces $f_i = -\partial U/\partial r_i$, in which case the model reduces to models previously considered by earlier workers [3, 4]. Note that the correlations imply $\langle \tilde{\rho}_i \rangle \neq \langle \tilde{\rho}_i \rangle \neq \rho$ [4].

Figure 4 shows the phase behaviour and interfacial density profiles for two parameter sets (see [5] for more details), and figure 5 shows the interfacial tensions and a measure of the interfacial width, also determined by these simulations. It is apparent that the many-body or ‘mono-potential’ construct has allowed us to build a liquid out of purely soft interactions, although in this particular case one can expand out the sums in equations (4), (8) and (10) to see that one has (density-independent) soft pair attractions plus soft three-body repulsions.

4. Discussion

The general proposal is to write the potential energy for a set of particles $i = 1, \dots, N$ as $U\{r_i\} = \sum_i u_i$ where u_i is a self-energy or ‘mono-potential’ which depends on the local environment in some way. In the first example, this dependence was on a local ionic

strength, and was used to construct a DFT. The approach is similar to a weighted local-density approximation (WLDA). In the second example, the dependence was on the local density, for a one-component fluid. The potential energy $U\{\mathbf{r}_i\}$ was used as to determine the forces on particles within the DPD framework.

We see that the whole formalism has quite a rich physics, and indeed one can cast density-independent pair potentials into this form by writing $u_i = (1/2) \sum_j U_2(r_{ij})$ (this is not in the form $u_i = u(\rho_i)$ but certainly falls into the general group of an environment-dependent self-energy). Thus the formalism contains the whole of classical pair potential theory for liquids. Moreover, features from the classical theory of liquids persist in the new approach; in particular the range of interaction is replaced by the sampling range for the local environment, and has important consequences for the behaviour. Multiple ranges can be introduced (and may need to be introduced). If there is a phase instability, it can be to bulk phase separation or microphase separation. Finally, care is needed to avoid ‘catastrophic’ potentials in the sense of Ruelle [8, 21]. An interesting open problem is the development of integral equation methods for these many-body fluids.

As a final remark, the focus on pair potentials perhaps derives from the traditions of liquid state theory originating with van der Waals and others. Density-dependent pair potentials and other many-body effects have been found to be necessary in soft condensed matter to describe complex fluids. One is tempted to speculate that density-dependent self-energies offer a simpler way to handle some of these complexities in a unified manner, without compromising the essential physics.

Acknowledgments

I thank Rob Groot for many discussions in the early stages of development of the many-body DPD model. Finally, I would like to dedicate this contribution to the memory of an old friend and mentor, Denver G Hall, who initiated me into the mysteries of charge-stabilized colloidal suspensions several years ago now.

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