Renormalization Group Theory for Fluids to Greater Density Distances from the Critical Point[1]

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ABSTRACT

A recently developed renormalization group (RG) theory for fluids begins with an expression for the free energy for repulsive interactions only, then employs an RG procedure to take into account contributions to the free energy that come from fluctuations of all wavelengths in the presence of attractive intermolecular interactions of limited range. The theory has had some success in describing volumetric properties of real fluids at the critical point and out to distances within approximately $\pm 50\%$ of the critical point density. In the calculations, density dependence of the radial distribution function for the repulsive interactions was ignored. The theory has now been modified to take that density dependence into account. Predictions of the theory as thus amended are compared with volumetric measurements made in argon near the critical point temperature for densities from zero to more than twice the critical point density.

KEY WORDS: critical point; density fluctuations; nonuniversal thermal behavior; radial distribution function; renormalization group; volumetric properties.

1. INTRODUCTION

In two previous papers [1,2] the authors have developed a renormalization group (RG) procedure for treating volumetric properties of fluids. The theory begins with an expression for the free energy of a gas of molecules that interact with steeply repulsive forces only. It then uses RG methods to take into account contributions to the free energy that come from attractive interactions among the molecules. Because those interactions have a limited range, they result in density fluctuations that can be substantially larger than would be predicted in a mean field approximation. Calculation of the enhancement of fluctuations is difficult because fluctuations of many different wavelengths interact with one another. RG methods were developed initially to treat such interactions for fluctuations whose wavelengths are all asymptotically long compared with the range of the attractive forces. Extensions of those methods were proposed in [1] to treat shorter wavelength fluctuations, down to the shortest that make appreciable contributions to the free energy. Extensions of the theory were proposed in [2] to make it possible to predict the location of the critical point and other aspects of nonuniversal behavior for given intermolecular potentials. A limitation of the theory as developed in [1] and [2] was the lack of any allowance for changes of the pair correlation function for the repulsive interactions as one moves away from the critical point. A method is proposed here for treating effects of this changing density distribution function in carrying through the RG calculations.

2. RENORMALIZATION METHOD

The free energy calculated for repulsive interactions only is assumed to take into account fully density fluctuations of the very shortest wavelengths. Those fluctuations

are little affected by the less rapidly varying attractive interactions; the attraction is averaged over the short wavelengths of the fluctuations. For fluctuations with longer wavelengths, the steeply repulsive interactions are too abrupt to affect their amplitudes greatly, but the attractive wells have a big effect. The renormalization procedure [1] begins with the shortest wavelength fluctuations that are affected appreciably by the attractive wells, then adds contributions from successively longer wavelength fluctuations. Mathematically, after taking into account all fluctuations with wavelengths shorter than some λ_s, the grand partition function for the fluid contained within a domain Ω of volume V(Ω) and chemical potential μ is expressed as [1]

$$\Xi(T,\mu,\Omega) = \sum_{[\rho_s(\mathbf{r})]} e^{\beta\mu \int_\Omega d\mathbf{r}\, \rho_s(\mathbf{r}) - \beta \int_\Omega d\mathbf{r}\, f_s(T,\rho_s) - \beta U_s}. \tag{1}$$

The summation is taken over all fluctuations $\rho_s(\mathbf{r})$ containing (only) wavelengths longer than λ_s. The $\rho_s(\mathbf{r})$, which appears also in the exponent, includes the constant (nonfluctuating) component of density, $\overline{\rho}$. In the exponential, the first term gives $\beta\mu$N, where β=1/k$_B$T, and N is the total number of molecules in Ω when the number density is given by $\rho_s(\mathbf{r})$. The f$_s$(T,ρ_s) is the portion of the local Helmholtz free energy density [a functional of $\rho_s(\mathbf{r})$] that includes all contributions from fluctuations with wavelengths $\lambda<\lambda_s$. And U$_s$, which includes the factor g$_{repulsive}$(T,ρ_s,r), is the contribution to the free energy in Ω when the density is given by $\rho_s(\mathbf{r})$ that is made by the potential energy of attraction among the molecules in the fluid, canonically averaged over the shortest wavelength fluctuations, those associated with the steeply repulsive portions of the interaction potentials.

The calculation now proceeds by summing first over all fluctuations with wave-

lengths between λ_s and a larger wavelength, λ_l. The result can be expressed as

$$\sum_{[\rho_D(\mathbf{r})]} e^{-\beta \int_\Omega d\mathbf{r}\, f_D - \beta U_D} = e^{-\beta \int_\Omega d\mathbf{r}\, \delta f_l(T,\rho_l)}, \tag{2}$$

where $\rho_D = \rho_s - \rho_l$ is the portion of ρ_s that depends on wavelengths between λ_s and λ_l, and ρ_l that portion which depends only on wavelengths $\lambda \geq \lambda_l$. In the exponents, f_D is shorthand for $\mathrm{f}_D(T,\rho_l,\rho_D)$=$\mathrm{f}_s(T,\rho_s)$-$\mathrm{f}_s(T,\rho_l)$, where $\mathrm{f}_s(T,\rho_l)$ is the portion of $\mathrm{f}_s(T,\rho_s)$ that does not depend on ρ_D [obtained from $\mathrm{f}_s(T,\rho_s)$ by setting ρ_D=0], and, analogously, U_D=U_s-U_l, where U_l is the portion of U_s that doesn't depend on ρ_D. The $\delta\mathrm{f}_l(T,\rho_l)$ is an increment of local free energy density that can now be added to $\mathrm{f}_s(T,\rho_l)$ to form a new - 'renormalized' - function $\mathrm{f}_l(T,\rho_l)$ for use in an expression for the grand partition function that requires summations only over the remaining fluctuations, those with wavelengths $\lambda \geq \lambda_l$:

$$\Xi(T,\mu,\Omega) = \sum_{[\rho_l(\mathbf{r})]} e^{\beta\mu \int_\Omega d\mathbf{r}\, \rho_l(\mathbf{r}) - \beta \int_\Omega d\mathbf{r}\, f_l(T,\rho_l) - \beta U_l}. \tag{3}$$

In the phase-space cell approximation used in [1], essentially that of Wilson [3], one sets $\lambda_l \simeq 2\lambda_s$ and treats the ρ_D as wave packets. They are taken to be coherent inside a volume V_D within which the variation of ρ_l can be neglected, and incoherent outside that volume. Designating within V_D the amplitude of the fluctuations ρ_D by x and writing U_D=$\mathrm{V}_D\mathrm{u}_D$, one then obtains from (2)

$$\delta f_l(T,\rho_l) = -\frac{1}{\beta V_D} \ln Q_D(T,\rho_l) \tag{4a}$$

where

$$Q_D(T,\rho_l) = Q_0(T,\rho_l)\int dx\, e^{-\beta V_D[f_D(T,\rho_l,x)+u_D(T,\rho_l,x)]}. \tag{4b}$$

The $Q_0(T,\rho_l)$ arises from the conversion of the summation over $\rho_D(\mathbf{r})$ to an integral over x, and can be treated as substantially constant (only) when T and ρ_l don't change much, as when one is close to the critical point.

For a two-body potential, when one has reached wavelengths λ_s that are long compared with the range of the potential, the potential energy density u_D has a large portion proportional to x^2 and independent of λ_s, and a smaller portion proportional to $\lambda_s^{-2}x^2$. In that long wavelength limit, *when one is sufficiently close to the critical point so that $Q_0(T,\rho_l)$ can be treated as a constant*, one makes contact with previous RG treatments. Specifically, when f_D is written as

$$f_D(T,\rho_l,x) = [f_s(T,\rho_l+x) + f_s(T,\rho_l-x)]/2 - f_s(T,\rho_l), \tag{5}$$

then, if $f_s(T,\rho_s)$ is assumed to be a symmetric function of the density distance from the critical point density, Eq. (4) yields - independently of the numerical value of Q_0 - the familiar, near-critical-point recursion relations of Wilson, and Wilson and Fisher [2,3,4].

We are concerned here with behavior also when *not* near the critical point, and also when near the critical point for wavelengths λ_s that are *not* asymptotically long. We thus need to know how Q_0 varies with temperature and density distance from the critical point and also its numerical value at the critical point. (The latter information is required in order to determine the *location* of the critical point, rather than be

limited to a theory of how thermal behavior varies as a function of distance from a critical point whose location remains uncalculated.)

To determine how Q_0 changes as one moves away from the critical point and also its *actual* value at T_c, ρ_c, one can use the fact that in the mean field approximation, and also when λ_s is sufficiently small compared with the range of the attractive potential, the u_D in Eq. (4b) is negligibly small and makes no contribution to $f_l(T, \rho_l)$. Mathematically, then $f_l(T, \rho_l) = f_s(T, \rho_l)$, i.e. $\delta f_l(T, \rho_l)=0$. According to (4a), the corresponding $Q_D(T,\rho_l)$ is simply equal to unity. Thus $Q_0(T, \rho_l)$ equals the reciprocal of the integral in (4b) when $u_D=0$. Designating the Q_D for $u_D=0$ by $Q_{D,LR}$, where "LR" refers to the attractive potential assumed to have a range that is sufficiently long compared with λ_s so that to good approximation $u_D=0$, then (4a) can be rewritten equivalently as

$$\delta f_l(T, \rho_l) = -\frac{1}{\beta V_D} \ln \frac{Q_D(T, \rho_l)}{Q_{D,LR}(T, \rho_l)}. \tag{4c}$$

The argument of the logarithm is now the ratio of two integrals, in which the common factor $Q_0(T,\rho_l)$ cancels out. The result (4c) takes into account the $Q_0(T,\rho_l)$ that enters in (4b), including its dependence on T and ρ; the increments δf_l given by (4c) are *fully* determined (not just to an unknown constant multiple) once one specifies the averaging volume, V_D, the central wavelength λ_D in the wavepacket ρ_D, and the intermolecular potential (which determines the u_D that appears in (4b)).

3. NEW CALCULATIONS

In the calculations that follow, the U_s in Eq. (1) has been expressed as

$$U_s = \int_\Omega d\mathbf{r}' \int_\Omega d\mathbf{r}\, \rho_s(\mathbf{r}')\rho_s(\mathbf{r}) U_2(\mathbf{r}' - \mathbf{r}) g_{repulsive}(T, \rho_s, \mathbf{r}' - \mathbf{r}). \tag{6}$$

Here U_2 is one-half of the attractive part of the pair potential and $g_{repulsive}$ is the pair correlation function for the repulsive part of the potential. We assume spherically symmetric $U_2(\mathbf{r})=U_2(r)$ and $g_{repulsive}(T,\rho_s,\mathbf{r}) = g_{repulsive}(T,\rho_s,r)$. If the range of $U_2(r)$ were sufficiently short compared with all wavelengths contained in ρ_s, then within a domain Ω' within which ρ_s is constant the energy density $u_s=U_s/V(\Omega')$ would be given by

$$u_s\,(T,\rho_s) = \rho_s^2 \int_{\Omega'} d\mathbf{r}\, U_2(r) g_{repulsive}(T,\rho_s,r) \tag{7a}$$

$$= -a(T,\rho_s)\rho_s^2. \tag{7b}$$

Within a larger volume $V_D>V(\Omega')$, fluctuations ρ_D of amplitude x would then yield for u_D, analogously to (5) for f_D,

$$u_{D,SR}(T,\rho_l,x) = [u_s(T,\rho_l+x) + u_s(T,\rho_l-x)]/2 - u_s(T,\rho_l). \tag{8a}$$

Here the subscript "SR" on u_D refers to the requirement that the attractive potential U_2 be sufficiently short-ranged that it can be treated within V_D as a local potential.

When the averaging over density variations within the actual, extended range of U_2 is taken into account, the u_D is smaller by a factor 1-D,

$$u_D = (1-D)u_{D,SR}, \tag{8b}$$

where D is a number between zero and one. For simple sinusoidally varying density fluctuation of the form $\rho_D=\rho_0\cos(\mathbf{k}\cdot\mathbf{r}+\phi)$ and $g_{repulsive}$ evaluated at density ρ, the

factor (1-D) is given by

$$1 - D = U_{2,k}(T, \rho)/U_{2,0}(T, \rho), \tag{9a}$$

where

$$U_{2,k} = \int_{\Omega} d\mathbf{r}\ \cos(\mathbf{k} \cdot \mathbf{r})\mathbf{U}_2(r) g_{repulsive}(T, \rho, r) \tag{9b}$$

is the cosine Fourier component of $\mathrm{U}_2(\mathbf{r}'\text{-}\mathbf{r})\mathrm{g}_{repulsive}(T,\rho,\mathbf{r}'\text{-}\mathbf{r})$, and $\mathrm{U}_{2,0}/\mathrm{V}(\Omega) = -\mathrm{a}(T,\rho)$. In calculations to follow, the density ρ used in $\mathrm{g}_{repulsive}$ in Eq. (9) has been taken to be the average density $\overline{\rho}$ in $\mathrm{V}(\Omega)$.

In our earlier work that focused on behavior closer to the critical point [1,2], a simplifying approximation was made. It is equivalent to replacing everywhere the actual $\mathrm{g}_{repulsive}(T,\rho,\mathrm{r})$ by $\mathrm{g}_{repulsive}(T_c,\rho_c,\mathrm{r})$ and the product $\mathrm{U}_2(\mathrm{r})\mathrm{g}_{repulsive}(T_c,\rho_c,\mathrm{r})$ by a temperature and density-independent 'effective' $\mathrm{U}_2(\mathrm{r})$. When this is done, it is easily verified that Eqs. (6)-(9) above yield Eqs. (10) and (11) in [1], with the $\mathrm{a}(T,\rho)$ in those equations and in Eq. (14) replaced by $\mathrm{a}=\mathrm{a}(T_c,\rho_c)=\mathrm{const}$. In the present investigation this simplifying approximation, and the further approximations expressed by Eq. (12) and choice $\mathrm{D}_0=1$ in [1] were *not* employed.

4. RESULTS FOR ARGON

Equations above were evaluated numerically for square-well potential $\mathrm{U}_2(\mathrm{r})$, and for hard-sphere $\mathrm{g}_{repulsive}(\rho,\mathrm{r})$ given in tables published by Throop and Bearman [5] for values of $\rho\sigma^3$ in the range 0-1.1 (σ=sphere diameter). After choosing parameters of the square-well potential (its depth and inner and outer boundaries), numerical results were obtained upon making decisions about the size of the coherence volume V_D, which appears in Eqs. (4), and the fluctuation wavelengths $\lambda_D=2\pi/\mathrm{k}$ employed in Eq. (9b). For work reported here, wavelengths λ_D were chosen to be multiples t^n

(t=2.0; n=1,2,3,...) of a reference wavelength λ_{D0}=yRσ (Rσ=range of the attractive square-well potential), with y=1.04; and the coherence volume V_D was chosen for each λ_D to be of size $V_D=(z\lambda_D/2)^3$, with z=1.12. [For wavelengths $\lambda=t^n\lambda_{D0}$, with n=0,-1,-2,-..., i.e. as small as or smaller than λ_{D0}, fluctuation contributions given by (4) can be expected to be negligible, owing to the then rapid oscillation of cos($\mathbf{k}\cdot\mathbf{r}$) in (9b).] From theoretical considerations one can expect best choices for y and z to be close to unity. It wasn't posible at this time to determine y and z more exactly from theory, so they were assigned somewhat arbitrarily empirical values quoted above.

Results using the approach just described for these values of y and z, when the square-well parameters were adjusted to give the correct critical point T_c, ρ_c, P_c for argon, are illustrated in Figs. 1 (a) and (b) for the two measured [6] argon pressure isotherms closest to critical temperature. The root-mean-square deviation (perpendicular distance between experimental data point and theoretical curve) for all of the data is less than 0.5% (to be exact, 0.41%), with maximum absolute deviations for these two isotherms of less than 1% (maximum deviations were +0.84% and -0.79%). Theoretical curves calculated *without* any fluctuation contributions (4a,b), i.e., calculated at the same temperatures in mean-field approximation, deviate from the experimental points at some densities for argon by as much as 69% (rms deviation 25.4%; greatest deviations are at densities about 35% larger than critical) with deviations of 20% or more for densities in the range approximately 0.9-1.7$\rho_{c.}$. [This illustrates how large is the aggregate contribution from the fluctuations resulting from deviations of the attractive potential from the constant depth potential well assumed in the mean-field approximation. The situation is essentially that shown previously in Fig. 1(d) in White [7] (difference between dashed and solid line), where calculations were performed in a

less accurate approximation.]

The calculated results for argon presented in Figs. 1 a,b assumed a square-well of depth ϵ/k_B=86.8 K, inner diameter σ=3.208 Å, and range parameter R=1.73. Comparison figures quoted in the literature (based on fits to second virial coefficient measured at low densities) in the above units for ϵ/k_B and σ include (ϵ/k_B, σ, R) = (69.4, 3.162, 1.85) quoted in Hirschfelder, et. al. [8] and (93.3, 3.067, 1.70) found by Sherwood and Prausnitz [9]. Although these sets of comparison numbers look rather dissimilar, they lead to rather similar energy-volume products for the attractive parts of the potentials; and the weighted average (86.1, 3.096, 1.745) of these two sets (30% Hirschfelder plus 70% S&P) all lie within 1-4% of the (86.8, 3.208, 1.73) used for Fig. 1. Better agreement probably shouldn't be expected, among other reasons because effective molecular diameters change appreciably over the wide range of temperatures used for the second virial coefficient fits.

5. CONCLUSION

Our earlier work that ignored density variation of $\mathrm{g}_{repulsive}(T,\rho,\mathrm{r})$ in the RG calculations exhibited increasingly large deviations between theory and experiment for densities farther than about $0.5\rho_c$ from the critical point [2]. A procedure has been suggested here [Eqs. (6)-(9)] for incorporating temperature- and density-dependence of $\mathrm{g}_{repulsive}$ into the theory. A test against experimental data for argon suggests that this results in substantially improved agreement for densities farther from critical, down to zero density and on up to somewhat greater than $2\rho_c$.

FIGURE CAPTION

Fig. 1. (a) Calculated pressure isotherms for argon at temperatures T_r=T/T_c=0.9986 and 1.0152 (solid lines) compared with measurements of Michels, Levelt, and De Graaff [6]. (b) Deviations (perpendicular distances) between the measured data points and calculated curves; deviations are here included also for out of range data not shown in (a), at measured ρ/ρ_c, P/P_c equal to (2.03, 4.35), (2.14, 6.23) for T_r=0.9986, and (2.02, 4.72), (2.13, 6.64) for T_r=1.0152.

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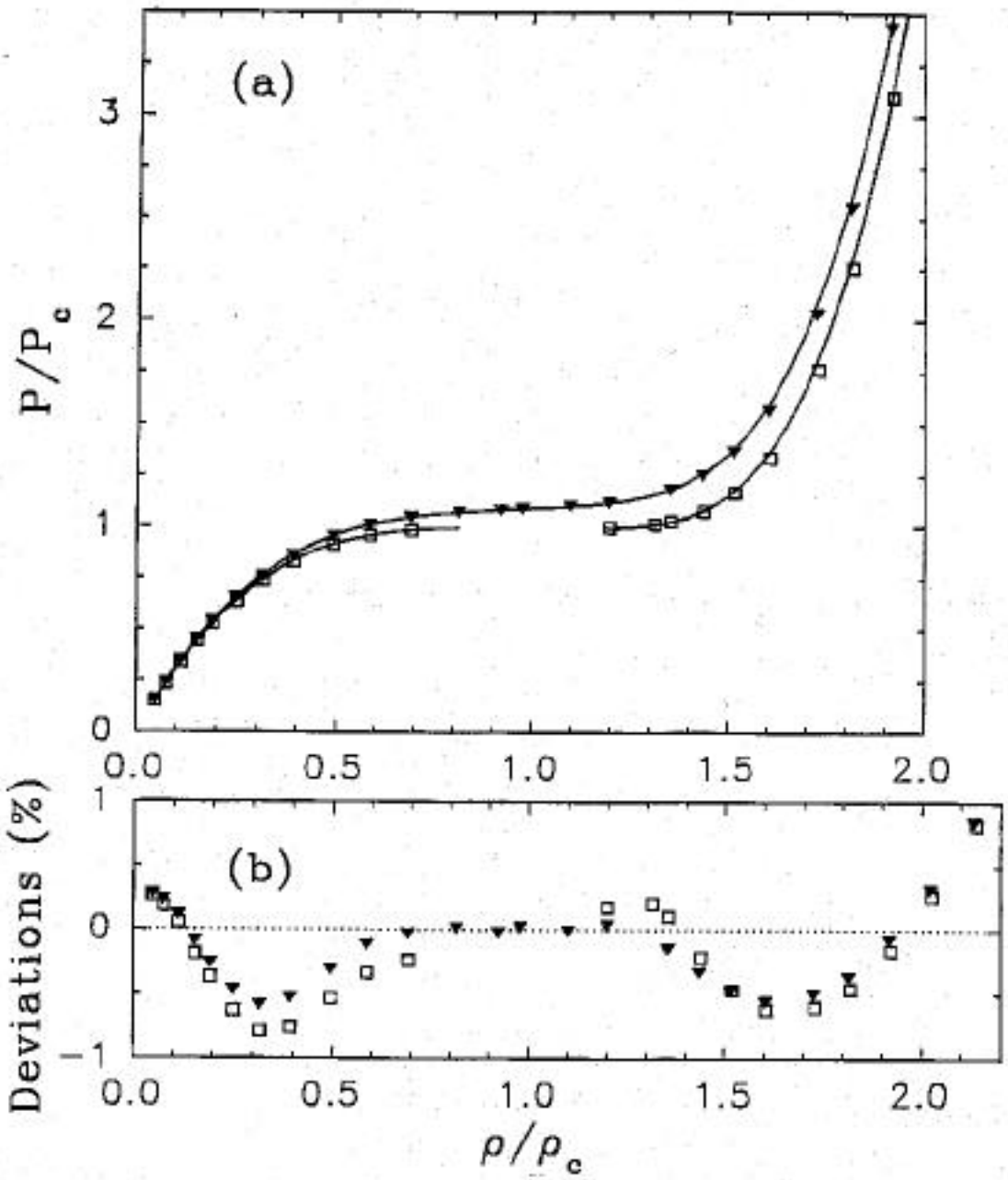

J. A. White and S. Zhang, Fig. 1