

Relevance of the local-density approximation to interfacial properties of ionic fluids within gradient theory

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 L705

(<http://iopscience.iop.org/0953-8984/10/42/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 17:36

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Relevance of the local-density approximation to interfacial properties of ionic fluids within gradient theory

Volker C Weiss and Wolfram Schröder

Institut für Anorganische und Physikalische Chemie der Universität Bremen, D-28359 Bremen, Germany

Received 14 August 1998, in final form 9 September 1998

Abstract. The effect of employing different approximations to the local density on properties of inhomogeneous systems as obtained from a gradient expansion of the local free energy (gradient theory) is investigated. We present liquid–vapour density profiles, surface tensions, correlation lengths, and Ginzburg temperatures for an ionic model fluid, the restricted primitive model (RPM), treated in the framework of Debye–Hückel theory. The dependence of the interfacial properties, density profile and surface tension, on the type of local-density approximation is comparatively weak (at most a factor of four in the surface tension). In contrast, the much more sensitive Ginzburg temperature, which estimates the extent of the critical region, varies over a range of four orders of magnitude depending on which local-density approximation is applied.

In this letter, we investigate the importance of the particular choice of local-density approximation for several quantities of nonuniform fluids that can be obtained from a gradient expansion of the local free energy, i.e. from gradient theory. In principle, the calculation of these properties (density profiles, surface tension etc) calls for correlation functions of the inhomogeneous system. Since these are unavailable in general, one usually relies on the correlation functions for a corresponding uniform system and approximates the density $\bar{\rho}$, at which these correlation functions are to be evaluated, by various reasonable expressions. Among the most commonly used approximations are [1] the ‘local average density approximation’ (LADA), which assumes $\bar{\rho} = (\rho(\mathbf{r}) + \rho(\mathbf{r}'))/2$, and the ‘density-at-average-position approximation’ (DAPA), $\bar{\rho} = \rho((\mathbf{r} + \mathbf{r}')/2)$. Furthermore, one may try to use the mean overall density of the system (MODA) [2] or the density at a Boltzmann-averaged position (BAPA), where the *ansatz* $\bar{\rho} = \rho(\mathbf{r} + z(\mathbf{r}' - \mathbf{r}))$ [3] is made, and z is subsequently averaged over using the free energy that the respective z values produce in a Boltzmann-weighting function. In the MODA approach, by adopting $\bar{\rho} = N/V$, where N is the number of particles in the whole system of volume V , it is assumed that the correlation functions are no longer functions of the absolute positions \mathbf{r} and \mathbf{r}' , so any local character of $\bar{\rho}$ is neglected in the gradient expansion. For a simple Lennard-Jones fluid, McCoy and Davis [4] conclude that the particular type of approximation hardly affects the numerical results for fluid–fluid interfaces. There is, however, reason to believe that the situation is a bit different when ionic fluids are considered. Many theoretical studies of ionic fluids have been concerned with the restricted primitive model (RPM). This model fluid consists of equisized hard spheres, half of which carry a charge of $+q$, the other half a charge of $-q$. These ions of diameter σ are immersed in a dielectric continuum of dielectric constant ϵ . In our analyses of the Ginzburg temperature ΔT_{Gi}^* [2, 3] of the RPM, which are based on the Debye–Hückel theory and its extensions, we demonstrate that ΔT_{Gi}^* is extremely sensitive

to the type of local-density approximation. Here, we shall investigate to what extent this sensitivity propagates to surface tensions and density profiles. Recently, Groh *et al* [5] have employed the LADA to evaluate liquid–vapour density profiles and the surface tension for the RPM using the mean-spherical approximation (MSA) and density-functional theory, so it may be of interest to assess the reliability of LADA.

In this study, we focus mainly on modified and extended versions of the van der Waals gradient theory [1], so there will be no explicit appearance of the direct correlation function. The only relevant correlation function is the pair distribution function g_{ik} . Furthermore, we are going to use the Debye–Hückel (DH) theory to account for the thermodynamic properties and to provide an approximate model pair distribution function. The local free-energy density $\phi(\mathbf{r}) = \beta A(\mathbf{r})\sigma^3/V$ is approximated by the free-energy density of a corresponding homogeneous system $\phi_{\text{hom}}(\mathbf{r})$ and the square-gradient term $\phi_{\nabla^2}(\mathbf{r})$

$$\phi(\mathbf{r}) = \phi_{\text{hom}}(\mathbf{r}) + \phi_{\nabla^2}(\mathbf{r}) \quad (1)$$

$$\phi_{\text{hom}}(\mathbf{r}) = \phi_{\text{hom}}^{\text{id}}(\mathbf{r}) + \frac{\sigma^3}{2} \sum_{i,k} \rho_i(\mathbf{r})\rho_k(\mathbf{r}) \int_0^\beta \int u_{ik}(r_{ik}) g_{ik}(r_{ik}, \beta, \rho(\mathbf{r})) d\mathbf{r}_{ik} d\beta \quad (2)$$

$$\begin{aligned} \phi_{\nabla^2}(\mathbf{r}) = & -\frac{\sigma^3}{12} \sum_{i,k} \nabla \rho_i(\mathbf{r}) \nabla \rho_k(\mathbf{r}) \int_0^\beta \int r_{ik}^2 u_{ik}(r_{ik}) \left[g_{ik}(r_{ik}, \beta, \rho(\mathbf{r})) \right. \\ & \left. + a_1 \rho(\mathbf{r}) \frac{\partial g_{ik}(r_{ik}, \beta, \rho(\mathbf{r}))}{\partial \rho(\mathbf{r})} + a_2 \rho(\mathbf{r})^2 \frac{\partial^2 g_{ik}(r_{ik}, \beta, \rho(\mathbf{r}))}{\partial \rho(\mathbf{r})^2} \right] d\mathbf{r}_{ik} d\beta \end{aligned} \quad (3)$$

where $\phi_{\text{hom}}^{\text{id}}$ stands for the ideal-gas part to be specified below. Within the RPM, the interaction potential u_{ik} for $r_{ik} > \sigma$ is given by $u_{ik}(r_{ik}) = q_i q_k / \varepsilon r_{ik}$, while the pair distribution function corresponding to the DH theory is

$$g_{ik} = 1 - \beta \frac{q_i q_k \exp[\kappa(\sigma - r_{ik})]}{\varepsilon r_{ik} (1 + \kappa \sigma)} \quad (4)$$

where κ is the inverse Debye length. Using these expressions the homogeneous part of the reduced free-energy density within pure DH theory is obtained to be

$$\phi_{\text{hom}} = \rho^* \left[\ln \left(\frac{1}{2} \rho \Lambda^3 \right) - 1 \right] - (1/4\pi) \left[\ln(1+x) - x + \frac{1}{2} x^2 \right] \quad (5)$$

where Λ is the de Broglie thermal wavelength and $\rho^* = \rho \sigma^3$ the reduced density; $x = \kappa \sigma$ denotes the reduced inverse Debye length. A reduced temperature is introduced via $T^* = k_B T \varepsilon \sigma / q^2$. The parameters a_1 and a_2 in (3) depend on the local-density approximation made before expanding the free energy expression for the nonuniform system [3]. In MODA, a_1 and a_2 are both zero, since no local variation of g_{ik} with ρ is taken into account. For LADA, we have $a_1 = 1$, $a_2 = 1/4$, while DAPA corresponds to $a_1 = 1/2$, $a_2 = 0$. In our treatment of BAPA [3], averaging over z with equal weights yields $a_1 = 2/3$, $a_2 = 0$.

The results obtained using different local-density approximations will be compared to predictions of an approach that employs an approximate hypernetted-chain (AHNC) relation for the direct correlation function C_{ik}

$$C_{ik} = -\beta u_{ik} + \frac{1}{2} h_{ik}^2 \quad (6)$$

used in conjunction with $h_{ik} = g_{ik} - 1$ taken from DH theory to compute the square-gradient term [3]. From the direct correlation function C_{ik} , the square-gradient term can be calculated after

$$\phi_{\nabla^2} = \frac{\sigma^3}{12} \sum_{i,k} \int r_{ik}^2 C_{ik}(r_{ik}) d\mathbf{r}_{ik} \nabla \rho_i(\mathbf{r}) \nabla \rho_k(\mathbf{r}). \quad (7)$$

Furthermore, we will present values for the generalized Debye–Hückel (GDH) theory developed by Lee and Fisher [6]. In this approach, the direct correlation function is obtained by means of functional differentiation from a DH equation generalized to be applicable to nonuniform systems. Note that in the AHNC approach and in the GDH theory, no additional assumption, such as a local-density approximation, is necessary as the square-gradient term is calculated from a theory for the bulk fluid. In this respect, the latter two treatments differ from the above approaches to calculate (approximately) the properties of an inhomogeneous fluid, which rely on a specific form of the local density.

The pure DH theory is certainly not the most accurate theory for the RPM [7] and we would like to emphasize that we do not attempt to obtain best estimates for density profiles and surface tensions in this work, but rather study the role of the local-density approximation. A numerical improvement of the results would certainly be obtainable by employing the Fisher–Levin theory [7].

From evaluating (3) and using $c = 2\phi_{\nabla^2}/(\nabla^*\rho^*)^2$, we obtain the following contributions to the coefficient of the square-gradient term c . This coefficient is a sum of up to three terms

$$c = c_0 + a_1c_1 + a_2c_2 \quad (8)$$

with

$$c_0 = \frac{1}{12\pi\rho^{*2}} \left[\ln(1+x) + x + \frac{1}{2}x^2 \right] \quad (9)$$

$$c_1 = -\frac{1}{24\pi\rho^{*2}} \frac{2x + 4x^2 + x^3 + 4(1+x)\ln(1+x)}{1+x} \quad (10)$$

$$c_2 = \frac{1}{48\pi\rho^{*2}} \frac{6x + 24x^2 + 23x^3 + 4x^4 + 24(1+x)^2\ln(1+x)}{(1+x)^2} \quad (11)$$

corresponding to the three terms in (3). While c_0 stems from the term that contains no derivative of g_{ik} with respect to the density [2], to obtain c_1 and c_2 , g_{ik} has been differentiated with respect to density once and twice, respectively. Note that the given c refers to an expansion of the reduced free-energy density $\phi = \beta A\sigma^3/V$.

From the AHNC relation, the following expression for the coefficient of the square-gradient term results:

$$c_{\text{AHNC}} = \frac{\pi}{12} \frac{1 + 2x + 2x^2}{x^3 T^{*2} (1+x)^2}. \quad (12)$$

Within GDH theory, c is given by [6]

$$c_{\text{GDH}} = \frac{1}{96\pi\rho^{*2}} \left[\ln \left(\frac{(1+x)^{10}}{(1+x + \frac{1}{3}x^2)^9} \right) - \frac{x - 5x^2 - 8x^3}{2(1+x)^2} \right]. \quad (13)$$

We expect the BAPA and the AHNC relation to give results closest to those of GDH theory. The reason for this expectation is based on the closely agreeing results for c_{2g} (c at the critical point) [3] and the expression for the correlation length in the low-density limit, for which Lee and Fisher [6] predict the presumably exact result $\xi = (b/9216\pi\rho)^{1/4}$, where $b = \sigma/T^*$ is the Bjerrum length. Explicitly, the mean-field correlation length (in units of σ) can be obtained from

$$\xi = \left[c \left(\frac{\partial^2 \phi_{\text{hom}}}{\partial \rho^{*2}} \right)^{-1} \right]^{1/2}. \quad (14)$$

As shown in table 1, MODA, LADA, and DAPA predict considerably larger amplitudes of ξ in the low-density limit, that is, larger than the Lee–Fisher result by a factor of $a_\xi = \sqrt{32}$, $\sqrt{14}$, and $\sqrt{8}$, respectively. The prefactor of $\sqrt{14}$ for LADA is also obtained from the MSA [5]. While AHNC gives the correct result including the numerical prefactor, for the ‘equal-weight’ BAPA, the coefficient of this leading term vanishes identically [3] and a higher-order term comes into play which causes ξ to vanish as $\xi \sim \rho^{1/4}$ in the low-density limit. As we will see, this incorrect behaviour affects the symmetry of the density profile.

The critical parameters of the pure DH theory are $\rho_c^* = 1/64\pi \approx 0.005$ and $T_c^* = 1/16 = 0.0625$. Judged by recent estimates from Monte-Carlo simulations for the RPM [8], which indicate $\rho_c^* = 0.08$ and $T_c^* = 0.049$, these DH values are not very accurate, as mentioned above. In particular, the critical density is much too low. We will calculate the density profiles and the surface tension for $T^* = 0.05$, i.e. $T^*/T_c^* = 0.8$. The bulk densities of the coexisting phases are roughly $\rho_l^* = 0.06$ and $\rho_v^* = 6.6 \times 10^{-5}$. We employ the gradient theory treatment as outlined by Davis [1], that is, the density profile is calculated according to

$$\int_{\rho_0^*}^{\rho^*} \left(\frac{T^* c(\rho^*)}{2\Delta\omega(\rho^*)} \right)^{1/2} d\rho^* = -z/\sigma = -z^* \quad (15)$$

where ρ^* denotes $\rho^*(z^*)$, $\rho_0^* = (\rho_l^* + \rho_v^*)/2$, and $\Delta\omega(\rho^*) = \omega(\rho^*) + P_{\text{bulk}}^*$. $P_{\text{bulk}}^* = P_{\text{bulk}}\varepsilon\sigma^4/q^2$ is the reduced bulk pressure and the quantity $\omega(\rho^*)$ is defined as $\omega(\rho^*) = T^*(\phi_{\text{hom}}(\rho^*) - \rho^*\mu_{\text{bulk}}^*)$. Here, $\mu_{\text{bulk}}^* = \beta\mu_{\text{bulk}}$ is the reduced bulk chemical potential. Equation (15) is obtained from the Euler–Lagrange equation that minimizes the square-gradient free-energy functional [9, 10]

$$I(\{\rho^*\}) = \int_{-\infty}^{+\infty} \left[\Delta\omega(\rho^*) + \frac{1}{2}T^*c(\rho^*) \left(\frac{\partial\rho^*}{\partial z^*} \right)^2 \right] dz^* \quad (16)$$

where the two terms in the integrand measure the gain and loss, respectively, of free-energy density that results from creating an interface of a certain thickness. The interplay of these contributions determines the equilibrium density profile of the interface. This minimization procedure is equivalent to imposing the condition that the chemical potential be constant throughout the system [9]. In this theory, the dimensionless surface tension is obtained from

$$\gamma^* = \gamma\varepsilon\sigma^3/q^2 = \int_{\rho_0^*}^{\rho_l^*} \sqrt{2T^*c(\rho^*)\Delta\omega(\rho^*)} d\rho^*. \quad (17)$$

The density profiles are shown in figure 1, while the reduced surface tensions $\tilde{\gamma} = \gamma^*/T^* = \beta\gamma\sigma^2$ following from the various local-density approximations are given in table 1 along with the correlation lengths in the coexisting phases. From figure 1, it is obvious that those theories which predict a larger correlation length also give rise to a broader interface. The liquid–vapour interface extends over roughly four particle diameters for AHNC and up to 20 diameters for MODA; thus, the estimate of Groh *et al* [5] that the interface thickness is about $4\xi_l$ is confirmed. Except for BAPA, the density profiles are rather symmetric. In the BAPA case, it can be seen that the decay to the bulk density is more rapid on the vapour side, as it was observed by Groh *et al* [5] in their MSA-based density functional theory. As they argue [5], in gradient theory such a behaviour can only be observed if $\xi_v < \xi_l$, which is not only at variance with their MSA-based prediction for the correlation length in the

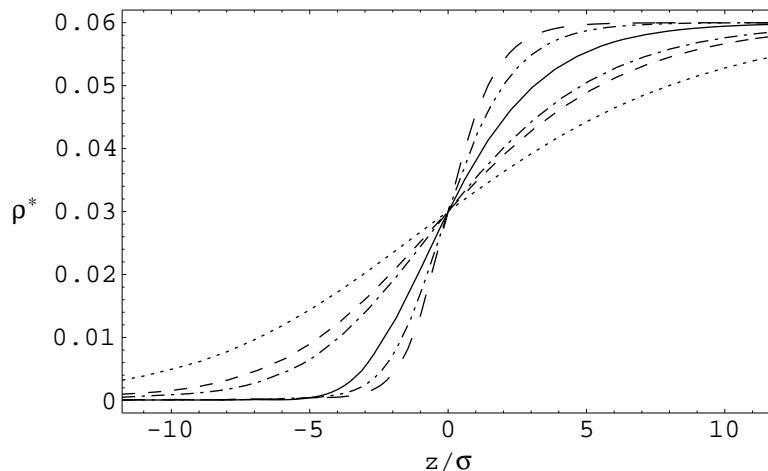


Figure 1. Density profiles for an ionic fluid within Debye–Hückel theory at $T^* = 0.05$. The profile is shown for various approximations to the local density: MODA (dotted), LADA (short-dashed), DAPA (dash-dotted), BAPA (continuous), for the GDH (dash-dot-dotted), and for the AHNC (long-dashed). Abbreviations are explained in the text.

Table 1. Results obtained using the listed local-density approximations, the GDH theory, and the approximate HNC relation for the reduced surface tension $\tilde{\gamma}$ and the correlation length ξ in the liquid and in the vapour phase at $T^* = 0.05$. The square of the prefactor a_ξ^2 of the Lee–Fisher result for the low-density limit correlation length, the coefficient of the square-gradient term c_{2g} at the critical point, and the Ginzburg temperature ΔT_{Gi}^* (taken from [2, 3, 6]) are also given.

Approximation	$\tilde{\gamma}$	ξ_l	ξ_v	a_ξ^2	c_{2g}	ΔT_{Gi}^*
MODA	0.0683	5.565	14.48	32	0.05818	0.006
LADA	0.0462	3.833	9.586	14	0.02619	0.068
DAPA	0.0381	3.429	7.259	8	0.01658	0.266
BAPA	0.0189	2.314	0.581	0	0.00271	60.80
GDH	0.0156	1.395	2.587	1	0.00267	63.67
AHNC	0.0127	0.971	2.574	1	0.00207	136.4

coexisting phases, but also with those of all other DH-based approaches we investigate; see table 1. For BAPA, however, the correlation length in the vapour phase is indeed smaller than in the liquid phase. This surprising result is due to the incorrect prediction for the correlation length in the low-density limit, which in this case vanishes as $\rho^{1/4}$. This effect is already at work for the low-density vapour phase and causes the small value of ξ_v . If a_1 is set to 31/48 instead of 2/3, the resulting c leads to the correct Lee–Fisher correlation length in the low-density limit and gives $\xi_l = 2.481$ and $\xi_v = 2.624$ at $T^* = 0.05$. Note that only the ‘equal-weight’ BAPA, not the BAPA approach in general, predicts $a_1 = 2/3$ and leads to qualitatively wrong behaviour in the low-density limit. In an earlier study based on gradient theory and the generalized (G)MSA, Telo da Gama *et al* [11], observed a slight asymmetry associated with a more rapid decay on the liquid side.

The broadest interface also corresponds to the highest surface tension. This quantity varies from $\tilde{\gamma} = 0.0127$ for AHNC to $\tilde{\gamma} = 0.0683$ for MODA. Nevertheless, it can be stated that interface thickness and surface tension do not depend too strongly on the local-density

approximation, although differences are noticeable. Thus, the conclusion of Groh *et al* [5] that their treatment gives the correct order of magnitude for the surface tension seems well justified. Note in this context that the MSA and the DH theory do not necessarily behave in exactly the same way towards the local-density approximation; however, it seems safe to say that both theories lead to roughly the same values for the surface tension for one particular type of local-density approximation: the agreement of the values of Groh *et al* for the surface tension at $T^*/T_c^* = 0.8$ from LADA–MSA1/MSA ($\tilde{\gamma} = 0.037/\tilde{\gamma} = 0.060$) and our LADA–DH estimate of $\tilde{\gamma} = 0.046$ is surprisingly good in view of the differences in absolute T^* and $\rho_l^* - \rho_v^*$, which result from using the MSA in place of DH theory.

A dilemma arises, however, when one focuses on the Ginzburg temperature: ΔT_{Gi}^* varies over four orders of magnitude depending on which local-density approximation is applied [2, 3]. Even the, at first sight, most reasonable approximations, LADA and DAPA, estimate the Ginzburg temperature of the ionic fluid to be smaller than the value of $\Delta T_{\text{Gi}}^* \approx 2$ obtained for a square-well fluid with short-range forces ($\lambda = 1.5$) [3]. This is in marked contrast to what has been found from GDH [6], from GMSA [12], from AHNC–DH, and from a BAPA–DH theory [3]. At this point, it might be worthwhile to emphasize again that for the AHNC, the GDH, and the GMSA treatment, no specific assumption on the form of the local density is made as the direct correlation function is obtained from bulk liquid-state theories. So it must be concluded that in the case of ionic fluids, at least for some particularly sensitive properties like the Ginzburg temperature, the ‘reasonable’ local-density approximations do not seem to suffice at all, but even for less sensitive quantities like the surface tension the results may vary by a factor of 3–5. The MSA may not be as sensitive towards the local-density approximation as the DH theory; this, however, remains to be checked explicitly.

Noteworthy from a computational point of view is the good agreement between the results of the convenient AHNC and the much more elaborate GDH theory. As expected the ‘equal-weight’ BAPA approach gives similar values as AHNC and GDH for all quantities except for those evaluated at very low densities.

Stimulating discussions with R Evans, M E Fisher, B Groh, G Stell, and S Wiegand are acknowledged. W S expresses his gratitude for support from the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie.

References

- [1] Davis H T 1995 *Statistical Mechanics of Phases, Interfaces, and Thin Films* (New York: VCH) and references therein
- [2] Weiss V C and Schröder W 1997 *J. Chem. Phys.* **106** 1930
Schröder W and Weiss V C 1997 *J. Chem. Phys.* **106** 7458
- [3] Schröder W and Weiss V C 1998 *J. Chem. Phys.* **109** (19)
- [4] McCoy B F and Davis H T 1979 *Phys. Rev. A* **20** 1201
- [5] Groh B, Evans R and Dietrich S 1998 *Phys. Rev. E* **57** 6944
- [6] Lee B P and Fisher M E 1996 *Phys. Rev. Lett.* **76** 2906
Fisher M E and Lee B P 1996 *Phys. Rev. Lett.* **77** 3561
- [7] Fisher M E and Levin Y 1993 *Phys. Rev. Lett.* **71** 3826
Levin Y and Fisher M E 1996 *Physica A* **225** 164
- [8] Caillol J M, Levesque D, and Weis J J 1997 *J. Chem. Phys.* **107** 1565
- [9] Cahn J W and Hilliard J E 1958 *J. Chem. Phys.* **28** 258
- [10] Rowlinson J S and Widom B 1982 *Molecular Theory of Capillarity* (Oxford: Clarendon)
- [11] Telo da Gama M M, Evans R and Sluckin T J 1980 *Mol. Phys.* **41** 1355
- [12] Leote de Carvalho R J F and Evans R 1995 *J. Phys.: Condens. Matter* **7** L575