Phase behaviour and the random phase approximation for ultrasoft restricted primitive models

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Phase separation of the ultrasoft restricted primitive model (URPM) with Gaussian charges is re-investigated in the random phase approximation (RPA)\textemdash the ‘Level A’ approximation discussed by Nikoubashman, Hansen and Kahl [J. Chem. Phys. 137, 094905 (2012)]. We find that the RPA predicts a region of low temperature vapour-liquid coexistence, with a critical density much lower than that observed in either simulations or more refined approximations (we also remark that the RPA critical point for a related model with Bessel charges can be solved analytically). This observation suggests that the hierarchy of approximations introduced by Nikoubashman et al. should be analogous to those introduced by Fisher and Levin for the restricted primitive model [Phys. Rev. Lett. 71, 3826 (1993)], which makes the inability of these approximations to capture the observed URPM phase behaviour even more worth of investigation.

Recently Coslovich, Hansen and Kahl (CHK) introduced a novel class of Gaussian charge cloud models for mixtures of interpenetrable polycations and polyanions in solution\textsuperscript{[1, 2]}. The low temperature phase behaviour of these models was explored both by Monte-Carlo and molecular dynamics simulations\textsuperscript{[1, 2]}, and in mean field theory by Nikoubashman, Hansen and Kahl (NHK)\textsuperscript{[3, 4]}. Our interest in this class of models stems from a different perspective. In mesoscale models, particularly in dissipative particle dynamics (DPD)\textsuperscript{[4]} soft interactions are the norm. Then it is both natural, and indeed essential, to smear out point charges into charge clouds. The divergence of the long-range Coulomb law as \( r \rightarrow 0 \) (where \( r \) is the center-center separation) is replaced by a smooth cutoff, thus ensuring thermodynamic stability according to a theorem by Fisher and Ruelle\textsuperscript{[5]}. The precise form of the charge smearing is often tuned to the numerical algorithm used to calculate the electrostatic interactions, and a consensus on the best approach has yet to emerge\textsuperscript{[6, 7]}. Whilst for mesoscale modelling applications the low temperature phase behaviour is not in itself of primary importance, the screening properties though are of great interest and our research into this aspect will be reported more thoroughly elsewhere.

The canonical example of this class of models, which CHK termed the ultrasoft restricted primitive model (URPM), is an equimolar mixture of Gaussian charge clouds, which are identical apart from the sign of the charges, and for which only the electrostatic interactions are kept. The URPM is a natural counterpart to the well-studied restricted primitive model (RPM) of equi-sized charged hard spheres\textsuperscript{[3, 10]} in which the short-range Coulombic divergence is hidden behind the hard core repulsion. For the URPM, CHK reported a region of low temperature vapour-liquid phase coexistence, for which the terminus on increasing temperature bears many of the hallmarks of a tricritical point. Above this point, and a likely reason for the apparent tricriticality, is either a weak second order transition or a rapid crossover between an insulating dielectric phase of neutral ‘molecules’ of paired opposite charges and a conducting ‘plasma’ phase containing a substantial fraction of free ions. Subsequently NHK investigated a hierarchy of mean-field approximations in an attempt to understand in detail the origin of the low temperature URPM phase behaviour. This hierarchy was built in analogy to the earlier work of Fisher and Levin on the RPM\textsuperscript{[11, 12]}. The simplest level of approximation, termed ‘Level A’ in NHK, is analogous to the Fisher-Levin DH (Debye-Hückel) approximation. It is identical to the random phase approximation (RPA) from integral equation theory, and incorporates the mutual attractions and repulsions in a linearised way. The next level of approximation, ‘Level B’ in Ref.\textsuperscript{[8]} and DHBj (Debye-Hückel-Bjerrum) in the Fisher-Levin classification, captures the formation of ion pairs—a crucial aspect of the non-linear physics at low temperatures.

NHK assert that “there is no phase separation at [the ‘Level A’] approximation” (below Eq. (30) in Ref.\textsuperscript{[3]})\textsuperscript{.}\textsuperscript{8} This caught our attention, as we have known for some time that the RPA for a related Bessel charge model (discussed below) does exhibit phase separation, with a critical point which can be determined analytically. Prompted by this discrepancy, our own further investigations reveal that the RPA for Gaussian charges does have a region of phase separation, but at a much lower density than investigated by NHK.

To set the problem up, we consider an equimolar mixture of \( N_+ = N_- = N/2 \) charge clouds (polyions) in a volume \( V \), with an overall density \( \rho = N/V \). Gaussian charge clouds interact with the following pair potential,

\[
u_{\pm\pm}(r) = \pm u(r), \quad \beta u(r) = \frac{\epsilon_0}{r} \text{erf}\left(\frac{r}{2\sigma}\right) \tag{1}\]

where \( u(r) \) is the pair potential between charge clouds.
of the same sign, $\beta = 1/k_B T$ is the inverse of the temperature measured in units of Boltzmann’s constant, $k_B$ is the Bjerrum length which plays the role of a coupling constant, $r$ is the separation, and $\sigma$ is a measure of the size of the charge cloud. For Gaussian charges the radial charge distribution corresponding to this potential is $(2\pi \sigma^2)^{-3/2} e^{-r^2/2\sigma^2}$. The function $\text{erf}(r/2\sigma) \sim r$ as $r \to 0$, thus ensuring the Coulombic divergence is replaced by a smooth cutoff.

An interesting alternative to the Gaussian charge URPM is provided by a Bessel charge model. For this case the interaction potential is simply

$$\beta u(r) = \frac{l_B}{r} (1 - e^{-r/\sigma})$$

This corresponds to a radial charge distribution $K_1(r/\sigma)/(2\pi^2 \sigma^2 r)$ where $K_1$ is a modified Bessel function (hence the name). Although this radial charge distribution diverges as $r \to 0$, the interaction potential itself is again smoothly cutoff.

Gaussian charges are blessed by being particularly well suited to the Ewald summation method for handling long range Coulomb interactions, as has been noted by CHK. Bessel charges, on the other hand, are not so well suited for simulations but provide perhaps the simplest non-trivial example of an ultrasoft primitive model when it comes to analytical work. Obviously, the definition of $\sigma$ in the two potentials cannot be exactly matched up and this should be born in mind when making comparisons.

In reciprocal space these potentials are

$$\beta \tilde{u}(k) = \frac{4\pi l_B}{k^2} w(k\sigma)$$

where, writing $q = k\sigma$,

$$w(q) = \begin{cases} e^{-q^2} & \text{(Gaussian)}, \\ 1/(1 + q^2) & \text{(Bessel)}. \end{cases}$$

The definition of $\sigma$ in the two models is chosen to match up the long wavelength behaviour here.

The random phase approximation (RPA) for this class of models takes the form $c_{\pm \pm} = -\beta u_{\pm \pm}$ for the direct correlation functions. Because the absence of hard cores, the RPA is also equivalent to the mean spherical approximation (MSA). From the RPA, the total correlation functions, $h_{\pm \pm}(r) = \pm \tilde{h}(r)$, follow by inversion of the Ornstein-Zernike equations. In reciprocal space the solution is

$$\tilde{h}(k) = \frac{-4\pi l_B w(k\sigma)}{k^2 + k_D^2 w(k\sigma)}.$$  

In this $k_D^2 = 4\pi l_B \rho$ is the square of the Debye wavevector. It follows from Eq. (5) that the density-density structure factor is given by $S_{NN}(k) = 1$ and, somewhat less trivially, the charge-charge structure factor is given by $S_{ZZ}(k) = \frac{k^2}{[k^2 + k_D^2 w(k\sigma)]}$.

In all these we notice the prominent role played by the denominator $D(k) = k^2 + k_D^2 w(k\sigma)$. As is well known the zeros of this function in the complex $k$-plane determine the asymptotic behaviour of the total correlation functions, and are crucial to understanding the screening properties of the system particularly for applications in mesoscale modelling. The asymptotic behaviour typically crosses over from being purely exponential to being damped oscillatory as one increases the density past the so-called Kirkwood line in the density-temperature plane and more generally, this is referred to as a Fisher-Widom line. For Gaussian charges the asymptotic behaviour is determined by the complex roots of $q^2 + q_D^2 e^{-q^2} = 0$, where $q_D = k_D \sigma$. The most relevant roots are given by $q^2_0 = W_0(-q_D^2)$ where $W_0$ is the principal branch of the Lambert $W$ function. From this, or by direct calculations, the Kirkwood line for Gaussian charges is given by $q_0 = e^{-1/2} \approx 0.6065$. The Kirkwood line for Bessel charges is determined by the complex roots of the biquadratic equation $q^4 + q^2 + q_D^2 = 0$. For $q_D \leq \frac{1}{3}$ the roots are all purely imaginary, whereas for $q_D > \frac{1}{3}$ they are all complex. Hence in this case the Kirkwood line takes the simple form $q_0 = \frac{1}{2}$.

Now we turn to the free energy. It follows from the density-density structure factor that the compressibility route equation of state is trivially that of an ideal gas, for which the free energy density is

$$\beta f_{id} = \rho (\ln \frac{1}{2} \rho - 1).$$  

Note there are two species of ions contributing to this, each at a density $\frac{1}{2} \rho$, and we have neglected the thermal de Broglie wavelength as it plays no role in phase coexistence. The virial route equation of state, and the energy route equation of state (via coupling constant integration) give rise to the same result, which can be integrated to a non-trivial excess free energy density. The result is

$$\beta f^{ex} = -\frac{1}{4\pi^2 \sigma^3} \int_0^\infty dq \left[ q^2 \ln \left( 1 + \frac{q_D^2}{q^2} w(q) \right) - q_D^2 w(q) \right].$$

![FIG. 1. RPA free energy for Gaussian URPM at $\sigma \sqrt{\pi/l_B} = \sqrt{\pi}/27 \approx 0.0656$, from Eqs. (6)–(8) with $w(q) = e^{-q^2}$. A function $A\rho$, with $\beta A = 4.03$, is added to the free energy to reveal the common tangent construction without perturbing the phase behaviour.](image)
FIG. 2. (color online) Vapour-liquid coexistence regions (binodals plus critical points) for the URPM with Gaussian or Bessel charges. Approximations are RPA (present work) and RPABj (‘Level B’ in Ref. [3]). Data for RPABj is taken from Fig. 7 of Ref. [3], and the simulation data is taken from Fig. 18 of Ref. [2]. See Table I for locations of critical points.

For point charges \( u(q) = 1 \) and this reduces to the exact DH limiting law \( \beta f^{\text{ex}} = -\kappa^3 / 12\pi \). The total free energy density, used in calculating the phase behaviour, is given by the sum of Eqs. (6) and (7):

\[
f = f^{\text{id}} + f^{\text{ex}}.
\]

In the Gaussian case Eq. (7) is exactly equal to Eq. (29) in Ref. [3]. Figure 1 shows the total free energy, from Eq. (8), as a function of density at a judiciously chosen temperature, illustrating the existence of a common tangent construction. The full phase behaviour is plotted in Fig. 2, marked ‘RPA’, where also are shown the ‘Level B’ results replotted from Ref. [3], here marked ‘RPABj’, and simulation results taken from Ref. [2]. The Gaussian RPA critical point, found numerically, is located at \( \rho^* = 0.085 \). For point charges \( u(q) = 1 \) and the hard sphere diameter for the RPM.

At this point we should comment on the choice of reduced (dimensionless) temperature. CHK and NHK use \( u_0 = u(0) \) as an energy scale but this frustrates direct comparison with the RPM. Our own preference is to use the long range behaviour of the potential characterised by the reduced Bjerrum length \( l_B / \sigma \). Since \( \beta u_0 = l_B / \sigma \sqrt{\pi} \) for Gaussian charges, to facilitate the comparison with CHK and NHK we universally use \( \sigma \sqrt{\pi} / l_B \) as a reduced temperature. In this, \( \sigma \) is the parameter entering the interaction potentials in Eqs. (1) and (2) for the URPM, and the hard sphere diameter for the RPM.

For the Bessel case, the RPA excess free energy can be obtained in closed form. The last term in Eq. (7) evaluates to \( -q_D^3 / (8\pi\sigma^3) = -l_B \rho / (2\sigma) \). On multiplying through by \( \sigma^3 \), the first part of the integral is

\[
I = \frac{1}{4\pi^2} \int_0^\infty dq q^2 \ln \left( 1 + \frac{q^2}{q^2(1+q^2)} \right).
\]

To solve this, we learn from the (Schwinger-)Feynman parameter trick [21] and rewrite it as

\[
I = \frac{1}{4\pi^2} \int_0^\infty dq \int_0^{q_D^2} du \frac{q^2}{q^2(1+q^2) + u}.
\]

Making for the time being the assumption that \( q_D^2 \leq \frac{1}{4} \), so that we are on the low density side of the Kirkwood line, the \( q \)-integral can now be done, by the method of partial fractions, to get

\[
I = \frac{1}{8\pi\sqrt{2}} \int_0^{q_D^2} du \sqrt{1+z} - \sqrt{1-z} z \int
\]

where \( z = \sqrt{1-4u} \) (hence the temporary restriction on \( q_D \)). We note that \( du = -\frac{1}{2}z dz \), so the \( u \)-integral can also be done. After taking careful account of the integration limits, the final result for the free energy is

\[
\sigma^3 \beta f^{\text{ex}} = \frac{2\sqrt{2} - (1+z)^{3/2} - (1-z)^{3/2}}{24\pi\sqrt{2}} - \frac{l_B \rho \sigma^2}{2}
\]

where now \( z = \sqrt{1-4q_D^2} \).Whilst this result has been derived for \( q_D^2 \leq \frac{1}{4} \), it holds by analytic continuation for all \( q_D \). As one crosses the Kirkwood line from low to high density, \( z \) crosses over from being purely real to purely imaginary, so that

\[
z = \begin{cases} 
\sqrt{1-4q_D^2} & (q_D \leq \frac{1}{2}) \\
\frac{1}{\sqrt{4q_D^2-1}} & (q_D > \frac{1}{2})
\end{cases}
\]

Nevertheless the free energy remains purely real and is continuous across the Kirkwood line. (Note that the roots of \( q^4 + q^2 + q_D^2 = 0 \) are given by \( q^2 = -\frac{1}{2} \pm \frac{i}{2}z \).)
Like the Gaussian case, the RPA free energy for the Bessel case has a region of vapour-liquid phase coexistence at low densities and temperatures. The critical point can be found by solving $\partial^2 f / \partial \rho^2 = \partial^3 f / \partial \rho^3 = 0$ from Eqs. (6), (8) and (12). An analytic solution can be obtained, which is $l_B / \sigma = 12\sqrt{3} \approx 20.78$ and $\rho \sigma^3 = 1/(48\pi \sqrt{3}) \approx 3.829 \times 10^{-3}$ (see also Table I). This corresponds to $z = i\sqrt{3}$ and $q_D = 1$, thus for Bessel charges the RPA critical point lies on the high density side of the Kirkwood line. The phase behaviour for the Bessel case, calculated numerically, is also shown in Fig. 2.

Table I compares the vapour-liquid critical points for the RPM and the URPM, using various approximations. We see that the DH approximation for the RPM, and the RPA for the URPM, both predict critical points at low densities and temperatures. When Bjerrum pairing is incorporated (i.e. DHBj for RPM, and RPABj for Gaussian URPM), the critical temperature remains unchanged but the critical density is considerably increased. For the RPM, this brings the predicted critical point quite close to the simulations, within 20% for the critical temperature (for a detailed discussion, see Ref. [11]). For the URPM with Gaussian charges though, the predicted critical point is still considerably distant from the simulations. In particular the predicted critical temperature is at least a factor of three above the observed value. We can to some extent confirm this observation, as we have looked for phase separation in the Gaussian URPM using Monte-Carlo methods, at temperatures in the vicinity of the RPA critical point, and have found no evidence of such. This singular aspect of the phase behaviour of the URPM stands in marked contrast to the RPM. Some possible explanations have been proposed by NHK [3].

The observation that the critical temperature remains unchanged in comparing RPA and RPABj can be traced to the fact that in the latter approximation the Bjerrum pairs are an ideal spectator species [10,12]. As such they cannot, in themselves, influence the phase behaviour of the unpaired ions. The quasi-chemical equilibrium between paired and unpaired ions changes the coexistence densities, in accordance with the law of mass action, but the critical temperature itself remains unaffected.

To summarise, the Fisher-Levin hierarchy of approximations developed for the RPM can be pursued also for the URPM, with similar trends, indicating the two models should show similar phase behaviour. The fact that they do not deepens the mystery uncovered by Nikoubashman, Hansen and Kahl in Ref. [3] and clearly warrants further investigation.

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