

## **Renormalization Group Theory for Fluids to Greater Density Distances from the Critical Point<sup>1</sup>**

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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, the 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.

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**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

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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 Ref. 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 Ref. 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 Refs. 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 account fully for 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  $\lambda_s$ , the grand partition function for the fluid contained within a domain  $\Omega$  of volume  $V(\Omega)$  and chemical potential  $\mu$  is expressed as [1]

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

The summation is taken over all fluctuations  $\rho_s(\mathbf{r})$  containing (only) wavelengths longer than  $\lambda_s$ . The  $\rho_s(\mathbf{r})$ , which appears also in the exponent, includes the constant (nonfluctuating) component of density,  $\bar{\rho}$ . In the exponential, the first term gives  $\beta\mu N$ , where  $\beta = 1/(k_B T)$ , and  $N$  is the total number of molecules in  $\Omega$  when the number density is given by  $\rho_s(\mathbf{r})$ . The  $f_s(T, \rho_s)$  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  $g_{\text{repulsive}}(T, \rho_s, r)$ , is the contribution to the free energy in  $\Omega$ , 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, the fluctuations associated with the steeply repulsive portions of the interaction potentials.

The calculation now proceeds by summing first over all fluctuations with wavelengths between  $\lambda_s$  and a longer wavelength,  $\lambda_1$ . The result can be expressed as

$$\sum_{[\rho_D(\mathbf{r})]} e^{-\beta \int_{\Omega} d\mathbf{r} f_D - \beta U_D} = e^{-\beta \int_{\Omega} d\mathbf{r} \delta f_1(T, \rho_1)} \quad (2)$$

where  $\rho_D = \rho_s - \rho_1$  is the portion of  $\rho_s$  that depends on wavelengths between  $\lambda_s$  and  $\lambda_1$ , and  $\rho_1$  is the portion that depends only on wavelengths  $\lambda \geq \lambda_1$ . In the exponents,  $f_D$  is shorthand for  $f_D(T, \rho_1, \rho_D) = f_s(T, \rho_s) - f_s(T, \rho_1)$ , where  $f_s(T, \rho_1)$  is the portion of  $f_s(T, \rho_s)$  that does not depend on  $\rho_D$  [obtained from  $f_s(T, \rho_s)$  by setting  $\rho_D = 0$ ], and analogously,  $U_D = U_s - U_1$ , where  $U_1$  is the portion of  $U_s$  that does not depend on  $\rho_D$ . The  $\delta f_1(T, \rho_1)$  is an increment of local free energy density that can now be added to  $f_s(T, \rho_1)$  to form a new—"renormalized"—function  $f_1(T, \rho_1)$  for use in an expression for the grand partition function that requires summations only over the remaining fluctuations, those with wavelengths  $\lambda \geq \lambda_1$ :

$$\Xi(T, \mu, \Omega) = \sum_{[\rho_1(\mathbf{r})]} e^{\beta \mu \int_{\Omega} d\mathbf{r} \rho_1(\mathbf{r}) - \beta \int_{\Omega} d\mathbf{r} f_1(T, \rho_1) - \beta U_1} \quad (3)$$

In the phase-space cell approximation used in Ref. 1, essentially that of Wilson [3], one sets  $\lambda_1 \simeq 2\lambda_s$  and treats the  $\rho_D$  as wave packets. They are taken to be coherent inside a volume  $V_D$  within which the variation of  $\rho_1$  can be neglected, and incoherent outside that volume. Designating within  $V_D$  the amplitude of the fluctuations  $\rho_D$  by  $x$  and writing  $U_D = V_D u_D$ , one then obtains from Eq. (2)

$$\delta f_1(T, \rho_1) = -\frac{1}{\beta V_D} \ln Q_D(T, \rho_1) \quad (4a)$$

where

$$Q_D(T, \rho_1) = Q_0(T, \rho_1) \int dx e^{-\beta V_D [f_D(T, \rho_1, x) + u_D(T, \rho_1, x)]} \quad (4b)$$

The  $Q_0(T, \rho_1)$  arises from the conversion of the summation over  $\rho_{\text{D}}(\mathbf{r})$  to an integral over  $x$ , and can be treated as substantially constant (only) when  $T$  and  $\rho_1$  do not change much, as when one is close to the critical point.

For a two-body potential, when one has reached wavelengths  $\lambda_s$  that are long compared with the range of the potential, the potential energy density  $u_{\text{D}}$  has a large portion proportional to  $x^2$  and independent of  $\lambda_s$  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  $Q_0(T, \rho_1)$  can be treated as a constant, one makes contact with previous RG treatments. Specifically, when  $f_{\text{D}}$  is written as

$$f_{\text{D}}(T, \rho_1, x) = [f_s(T, \rho_1 + x) + f_s(T, \rho_1 - x)]/2 - f_s(T, \rho_1) \quad (5)$$

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 the familiar near-critical-point recursion relations of Wilson and of Wilson and Fisher [2–4], independently of the numerical value of  $Q_0$ .

We are also concerned here with behavior when *not* near the critical point, and also when near the critical point for wavelengths  $\lambda_s$  that are *not* asymptotically long. We thus need to know how  $Q_0$  varies with temperature and with 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 to be limited to a theory of how thermal behavior varies as a function of distance from a critical point whose location remains unknown.)

To determine how  $Q_0$  changes as one moves away from the critical point and also its *actual* value at  $(T_c, \rho_c)$ , one can use the fact that in the mean field approximation, and also when  $\lambda_s$  is sufficiently small compared with the range of the attractive potential, the  $u_{\text{D}}$  in Eq. (4b) is negligibly small and makes no contribution to  $f_1(T, \rho_1)$ . Mathematically, then  $f_1(T, \rho_1) = f_s(T, \rho_1)$ , i.e.,  $\delta f_1(T, \rho_1) = 0$ . According to Eq. (4a), the corresponding  $Q_{\text{D}}(T, \rho_1)$  is simply equal to unity. Thus,  $Q_0(T, \rho_1)$  equals the reciprocal of the integral in Eq. (4b) when  $u_{\text{D}} = 0$ . Designating the  $Q_{\text{D}}$  for  $u_{\text{D}} = 0$  by  $Q_{\text{D, LR}}$ , where “LR” refers to the attractive potential assumed to have a range that is sufficiently long compared with  $\lambda_s$  so that to good approximation  $u_{\text{D}} = 0$ , then Eq. (4a) can be rewritten equivalently as

$$\delta f_1(T, \rho_1) = -\frac{1}{\beta V_{\text{D}}} \ln \frac{Q_{\text{D}}(T, \rho_1)}{Q_{\text{D, LR}}(T, \rho_1)} \quad (4c)$$

The argument of the logarithm is now the ratio of two integrals, in which the common factor  $Q_0(T, \rho_1)$  cancels out. The result in Eq. (4c) takes into

account the  $Q_0(T, \rho_1)$  that enters in Eq. (4b), including its dependence on  $T$  and  $\rho$ ; the increments  $\delta f_1$  given by Eq. (4c) are *fully* determined (not just to an unknown constant multiple) once one specifies the averaging volume,  $V_D$ , the central wavelength  $\lambda_D$  in the wavepacket  $\rho_D$ , and the intermolecular potential [which determines the  $u_D$  that appears in Eq. (4b)].

### 3. NEW CALCULATIONS

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

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

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

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

$$= -a(T, \rho_s) \rho_s^2 \quad (7b)$$

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

$$u_{D, \text{SR}}(T, \rho_1, x) = [u_s(T, \rho_1 + x) + u_s(T, \rho_1 - x)]/2 - u_s(T, \rho_1) \quad (8a)$$

Here the subscript "SR" to  $u_D$  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,  $u_D$  is smaller by a factor  $(1 - D)$ ,

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

where  $D$  is a number between zero and one. For a simple sinusoidally varying density fluctuation of the form  $\rho_D = \rho_0 \cos(\mathbf{k} \cdot \mathbf{r} + \phi)$ , and  $g_{\text{repulsive}}$  evaluated at density  $\rho$ , the factor  $(1 - D)$  is given by

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

where

$$U_{2,k} = \int_{\Omega} d\mathbf{r} \cos(\mathbf{k} \cdot \mathbf{r}) U_2(r) g_{\text{repulsive}}(T, \rho, r) \quad (9b)$$

is the cosine Fourier component of  $U_2(\mathbf{r}' - \mathbf{r}) g_{\text{repulsive}}(T, \rho, \mathbf{r}' - \mathbf{r})$ , and  $U_{2,0}/V(\Omega) = -a(T, \rho)$ . In calculations to follow, the density  $\rho$  used in  $g_{\text{repulsive}}$  in Eq. (9) has been taken to be the average density  $\bar{\rho}$  in  $V(\Omega)$ .

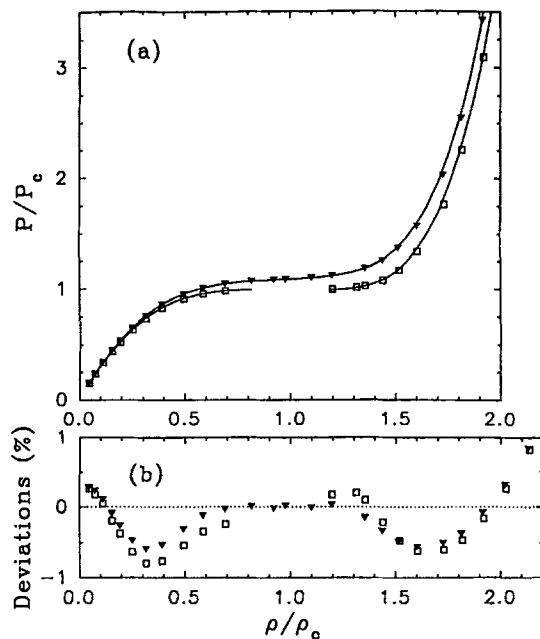
In our earlier work that focused on behavior closer to the critical point [1, 2], a simplifying approximation was made. It is equivalent to replacing everywhere the actual  $g_{\text{repulsive}}(T, \rho, r)$  by  $g_{\text{repulsive}}(T_c, \rho_c, r)$ , and the product  $U_2(r) g_{\text{repulsive}}(T_c, \rho_c, r)$  by a temperature- and density-independent "effective"  $U_2(r)$ . When this is done, it is easily verified that Eqs. (6)–(9) above yield Eqs. (10) and (11) in Ref. 1, with the  $a(T, \rho)$  in those equations and in Eq. (14) replaced by  $a = a(T_c, \rho_c) = \text{const}$ . In the present investigation this simplifying approximation and the further approximations expressed by Eq. (12) and the choice  $D_0 = 1$  in Ref. 1 were *not* employed.

#### 4. RESULTS FOR ARGON

Equations (4)–(6), (8), and (9) were evaluated numerically for the square-well potential  $U_2(r)$  and for hard-sphere  $g_{\text{repulsive}}(\rho, r)$  given in tables published by Throop and Bearman [5] for values of  $\rho\sigma^3$  in the range 0 to 1.1 ( $\sigma = \text{sphere diameter}$ ). 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  $\lambda_D = 2\pi/k$  employed in Eq. (9b). For the work reported here, wavelengths  $\lambda_D$  were chosen to be multiples  $t^n$  ( $t = 2.0$ ;  $n = 1, 2, 3, \dots$ ) of a reference wavelength  $\lambda_{D0} = yR\sigma$  ( $R\sigma = \text{range of the attractive square-well potential}$ ), with  $y = 1.04$ ; and the coherence volume  $V_D$  was chosen for each  $\lambda_D$  to be of size  $V_D = (z\lambda_D/2)^3$ , with  $z = 1.12$ . [For wavelengths  $\lambda = t^n\lambda_{D0}$ , with  $n = 0, -1, -2, -\dots$ , i.e., as small as or smaller than  $\lambda_{D0}$ , fluctuation contributions given by Eq. (4) can be expected to be negligible, resulting from the then rapid oscillation of  $\cos(\mathbf{k} \cdot \mathbf{r})$  in Eq. (9b).] From theoretical considerations one can expect best choices for  $y$  and  $z$  to be close to unity. It was not possible at this time to determine  $y$  and  $z$  more exactly from theory, so they were assigned the somewhat arbitrary, empirical values given 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  $(T_c, \rho_c, P_c)$  for argon, are illustrated in Figs. 1a and b for the two measured [6] argon pressure isotherms closest to the critical temperature. The root-mean-square deviation (perpendicular distance between the experimental data point and the theoretical curve) for all of the data is less than 0.5% (to be exact, 0.41%), with maximum absolute deviations of less than 1% for these two isotherms (maximum deviations were +0.84 and  $-0.79\%$ ). Theoretical curves calculated *without* any fluctuation contributions [Eqs. (4a) and (4b)], 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 of approximately 0.9 to  $1.7\rho_c$ . [This illustrates the size of the aggregate contribution of the fluctuations



**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 by Michels et al. [6]. (b) Deviations (perpendicular distances) between the measured data points and the calculated curves; deviations are also included for out-of-range data not shown in a, at measured  $\rho/\rho_c, P/P_c$  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  $T_r = 1.0152$ .

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. 1d of White [7] (difference between dashed and solid lines), where calculations were performed using a less accurate approximation.]

The calculated results for argon presented in Figs. 1a and b assumed a square-well of depth  $\varepsilon/k_B = 86.8$  K, an inner diameter of  $\sigma = 3.208$  Å, and a range parameter  $R = 1.73$ . Values quoted in the literature (based on fits to second virial coefficients measured at low densities) in the above units for  $\varepsilon/k_B$  and  $\sigma$  include  $(\varepsilon/k_B, \sigma, R) = (69.4, 3.162, 1.85)$  quoted by Hirschfelder et al. [8] and  $(93.3, 3.067, 1.70)$  found by Sherwood and Prausnitz [9]. Although these sets of values 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% [8] plus 70% [9]) all lie within 1 to 4% of the  $(86.8, 3.208, 1.73)$  used for Fig. 1. Better agreement probably should not 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 the density variation of  $g_{\text{repulsive}}(T, \rho, r)$  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 proposed here [Eqs. (6)–(9)] for incorporating the temperature- and density dependence of  $g_{\text{repulsive}}$  into the theory. A test against experimental data for argon suggests that this procedure results in substantially improved agreement for densities farther from critical, down to zero density, and up to somewhat greater than  $2\rho_c$ .

A recent review [10] discusses in detail an alternative to the present approach for treating the liquid-state and critical phenomena and includes some background discussion and an extensive list of references.

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