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On the Phase Equilibrium of Polar Fluids Using the Dipolar Yukawa Fluid Molecular Model[†]

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The fluid phase equilibrium of polar fluids is investigated using the dipolar Yukawa fluid (DY) molecular model. The dispersion forces and the electrostatic interactions are represented by the hard core Yukawa fluid molecular model and the dipole−dipole interaction, respectively. It is shown that the liquid−vapor (L−V) coexistence phase equilibrium, similar to that for the Stockmayer fluid model (STM), that uses the Lennard-Jones (LJ) potential model plus the dipole−dipole interaction can be obtained using the DY molecular model. Results show that for the special case of the parameter value of the Yukawa potential, $z = 1.8/\sigma$, the thermodynamic functions of the Yukawa fluid are very similar to those of the LJ 12:6 fluid, and the STM potential model can be replaced by the more easily employed DY. Results for the L−V coexistence phase equilibrium of polar liquids are presented for polar fluids with dipolar strength of $\mu^2/\varepsilon\sigma^3 = 1$, 2, 3, and 4 and show good agreement with GEMC computer simulations of the STM fluid. It is also shown that as the dipolar strength of the polar fluid increases, similarly to accurate calculations using the STM, the L−V phase equilibrium coexistence curves do not present any undesirable unusual behavior that has been seen in some approximate calculations.

1. Introduction

The properties of polar liquids have been investigated using different theoretical[1,2] and computing simulation techniques.[3−5]

A great deal of information for polar fluids has been obtained using the Stockmayer (STM) molecular model. Although that model is a considerable idealization for real polar molecule interactions, it has been successfully used for describing the properties of polar pure fluids[1,2,6] and their mixtures.[7] The STM molecular model has been used in pioneering work for investigating the properties of polar fluids. However the STM fluid molecular model does not yield an analytic solution with any of the usual integral equations of the theory of liquids. This makes its use somewhat awkward. For example, multiparameter fits of the properties of the STM are often required.

Recently, Henderson et al.[8] presented an alternative procedure for studying the polar fluid properties using the Yukawa potential for representing the dispersion forces, and so replacing the Lennard-Jones (LJ) potential model but still considering the polar−polar interactions as those coming from the dipolar−dipolar interactions. This molecular model for representing the interactions of polar molecules is the so-called dipolar Yukawa molecular model (DY), which *does* yield an analytic solution within the framework of the Mean Spherical Approximation (MSA) integral equation theory that has been found useful for studying properties of polar fluids.

Since the DY molecular model presents both a radial and the angle-dependent part, it is also suitable for perturbation theoretical (PT) approaches such as the reference system and the perturbation potential, respectively, represented by the hard core Yukawa fluid and the dipole−dipole interactions.

2. Theory

2.1. Molecular Model. In modeling the interaction of the molecules in a polar fluid, it is assumed that the constituent molecules are rigid spheres of equal size with an embedded nonpolarizable permanent point dipole moment that interacts via the Yukawa pair potential. Consequently, the total pair potential between two polar molecules, say 1 and 2, reads as follows

$$u(\mathbf{r}_{12}) = u_0^{\mathrm{Y}}(r_{12}) + u_{\mathrm{dd}}(\mathbf{r}_{12}) \tag{1}$$

$u_0^{\mathrm{Y}}(..)$ is the hard Yukawa pair potential interaction and $u_{\mathrm{dd}}(..)$ is the dipolar−dipolar interaction between two permanent dipole moments of strength μ.

The Yukawa potential $u_0^{\mathrm{Y}}(..)$ with a hard core is given by

$$u_0^{\mathrm{Y}}(r_1, r_2) = \begin{cases} \infty, & r_{12} < \sigma \\ -\dfrac{\varepsilon\sigma}{r_{12}} \exp[-z(r_{12} - \sigma)], & r_{12} \geq \sigma \end{cases} \tag{2}$$

where ε and z are, respectively, the depth and the range of the dispersion interaction. The separation of the centers of molecules, 1 and 2, is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and σ is the diameter of molecules. Further, $u_{\mathrm{dd}}(\mathbf{r}_{12})$ is the intermolecular potential energy between two point dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ of strength μ located at the centers of molecules 1 and 2 given by

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$$u_{\mathrm{dd}}(\mathbf{r}_{12}) = \left[\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r_{12}^3} - \frac{3}{r_{12}^5}(\boldsymbol{\mu}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12})\right] \tag{3}$$

2.2. The Helmholtz Free Energy. We have assumed that for the reference system fluid the molecules interact via the hard Yukawa potential function. Then the nonorientation-dependent forces of the interaction potential are represented by the HS plus the Yukawa potential function. The angular-dependent part of the total intermolecular potential is assumed to be that of the dipole−dipole interaction function.

In this section, a brief description of the theoretical approach is given as follows. Waisman[9] solved the MSA for the Yukawa fluid obtaining six nonlinear equations in six unknowns. Ginoza[10] simplified this result and presented the MSA solution for the Yukawa fluid given in terms of the Γ parameter which is given in the following equation

$$\Gamma(1 + z\Gamma)(1 + \Psi\Gamma)^2 + xw = 0 \tag{4}$$

where $x = \varepsilon/kT$ (k is the Boltzmann constant and T is the temperature). Also, $w = 6\eta/\Phi_0^2$ and

$$\Phi_0 = \frac{e^{-z}L(\eta, z) + S(\eta, z)}{z^3(1 - \eta)^2} \tag{5}$$

in which

$$\psi = z^2(1 - \eta)^2 \frac{1 - e^{-z}}{e^{-z}L(\eta, z) + S(\eta, z)} \tag{6}$$

The above equations are given in terms of the packing fraction, $\eta = \pi\rho\sigma^3/6$, with $\rho = N/V$ the number density in which N and V are the number of particles and the volume, respectively, and $L(\eta, z)$ and $S(\eta, z)$ are functions given in ref 11. The parameter Γ is the parameter of fundamental importance in Ginoza's theoretical approach. By expanding Γ, as was done by Henderson et al.,[11] one obtains an inverse temperature expansion of the Γ parameter as follows

$$\Gamma = \sum_n x^n \Gamma_n \tag{7}$$

in which Γ_n are functions of w, z, and Ψ (see ref 11 for details). Using the values of the Γ_n, the so-called Waisman[9] parameter, $v = -2U$, can be obtained. By expanding the v parameter in powers of $x = \varepsilon/kT$ in a series similar to that of eq 7, the corresponding v_n are obtained. Thus (see ref 11 for details), the Helmholtz free energy (HFE) for the Yukawa fluid reads

$$(A - A_0)/NkT = -\frac{1}{2}\sum_n \frac{x^n}{n} v_n \tag{8}$$

$$(p - p_0)/NkT = -\frac{1}{2}\sum_n \frac{x^n}{n}(\eta\, \partial v_n/\partial\eta) \tag{9}$$

where A_0 and p_0 are, respectively, the HFE and the pressure of the hard sphere fluid[12]

$$A_0/NkT = 3 \ln \lambda - 1 + \ln \rho + \eta\frac{4 - 3\eta}{(1 - \eta)^2} \tag{10}$$

$$p_0V/NkT = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \tag{11}$$

In employing eqs 8 and 9, we use five terms in the temperature series.

In eq 10, $\lambda = h/(2\pi mkT)^{1/2}$, where h is the Planck's constant and m is the molecular mass, is the contribution of the kinetic energy.

The MSA HFE of the DY fluid can be written as follows[8]

$$A_{\mathrm{DY}}/NkT = A_{\mathrm{Y}}/NkT + A_{\mathrm{DD}}/NkT \tag{12}$$

where the first and second terms on the right-hand side of eq 12 are the HFE of the hard Yukawa fluid, given by the above written eq 8, and the HFE of the dipole−dipole contribution to the total DY fluid. The additivity of A_{Y} and A_{DD} is not an additional approximation but is rigorously correct within the MSA.

A_{DD}/NkT is given by Wertheim[13]

$$A_{\mathrm{DD}}/NkT = -\frac{3}{\eta}I(y) \tag{13}$$

where η is the packing fraction already defined and $y = 4\pi\rho\mu^2/(9kT)$ is the dipole strength function. $I(y)$ is given as follows

$$I(y) = \frac{8}{3}\xi^2\left\{\frac{(1 + \xi)^2}{(1 - 2\xi)^4} + \frac{(2 - \xi)^2}{8(1 + \xi)^4}\right\} \tag{14}$$

where ξ is the solution of the following equation

$$y(\xi) = \frac{1}{3}\left\{\frac{(1 + 4\xi)^2}{(1 - 2\xi)^4} - \frac{(1 - 2\xi)^2}{(1 + \xi)^4}\right\} \tag{15}$$

By expanding eq 15, one gets $y(\xi)$ as follows

$$y(\xi) = 8\xi + 30\xi^2 + 228\xi^3 + 775\xi^4 + O(\xi)^5 \tag{16}$$

Inversion of the above equation yields $\xi(y)$

$$\xi(y) = \frac{1}{8}y - \frac{15}{256}y^2 - \frac{3}{4096}y^3 + \frac{11125}{262144}y^4 + O(y)^5 \tag{17}$$

The above series can be summed by means of the following Padé

$$\xi(y) = \frac{y}{8\left(1 + \frac{15}{32}y\right)} \tag{18}$$

We have examined both eqs 17 and 18 by comparison with the corresponding results obtained by numerical inversion of eq 15 and have found that eq 18 is quite satisfactory, whereas the truncated series converges slowly and is very poor. Accordingly, our procedure is to substitute eq 18 into eqs 13 and 14 to obtain A_{DD}.

2.3. Critical Point. The critical point of the DY pure fluid is obtained by numerically solving the following equations

$$\left[\frac{\partial p}{\partial \rho}\right]_{T_c} = 0 \tag{19}$$

and

$$\left[\frac{\partial^2 p}{\partial \rho^2}\right]_{T_c} = 0 \tag{20}$$

where $p = -[(\partial A)/(\partial V)]_T$ is the total pressure of the fluid and A is the HFE of the DY fluid by the above given eq 12.

2.4. Phase Equilibrium. For a liquid and its vapor to coexist at a given temperature, say T, they must have the same pressure and the same chemical potential μ.

$$p(\rho_{\mathrm{v}}, T) = p(\rho_{\mathrm{l}}, T) = p \tag{21}$$

$$\mu(\rho_{\mathrm{v}}, T) = \mu(\rho_{\mathrm{l}}, T) = \mu \tag{22}$$

The numerical solution of the above equations gives ρ_{v} and ρ_{l}, the vapor and liquid equilibrium densities, respectively.

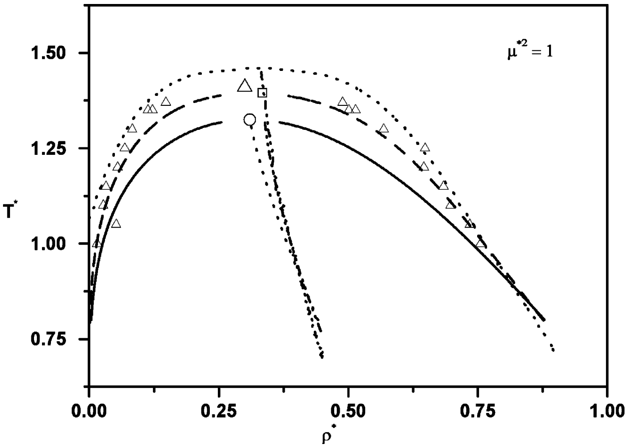

Figure 1. DY and STM results for L−V equilibrium of a polar fluid with the strength of the dipole moment $\mu^2/\varepsilon\sigma^3 = 1$. Δ, the STM GEMC computer simulations values from ref 17; dotted lines, the digitized values of the STM coexistence curve of ref 18; dashed line and □, the STM liquid−vapor coexistence curve and the critical point of ref 19; full line and ○, results for the liquid−vapor coexistence curve and the critical point using the DY fluid molecular model with $z = 1.8/\sigma$.

3. Results

In this section, we present results on the phase equilibrium and the critical behavior of the DY fluid, obtained using the molecular model given by eq 1. Part of the results of this work were presented previously at both national[14] and international[15] meetings. Recently, a similar independent study for polar fluids has been published[16] that arrives at results for the L−V equilibrium of polar fluids similar to those we present here.

It is worth noting that the DY molecular model can be used to obtain the fluid phase equilibrium properties of a polar fluid with similar accuracy as would be obtained using the STM potential. This is because for the special case of the range parameter value $z = 1.8/\sigma$ the Yukawa potential function mimics the LJ potential 12:6 function. Thus, the STM potential is approximated by only adding the DD interaction to the Yukawa function with that value for the parameter z. This addition of the Yukawa and dipolar terms is rigorously correct for the dipolar Yukawa fluid within the MSA. However, our goal is not to present the DY as an approximation to the STM but to present the DY model as an independent model. However, in view of the widespread use of the STM, it is informative to compare the results of the two models.

Using the HFE of the DY fluid, results for both the critical point and the liquid−vapor (L−V) equilibrium coexistence curve are obtained for our model polar fluid by solving numerically the equations presented in Section 2. We have calculated the L−V equilibrium coexistence curves and the critical points for polar fluids with a dipolar strength of $\mu^2/\varepsilon\sigma^3 = 1$, 2, 3, and 4.

In Figure 1, we compare our calculated L−V coexistence curve of a polar fluid using the STM molecular model and the DY fluid with the range parameter value $z = 1.8/\sigma$ and with the dipolar strength $\mu^2/\varepsilon\sigma^3 = 1$. The Gibbs ensemble Monte Carlo (GEMC) computer simulations,[17] the digitized results of van Leeuwen et al.,[18] and recent published results[19] that are based on the MBWR equation of state are also shown. We note that our results are in better agreement with the GEMC computer simulations than are the approximate results based on a multiparameter fit EOS.

It also can be noted that the calculated critical point is in good agreement with the GEMC computer simulation value (see Table 1). The digitized results of ref 18 also are in good agreement with GEMC computer simulations; however, as seen at the critical point region, the temperature is generally overestimated by the procedure of van Leeuwen et al. On the other hand, the DY critical temperature is somewhat below that of the STM. Since the DY and STM are different models, there is no a priori reason to expect exact agreement. Nonetheless, it is gratifiying that the agreement is close.

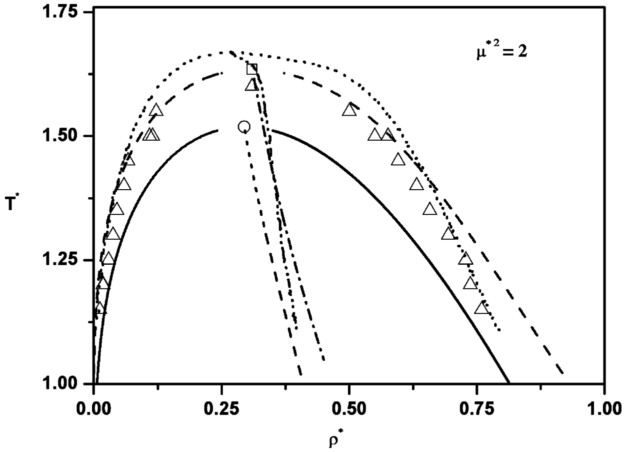

Figure 2. Vapor−liquid equilibrium results for the DY fluid molecular model with $z = 1.8/\sigma$ and dipolar strength $\mu^2/\varepsilon\sigma^3 = 2$. The symbols and curves are as in Figure 1.

Table 1. Critical Point Parameters for Polar Fluids

μ^{*2}	ρ^*	T^*	p^*	source
1.	0.30	1.41		STM ref 17
1.	0.315	1.394	0.145	STM ref 19
1.	0.31	1.325	0.148	DY this work
2.	0.31	1.60		STM ref 17
2.	0.310	1.634	0.179	STM ref 19
2.	0.294	1.518	0.161	DY this work
3.	0.312	1.82		STM ref 18
3.	0.301	1.906	0.206	STM ref 19
3.	0.280	1.76	0.177	DY this work
4.	0.289	2.06		STM ref 18
4.	0.293	2.174	0.227	STM ref 19
4.	0.265	2.028	0.194	DY this work

In Figure 2, results for the DY fluid with $\mu^2/\varepsilon\sigma^3 = 2$ are shown. Again, the digitized results of ref 18 for the STM fluid overestimate the values of temperature and on the vapor branch of the coexistence curve begin to show a nonphysical deformation of the liquid branch of the coexistence curve that has not been reported for any experimental data. Our calculated L−V equilibrium coexistence curve on the vapor branch exhibits good agreement with the GEMC computer simulation data of ref 17 for the STM fluid and does not show the extraneous behavior on the liquid branch that is predicted by the approximate MBWR fluid molecular model[18] for the STM fluid.

In Figure 3, our results using the DY fluid are shown and compared with results for a Stockmayer fluid with $\mu^2/\varepsilon\sigma^3 = 3$. As shown, theoretical results for the L−V coexistence curve of ref 18 do not agree with GEMC computer simulations. Again, our calculations using the DY fluid do show the expected L−V equilibrium coexistence curve.

Finally, in Figure 4, our results using the DY fluid are compared with those reported for STM fluid with $\mu^2/\varepsilon\sigma^3 = 4$. It is worth noting that even for such a large value of the dipole moment strength our calculated L−V equilibrium coexistence curve presents a reasonable agreement with GEMC computer simulations of ref 18 and does not predict any extraneous behavior on the liquid branch of the coexistence curve.

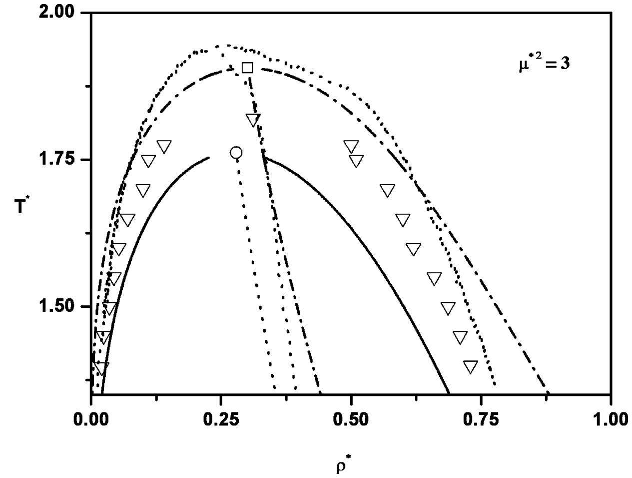

Figure 3. Vapor−liquid equilibrium results for the DY fluid molecular model with $z = 1.8/\sigma$ and dipolar strength $\mu^2/\varepsilon\sigma^3 = 3$. ∇, STM GEMC computer simulation values from ref 18. Captions are as in Figure 1.

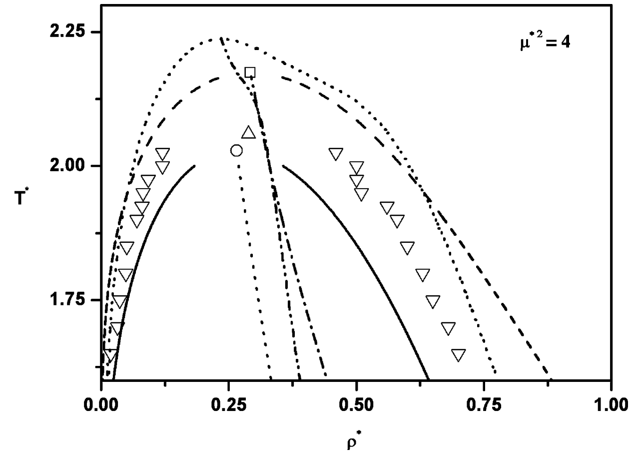

Figure 4. Vapor−liquid equilibrium results for the DY fluid molecular model with $z = 1.8/\sigma$ and dipolar strength $\mu^2/\varepsilon\sigma^3 = 4$. ∇, STM GEMC computer simulation values from ref 18. Captions are as in Figure 1.

In closing, in this work it has been shown that for moderate values of the strength dipole moment a polar fluid can be described satisfactorily using the DY fluid molecular model given by eq 1.

4. Discussion

In this work, the fluid phase behavior of polar fluids is investigated using the DY fluid molecular model given by eq 1. It has been shown that it can describe the fluid phase equilibrium properties of polar fluids as well as models such as the very well-known STM fluid. As it is well-known, the STM molecular model has been used for many years to describe the properties of polar fluids. However, by using the STM molecular model, one must resort to using theoretical approaches that require numerical solution of some equation or a multiparameter EOS to obtain the Helmholtz free energy of the nonorientation part of the STM potential function. On the other hand, using the DY fluid molecular model, this nonorientational contribution is given analytically by the hard sphere Yukawa potential function, with the given value $z = 1.8/\sigma$ of the range parameter. Since the Yukawa potential yields an analytical function, it is much easier to obtain more accurate fluid phase equilibrium properties than by using a multiparameter EOS to represent the LJ fluid properties. Further, we have shown that calculations performed using the DY fluid molecular model do not predict any unusual behavior for the L−V equilibrium coexistence curve such as those found using multiparameter EOS, as has been shown in this work.

Taking into consideration the results obtained for STM fluids, the DY molecular model can be used with confidence when predicting fluid phase behavior properties of polar fluids.

5. Conclusions

In this work, the DY fluid molecular model is used to investigate the fluid phase behavior of polar fluids. The radial interactions of molecules are assumed to be represented by the hard Yukawa potential function and the angular-dependent part of molecule interactions by that of the dipolar−dipolar interaction. Results for both the critical point and the fluid phase behavior for the STM fluid using the DY fluid are compared with both multiparameter EOS and GEMC computer simulation results.

The conclusion of this work are the following. The DY fluid molecular model is an important advance as compared with both the DHS and STM molecular models, due to:

(1) The properties of dipolar fluids can be obtained from simple analytic formulas.

(2) With the MSA, the DY does not form chain structures.

(3) The calculated critical points for different values of the strength of the dipole moment are in better agreement with GEMC computer simulation data than previously reported data using multiparameter EOS.

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Appendix

List of Symbols

A^*	Reduced Helmholtz free energy, $A^* = \beta A/N$
k	Boltzmann constant
N	total number of molecules in the system
p	pressure
p^*	reduced pressure, $p\sigma^3/\varepsilon$
T	absolute temperature
T^*	reduced temperature, β^{-1}/ε, where $\beta^{-1} = kT$
U	thermodynamic energy in excess of the ideal gas energy
V	volume

List of Abbreviations

DHS	dipolar hard sphere fluid
DY	dipolar Yukawa fluid molecular model
EOS	equation of state of a pure fluid
HFE	Helmholtz free energy
LJ	Lennard-Jones 12:6 potential model
L−V	liquid−vapor
MBWR	modified Bennet−Webb−Rubin equation of state
STM	Stockmayer fluid molecular model
Y	Yukawa potential

Greek Letters

η	packing fraction
β	$1/kT$
ρ	density
ρ^*	reduced density, $N\sigma^3/V$
ρ_v	saturated vapor density
ρ_l	saturated liquid density

σ	hard spheres diameter
μ	strength of the dipole moment
μ^*	$= \mu/(\varepsilon\sigma^3)^{1/2}$ reduced dipole moment

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