

# Application of the Functional Renormalization Group Method to Classical Free Energy Models

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*A simple functional renormalization group method is presented to correct the behavior of classical free energy models near the critical point. This approach is applied to the Soave–Redlich–Kwong equation of state to illustrate its ability to better reproduce the phase behavior of simple fluids and to understand the influence of its parameters on the shape of the vapor–liquid phase diagram. The method is then extended to account for the correlations induced by intramolecular bonds. It is then applied to a first-order thermodynamic perturbation theory for chain fluids to examine fluids composed of linearly bonded Lennard–Jones atoms. Unlike previous approaches for applying renormalization group corrections to chain fluids, this is able to accurately reproduce the critical point without predicting an overly flat liquid–vapor coexistence region. © 2015 American Institute of Chemical Engineers AIChE J, 61: 2985–2992, 2015*

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## Introduction

Large-scale density fluctuations lead to universal scaling behavior of the free energy of a fluid near the critical point. These take the form of nonanalytic behavior of the free energy, which are not present in the classical free energy models typically used by engineers to describe the thermodynamic behavior of fluids. As a consequence, there can be significant deviations of the predictions of these free energy models from experimentally observed results.

Much of the early work in describing this nonclassical phenomena originally focused only on states near the critical region. Phenomenological approaches have been used to combine the results of this work with classical thermodynamic models in order to construct a free energy model that has the correct scaling behavior in the critical regime and the classical behavior of the original model away from the critical point. This crossover approach has been applied to several classical free energy models, including cubic equations of state,<sup>1–3</sup> the perturbation theory for square-well fluids,<sup>4</sup> and statistical associated fluid theory (SAFT).<sup>5,6</sup>

Another method which gained popularity is the phase-space cell approximation, which was originally developed by Wilson<sup>7,8</sup> and extended to describe the behavior of simple fluids by White and coworkers.<sup>9–11</sup> This approach was later modified,<sup>12</sup> including mixtures,<sup>13</sup> and cubic equations of state.<sup>14</sup> This method is relatively easy to apply to any free energy model.

There have been several attempts in recent years to apply the phase-space cell method to fluids containing chain mole-

cules.<sup>15–17</sup> Typically, these formulations are based on the SAFT or related equations of state. These types of theories account for the connectivity of the molecules only in a local fashion. When the phase-space cell method has been applied to long chain systems, it has been observed that the predicted vapor–liquid coexistence curve becomes spuriously broad and flat.<sup>15–17</sup> This artifact is due, in part, to the neglect of density correlations that arise from the intramolecular bonding in the system.

It has been recognized that forms of the free energy of chain molecules that only depend on the polymer concentration through the monomer packing fraction lead to the wrong scaling behavior of the second virial coefficient with polymer molecular weight.<sup>18</sup> These include SAFT and the Flory–Huggins models. Attempts have been made to combine the renormalization group for polymers with the SAFT equation for linear<sup>19</sup> and star polymers,<sup>20</sup> however, these were limited to the good solvent regime and do not apply to phase separating systems.

A rigorous, molecularly based approach to applying the renormalization group method to classical fluids is the hierarchical reference theory (HRT).<sup>21–23</sup> This method accounts for the influence of long-range density fluctuations by examining the changes in the free energy of a fluid with changes in the underlying interaction potential. Using a theory for fluid structure, such as an integral equation theory, a direct connection is made with the underlying molecular properties of the system. HRT is able to accurately describe the crossover from the universal behavior of the free energy near the critical point to its more specific, molecularly dependent properties outside the critical region. This method has been successful in describing the properties of simple fluids<sup>21,22</sup> and mixtures.<sup>24</sup> The main shortcomings of this approach are its complexity and computational requirements.

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Still another approach is the functional renormalization group (FRG) method,<sup>25</sup> which has found many applications in the areas of quantum field theory and condensed matter physics. Recently, a close connection between FRG and HRT has been found.<sup>26</sup>

Ionescu et al. have formulated<sup>27</sup> a smooth cutoff version of HRT and demonstrated its application to the  $\phi^4$  model. This functional renormalization approach offers a simple method for providing critical corrections to classical free energy models. In this work, we demonstrate its application. In addition, we provide a slight generalization of this method to account for the correlations in chain molecules.

The remainder of this article is organized as follows. In the next section, we discuss the functional renormalization method and present a rough derivation for its application to free energy models for classical fluids. Afterward, we apply this functional renormalization method to a cubic equation of state. We then discuss the issue of critical corrections for chain molecules, and then generalize the method to apply to fluid composed of extended molecules. Finally, this method is used to describe the phase behavior of a Lennard-Jones chain fluid.

## Functional Renormalization Group Method

In this section, the basic ideas behind the FRG method and its application to classical fluids are discussed. We consider a simple fluid that interacts with a pairwise additive potential  $u$ , which can be divided as

$$u(r) = u_{\text{ref}}(r) + u_l(r) \quad (1)$$

where  $u_l$  is the attractive portion of the interaction potential between molecules in the system, and  $u_{\text{ref}}$  is the shorter ranged repulsive portion of the interaction potential. Typically, we assume that the free energy functional  $F_{\text{ref}}[\rho]$  (where  $\rho(\mathbf{r})$  is some density profile) of a fluid that interacts only with the reference portion of the potential  $u_{\text{ref}}$  is known.

The grand partition function  $\Xi$  of the classical molecular system can be formally written as a functional integral<sup>12</sup>

$$\Xi[\gamma] = \int \mathcal{D}\rho(\cdot) \exp \left\{ \int d\mathbf{r} \gamma(\mathbf{r}) \rho(\mathbf{r}) - \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) u_l(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') - F_{\text{ref}}[\rho] \right\} \quad (2)$$

where  $\beta = (k_B T)^{-1}$  with  $T$  being the absolute temperature of the system and  $k_B$  being the Boltzmann constant, and  $\gamma$  is an applied external field. The functional integral over  $\rho$  represents the summation of the exponential term evaluated at all permissible “shapes” of the density profile in the system. This expression is formally exact, however, in practice it is not possible to evaluate without making further approximations.

One method to approximate the functional integral is to completely neglect the fluctuations in the density profile, and to simply take the largest value of the integrand. This leads directly to the mean-field approximation<sup>28</sup>

$$F[\rho] \approx F_{\text{ref}}[\rho] + \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) u_l(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') \quad (3)$$

where  $F$  is the free energy function of the fluid with the pairwise interaction potential  $u = u_{\text{ref}} + u_l$ . This approximation is fairly good away from the critical point; however, near the critical regime, density fluctuations make a significant contri-

bution to the properties of the system, and the mean-field approximation becomes increasingly poor.

Rather than attempting to evaluate the entire contribution of the density fluctuations at once, another approach is to try to sequentially integrate the density fluctuations of increasing wavelength in order to obtain a series of approximations to the free energy. The rationale behind this is that it may be easier to approximate the change of the free energy due to a limited set of fluctuations. This is the idea behind the renormalization group method.

The starting point of this method is to assume that we know the free energy functional  $F_\Lambda[\rho]$ , which is the free energy functional that includes fluctuations on length scales less than  $2\pi\Lambda^{-1}$  and neglects those with a lower wavenumber. Note that a good approximation for  $F_\Lambda[\rho]$  is easier to obtain than  $F[\rho]$ , because small wavelength fluctuations (i.e., fluctuations with wavenumbers greater than  $2\pi/\sigma$ , where  $\sigma$  is the size of a molecule) are usually strongly suppressed by excluded volume interactions. We assume that a good approximation for the functional  $F_\Lambda$  is available, for some value of  $\Lambda \sim 2\pi/\sigma$ . The grand partition function given in Eq. 2 can be rewritten as<sup>12</sup>

$$\Xi[\gamma] = \int_\Lambda \mathcal{D}\rho(\cdot) \exp \left\{ \int d\mathbf{r} \gamma(\mathbf{r}) \rho(\mathbf{r}) - \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) u_l(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') - F_\Lambda[\rho] \right\} \quad (4)$$

where the functional integral over the density is now restricted to fluctuations with wavenumbers less than  $\Lambda$ .

To implement the renormalization group method, we construct a series of approximations to the grand partition function  $\Xi_Q$ , where only density fluctuations of wavenumber greater than  $Q$  and less than  $\Lambda$  are integrated over. If  $Q \geq \Lambda$ , then the free energy functional associated with  $\Xi_Q$  will be equal to

$$F_\Lambda[\rho] + \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) u_l(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}')$$

as all density fluctuations will be suppressed, and the mean-field approximation will be valid.

The grand partition function of a system in the absence of density fluctuations with a wave number below  $Q$  can in principle be evaluated by adding an additional two-body interaction  $R_Q$  to the system which will suppress long-range fluctuations

$$\Xi_Q[\gamma] = \int_\Lambda \mathcal{D}\rho(\cdot) \exp \left\{ \int d\mathbf{r} \gamma(\mathbf{r}) \rho(\mathbf{r}) - \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) u_l(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) R_Q(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') - F_\Lambda[\rho] \right\} \quad (5)$$

The precise form of the cutoff function  $R_Q$  is arbitrary, however, it must satisfy some key requirements.<sup>23</sup> First, its Fourier transform  $\hat{R}_Q(q)$  must be a monotonic function of  $q$  and vanish rapidly as  $q$  becomes very large. This ensures that it does not influence the functional integration over density profiles with a short wavelength. In addition, it should become large as  $q \leq Q$ ; this is the mechanism by which it suppresses the contribution of large wavelength fluctuations. In this work, we use the “optimized” cutoff function suggested by Litim<sup>29,30</sup>

$$\hat{R}_Q(q) = K(Q^2 - q^2) \Theta(Q - q) \quad (6)$$

where  $\Theta$  is the Heaviside step function, and  $K$  is an arbitrary constant.

We do not want to directly evaluate the functional integral in Eq. 5. Rather, we want to know how the free energy changes with respect to changes in  $Q$ , given by changes in  $R_Q$  which can be interpreted as changes in the interaction potential in the system. The functional derivative of the free energy functional with respect to the pair potential  $u$  between molecules in the system is given by<sup>28,31</sup>

$$\frac{\delta F}{\delta u(|\mathbf{r}-\mathbf{r}'|)} = \frac{\beta}{2} \rho_2(\mathbf{r}, \mathbf{r}') \quad (7)$$

where  $\rho_2$  is the two-body density function.

Therefore, the change in the free energy  $F_Q$  of the system, corresponding to the grand partition function  $\Xi_Q$ , due to a change in  $Q$  can be written as

$$\frac{\partial F_Q}{\partial Q} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_Q^{(2)}(\mathbf{r}, \mathbf{r}') \frac{\partial R_Q(|\mathbf{r}-\mathbf{r}'|)}{\partial Q} \quad (8)$$

For convenience, a modified free energy  $\mathcal{F}_Q$  is introduced, which excludes the interaction energy introduced by the cutoff function

$$\mathcal{F}_Q[\rho] = F_Q[\rho] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) R_Q(|\mathbf{r}-\mathbf{r}'|) \rho(\mathbf{r}') \quad (9)$$

which approaches the original free energy functional in the limit  $Q \rightarrow 0$ . This removes the influence of the cutoff function on the properties of the system at a mean-field level. The variation of the modified free energy with  $Q$  is then given by

$$\frac{\partial \mathcal{F}_Q}{\partial Q} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left[ \rho_Q^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}) \rho(\mathbf{r}') \right] \frac{\partial R_Q(|\mathbf{r}-\mathbf{r}'|)}{\partial Q} \quad (10)$$

The term in the square brackets in Eq. 10 can be written in terms of the direct correlation function  $c_Q$  of the system, which is related to the free energy functional as

$$\frac{\delta^2 F_Q}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = \frac{1}{\rho(\mathbf{r})} \delta^d(\mathbf{r}-\mathbf{r}') - c_Q(\mathbf{r}, \mathbf{r}') \quad (11)$$

where  $\delta^d$  is Dirac delta function in  $d$  dimensions ( $d = 3$  in this work). Substituting the direct correlation function, we find<sup>27</sup>

$$\frac{\partial \mathcal{F}_Q}{\partial Q} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left[ \frac{1}{\rho(\mathbf{r})} \delta^d(\mathbf{r}-\mathbf{r}') - c_Q(\mathbf{r}, \mathbf{r}') + R_Q(|\mathbf{r}-\mathbf{r}'|) \right]^{-1} \frac{\partial R_Q(|\mathbf{r}-\mathbf{r}'|)}{\partial Q} \quad (12)$$

For a uniform fluid, where the average properties of the system do not vary spatially, this reduces to

$$\frac{\partial f_Q}{\partial Q} = \frac{\rho}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[ 1 - \rho \hat{c}_Q(q) + \rho \hat{R}_Q(q) \right]^{-1} \frac{\partial \hat{R}_Q(q)}{\partial Q} \quad (13)$$

where  $f_Q = \mathcal{F}_Q/V$  is the modified free energy density. This equation is exact and gives the flow of the free energy with respect to the cutoff wavenumber  $Q$ .<sup>27</sup>

To implement this renormalization process, we require a model for the direct correlation function in the fluid. Within the HRT, this is typically done through using the Ornstein–Zernike equation combined with an approximate closure relation (e.g., mean spherical approximation, hypernetted chain approximation, self-consistent Ornstein–Zernike approximation, etc.).

The key element of HRT is that although simple approximations do not lead to the correct long-range behavior of the cor-

relation function, they do give a fairly accurate description of the short-ranged correlations in a fluid. Consequently, rather than directly trying to compute all the correlations in a fluid, a better strategy is to approximate the difference in the correlation function between fluids with slightly differing interaction potentials.

To develop a practical procedure, we assume that the free energy can be approximated by a local functional given by a truncated gradient expansion in terms of the density

$$F_Q[\rho] \approx \int d\mathbf{r} \left[ f_Q(\rho(\mathbf{r})) - \frac{B}{2} \nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r}) + \dots \right] \quad (14)$$

where  $B$  is a parameter that is related to the range of the interactions/correlations in the system. In general, when a free energy functional is put through the RG process, new terms will be generated. A free energy which is originally local will have nonlocal terms. Nonlocal terms that are generated by the renormalization process are neglected.

For this simple form for the free energy, the direct correlation function is given by (see Eq. 11)

$$\rho^{-1} - c_Q(q) = f_Q''(\rho(\mathbf{r})) + Bq^2 + \dots \quad (15)$$

where prime denotes a derivative with respect to density. This makes the assumption that the parameter  $B$  is independent of density, although it can still be temperature dependent. To get a rough idea of the value of  $B$ , we note that the direct correlation function is equal to the interaction potential at very large separations. Therefore, at small values of  $q$ , we have approximately<sup>28</sup>

$$\hat{c}_Q(q) \approx -\beta \hat{u}_l(q) + \dots \quad (16)$$

By expanding the above relation in powers of  $q$ , we can estimate

$$B \approx -\frac{4\pi}{3!} \int_0^\infty dr r^4 \beta u_l(r) \quad (17)$$

From this, we ascertain that  $B$  is roughly proportional to the strength of the attractive potential and inversely proportional to temperature.

By substituting the simple approximation for the direct correlation function given in Eq. 15 into Eq. 13 and choosing  $K = B$  in the cutoff function (see Eq. 6), we find that the integral over the wavevector  $q$ , which appears in Eq. 13, can be performed analytically. This leads to a nonlinear partial differential equation for the free energy as a function of the cutoff wavevector  $Q$ .<sup>27</sup>

$$Q \frac{\partial f_Q}{\partial Q} = \frac{K_d B Q^5}{f_Q'' + B Q^2} \quad (18)$$

where in three dimensions the constant  $K_d = 1/(6\pi^2)$ .

In general, Eq. 18 can be applied to any free energy model in order to correct its behavior near the critical point. This nonlinear partial differential equation can be solved to determine the evolution of the free energy with  $Q$ , where density fluctuations of larger and larger wavelengths are taken into account. The initial condition is taken at the cutoff  $Q = \Lambda$  of the original free energy<sup>27</sup>

$$f_\Lambda = f$$

where  $f$  is the original, classical model for the free energy. The corresponding boundary conditions are that  $f_Q$  is fixed at the

**Table 1. Estimates of the Critical Exponents from the Phase-Space Cell (PSC) Approximation and the Functional Renormalization Group (FRG) Method**

| Exponent | Exact <sup>32</sup> | Classical | PSC <sup>8</sup> | FRG <sup>27</sup> |
|----------|---------------------|-----------|------------------|-------------------|
| $\alpha$ | 0.110               | 0.000     | 0.17             | 0.050             |
| $\beta$  | 0.327               | 0.500     | 0.34             | 0.330             |
| $\gamma$ | 1.237               | 1.000     | 1.22             | 1.300             |
| $\delta$ | 4.789               | 3.000     | 4.80             | 5.000             |
| $\eta$   | 0.036               | 0.000     | 0.00             | 0.000             |

original value of  $f$  at  $\rho = 0$  and for some high value of  $\rho$ , which is always far from the critical density. The actual free energy of the system corresponds to the limit  $Q \rightarrow 0$ .

Typically, the original free energy will have classical values of the critical exponents, which are summarized in Table 1. This renormalization process leads to a free energy with non-classical critical exponents,<sup>27</sup> which are shown in the final column of Table 1. Note that the critical exponent  $\beta$ , which is related to the shape of the coexistence curve, should not be confused with the inverse temperature  $\beta = (k_B T)^{-1}$ . As a comparison, estimates of the “exact” values of the critical exponents,<sup>32</sup> as well as the predictions from the phase-space cell renormalization method, are also shown.

### Application to a Cubic Equation of State

To concretely illustrate the utility of Eq. 18, we apply the approximate FRG method presented in the previous section to the Soave–Redlich–Kwong (SRK) equation of state.<sup>33,34</sup> This is a cubic equation which is widely used in industry to describe the thermodynamic properties of fluids and fluid mixtures. The pressure is given by

$$p = \frac{\rho k_B T}{1 - \rho b} - \frac{\rho a(T)}{1 + \rho b} \quad (19)$$

where  $a(T)$  is a temperature dependent parameter relating to the strength of the intermolecular attractions, and  $b$  is a parameter relating to the size of the molecules. The corresponding expression for the Helmholtz free energy density is

$$f(\rho, T)b = (\rho b)(\ln \rho b - 1) - (\rho b) \ln(1 - \rho b) - (\rho b) \frac{\beta a(T)}{b} \ln(1 + b\rho) \quad (20)$$

The critical point of the SRK equation of state is<sup>33,34</sup>

$$k_B T_c b / a(T_c) = 0.202677$$

$$p_c b^2 / a(T_c) = 0.0175999$$

$$\rho_c b = 0.259921$$

where  $T_c$  is the critical temperature,  $p_c$  is the critical pressure, and  $\rho_c$  is the critical density. The critical compressibility factor for this equation of state is  $Z_c = 1/3$ . The vapor-liquid coexistence curve of the SRK equation is shown in as the dashed line in Figure 1a. Because the SRK equation is analytical at the critical point, it has a critical exponent  $\beta = 0.5$ —the classical value. As a result, the coexistence curve has a shape which is much too sharp as compared to that typically found experimentally.

To apply the renormalization group transformation to the model free energy, the parameters  $\Lambda$  and  $B$  must first be specified. The parameter  $\Lambda$  represents the length scale for which fluctuations have already been incorporated in the classical free energy. For this, we expect  $\Lambda b^{1/3}$  of the order or smaller

than one and use it as a dimensionless parameter that can be varied. The parameter  $B$  which appears in the free energy functional shown in Eq. 14 relates to the gradient term of the density. Consequently, we expect it to be proportional to the strength of the intermolecular interactions. In addition, its range should be in the order on which the fluctuations have already been captured in the system. Therefore, for the SRK equation of state, we select  $B$  as

$$B = \beta a(T) \Lambda^{-2} \bar{B} \quad (21)$$

where  $\bar{B}$  is a dimensionless parameter, which can be adjusted to fit experimental data, and  $\beta = (k_B T)^{-1}$ .

The nonlinear partial differential equation in Eq. 18 is solved using the method of lines. The partial derivatives of the free energy with respect to density are performed using the central difference method. The resulting set of first-order ordinary differential equations are solved using the SUNDIALS 2.5.0 software library.<sup>35</sup>

Figure 1 shows the vapor-liquid phase diagram as predicted by the SRK equation of state and as modified by the renormalization group transformation given by Eq. 18. In this figure, the  $\bar{B}$  parameter is held fixed, while  $\Lambda b^{1/3}$  is varied. Note that we assume that density fluctuations with a wavelength smaller than  $2\pi/\Lambda$  have already been incorporated into the original free energy. Applying the renormalization group process will incorporate density fluctuations of larger wavelengths  $2\pi/Q$  by integrating the flow equation, Eq. 18, over  $Q$  toward increasingly smaller values. If the parameter  $\Lambda$  is set to zero, then the original free energy is retained because all size fluctuations have already been incorporated. The larger the value of  $\Lambda$ , the more fluctuations need to be added to the original free energy, which tends to have a stabilizing influence. From Figure 1a, we see that increasing the value of  $\Lambda$  decreases the critical temperature and increases the flatness of the vapor-liquid phase envelop. This is a consequence of increasing the size of the critical region. Inside the critical region, the system is dominated by fluctuations, and the value of the critical exponent  $\beta$  (which is equal to 0.330 within the approximate FRG method that is used in this work) dictates the shape of the vapor-liquid coexistence curve. Outside this region, the shape of the coexistence curve is well described by mean-field theory, which has  $\beta = 0.5$ , leading to a “sharper” shape. In addition, the coexistence pressure tends to increase (see Figure 1b).

The affect of varying the parameter  $\bar{B}$ , while holding  $\Lambda$  fixed, on the phase diagram is shown in Figure 2. Increasing the value of  $\bar{B}$  decreases the critical temperature, gradually flattening the top of vapor-liquid phase envelop. Recall that the  $B$  parameter is the prefactor to the gradient term in the free energy functional (see Eq. 14). It gives a penalty for variations in the density distribution in the system: large values of this parameter disfavor density fluctuations. Therefore, increasing  $\bar{B}$  suppresses these stabilizing fluctuations and, consequently, increases the size of the vapor-liquid coexistence region.

The parameter  $\bar{B}$  does not have as pronounced an affect on the vapor pressure curve, as on the coexistence phase envelop (see Figure 2b). The vapor pressure curves calculated with different values of  $\bar{B}$  appear to be quite similar, although they stop at lower values of the pressure and temperature for larger values of  $\bar{B}$ .

### The Influence of Intramolecular Correlations

The renormalization group method described above accounts for large scale density fluctuations, where different



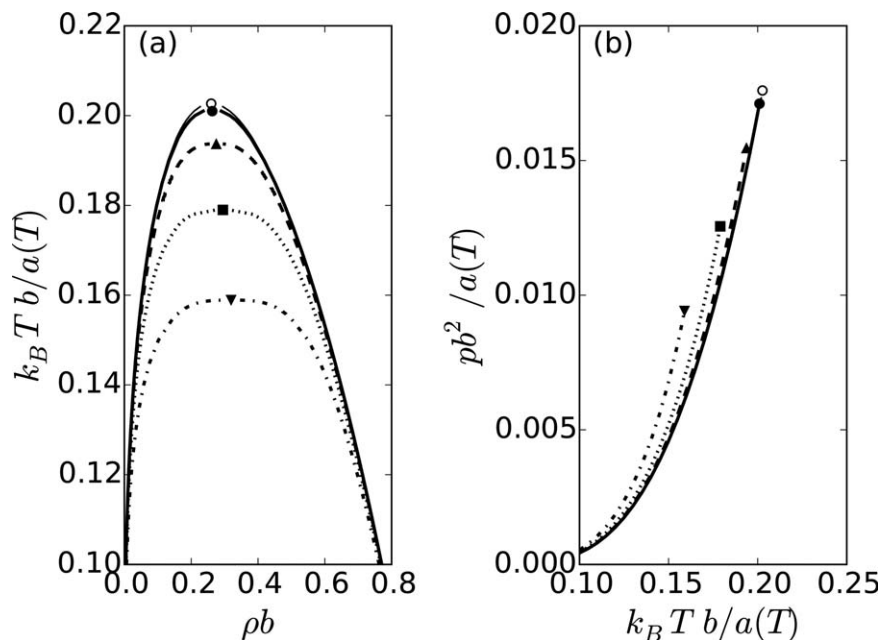


Figure 1. The vapor-liquid coexistence curve (a) and the vapor pressure (b) as determined by the SRK equation of state and the renormalization group with  $B=1$  and (1)  $\Lambda b^{1/3}=0.5$  (solid line, filled circle), (2)  $\Lambda b^{1/3}=1$  (dashed line, filled triangle up), (3)  $\Lambda b^{1/3}=1.5$  (dotted line, filled square), and (4)  $\Lambda b^{1/3}=2$  (dashed-dotted line, filled triangle down).

The thin solid line is for the SRK equation of state. The symbols denote the critical point. The open circle denotes the critical point of the SRK equation of state.

sections of the system are coupled mainly by intermolecular interactions. The extent and strength of these correlations are characterized by the parameter  $B$ . However, the method does not account for other types of correlations that may occur in

the system. In the case of chain molecules, the bonds which connect the monomers within the molecule lead to correlations between them. While at moderate to high monomer concentrations, these correlations are typically screened down to

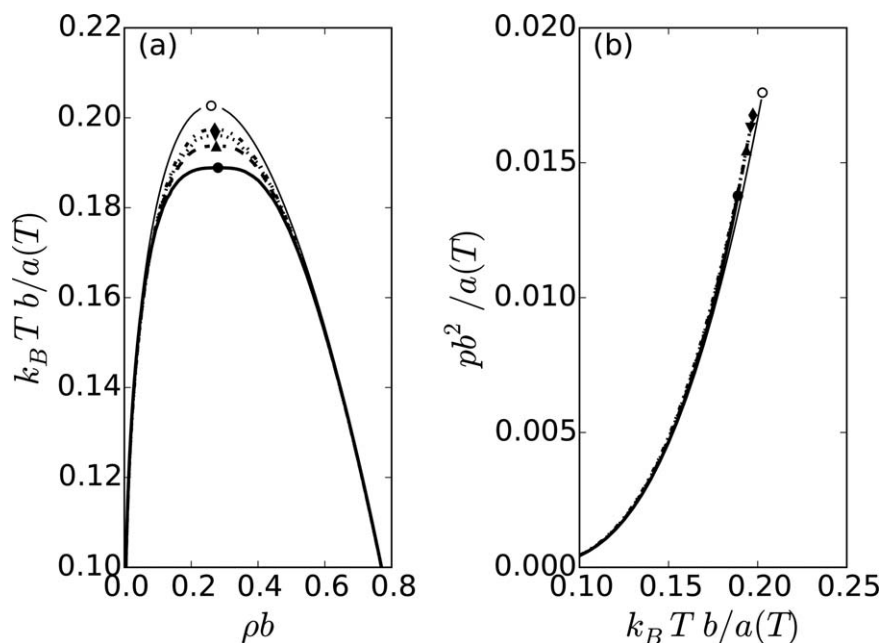


Figure 2. The vapor-liquid coexistence curve (a) and the vapor pressure (b) as determined by the SRK equation of state and the renormalization group with  $\Lambda b^{1/3}=1$  and (1)  $\bar{B}=0.5$  (solid line, filled circle), (2)  $\bar{B}=1$  (dashed line, filled triangle up), (3)  $\bar{B}=1.5$  (dotted line, filled square), and (4)  $\bar{B}=2$  (dashed-dotted line, filled triangle down).

The thin solid line is for the SRK equation of state. The symbols denote the critical point. The open circle denotes the critical point of the SRK equation of state.

monomer length scales, at low densities, these correlations extend to the size of the molecules, which for polymers or other macromolecules can be much larger than the monomer size.

These correlations tend to reduce the density fluctuations in the system.<sup>36</sup> In the renormalization group methods developed to correct the critical behavior of classical free energies for simple liquids (such as the phase-space cell method or the method described in the previous section of this work), the correlations due to intramolecular bonding are neglected. As a consequence, attempting to empirically adjust the parameters of the method to fit empirical or simulation data can lead to anomalies, such as the vapor-liquid coexistence curve being much too flat (e.g., see Figs. 1 and 7 in Ref. 15 or Fig. 5 in Ref. 16).

To better understand the influence of chain connectivity on the correlations in a solution, we examine an ideal gas of linear chains, each consisting of  $N$  bonded monomers. In this case, the scattering function  $S(q)$  of the monomers in the system<sup>36</sup>

$$S(q) \approx N[1 + q^2 R_g^2/3 + \dots]^{-1} \quad (22)$$

where  $R_g$  is the radius of gyration of the molecules, and  $\rho$  is the monomer number density. The corresponding expression for the direct correlation function is

$$\rho^{-1} - \hat{c}(q) \approx \frac{1}{N\rho} [1 + q^2 R_g^2/3 + \dots] \quad (23)$$

The prefactor outside the square brackets on the right of Eq. 23 represents the inverse isothermal compressibility of an ideal gas. This characterizes the strength of the monomer density fluctuations in the system. The second term inside the square brackets denotes the influence of bonding on the correlations in the system.

Generalizing this ideal gas expression for the direct correlation function to a system where the monomers have size and interact, we find<sup>36</sup>

$$\rho^{-1} - \hat{c}_Q(q) = f_Q''(\rho) + Bq^2 + \frac{1}{3} \frac{R_g^2}{N\rho} q^2 + \dots \quad (24)$$

The first two terms in Eq. 24 are precisely the same as those for the simple liquid. The third term represents the correlations in the system due to the connectivity of the monomers in the chain. At low densities, the connectivity induces correlations in the monomer density profile on length scales larger than the monomer size. As the density increases, these correlations are screened, with a characteristic decay length  $\lambda$  that varies as<sup>36</sup>

$$\lambda^2 = \frac{1}{3} \frac{R_g^2}{N\rho f_Q''(\rho)}$$

Substituting this expression for the direct correlation function into Eq. 13, we can again analytically evaluate the integral over  $q$ . In this case, the flow equation for the free energy becomes

$$Q \frac{\partial f_Q}{\partial Q} = \frac{K_d B Q^5}{(f_Q'' + B Q^2)} \frac{3}{(Ql)^2} \left[ 1 - \frac{1}{Ql} \arctan Ql \right] \quad (25)$$

where  $\xi^2 = R_g^2/(3N)$  is a length scale relating to a scaled size of the molecules in the system, and  $l^2 = \rho^{-1} \xi^2 / (f_Q'' + B Q^2)$ .

In the limit that the molecules are small compared to the other correlation lengths in the system,  $\xi \rightarrow 0$ , and this equa-

tion reduces to Eq. 18. The critical corrections only become significant when the wavelength of the density fluctuations becomes larger than the size of the molecules (which may be much larger than the monomer size).

## Application to Chain Molecules

In this section, the properties of linear chains composed of atoms interacting through the Lennard-Jones potential (where  $\varepsilon$  is the energy scale, and  $\sigma$  is the size parameter) are examined. Each chain in the system consists of  $N$  Lennard-Jones atoms bonded to each other with a bond length  $l$ . The thermodynamics of the system is modeled using the first-order thermodynamic perturbation theory (TPT; also referred to as the soft-SAFT theory) developed by Johnson et al.<sup>37</sup>

The Helmholtz free energy is considered to be composed of a contribution from a fluid of disconnected Lennard-Jones atoms  $f^{\text{ref}}$  and a contribution due to the bonding of the atoms within the chains. The resulting expression for the residual Helmholtz free energy density  $f^{\text{res}}$  (the difference between the Helmholtz free energy density of the system and that of an ideal gas at the same temperature and density) is

$$f^{\text{res}} = f^{\text{ref}} + f^{\text{chain}} \quad (26)$$

where  $f^{\text{ref}}$  is the residual Helmholtz free energy density of a Lennard-Jones monomer fluid, and  $f^{\text{chain}}$  is the chain bonding contribution to the Helmholtz free energy density of the chain system.

The free energy of the monomer Lennard-Jones fluid is computed from the equation of state developed by Johnson et al.<sup>38</sup> The chain contribution is given by the work required to hold two Lennard-Jones atoms together at a distance of the bond length  $l$  in the monomer fluid

$$f^{\text{chain}} = \frac{\rho}{N} (N-1) \ln y^{\text{ref}}(l)$$

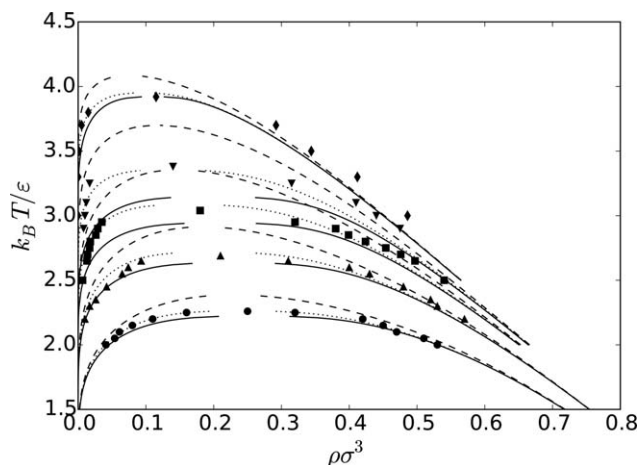
where  $y^{\text{ref}}$  is the indirect correlation function of the disconnected Lennard-Jones fluid. The mathematical form for this term is taken from Ref. 37.

The predictions of the first-order TPT for the vapor-liquid coexistence curve of Lennard-Jones chains with bond length  $l = \sigma$  are shown as the dashed lines in Figure 3. The corresponding Monte Carlo simulation data<sup>39,40</sup> are given by the symbols. TPT consistently predicts a much larger coexistence region and a higher critical temperature than found by simulation.

We apply the functional RG method to a first-order TPT approximation for the free energy. For the chains with  $N = 4, 8, 16$ , and  $32$ , the solid lines are the results of the RG transformation with the parameters  $\Lambda\sigma = 1$ ,  $B\Lambda^2/(\beta\varepsilon\sigma^3) = 5$ , and  $\xi/\sigma = 0$ . While the RG predictions are reasonably good for  $N = 4$ , they get progressively worse as  $N$  increases for these fixed values of the parameters, severely underestimating the height of the coexistence curve.

For the same chain lengths, the dotted lines for the RG transformation with the parameters  $\Lambda\sigma = 1$ ,  $B\Lambda^2/(\beta\varepsilon\sigma^3) = 5$ , and  $\xi/\sigma = 0.5$ . By adding the size correction, given by the parameter  $\xi$ , the low density arm of the coexistence curve shifts slightly up and to the left, leaving the high density arm relatively unmoved for the longer chain lengths. These curves are able to describe the coexistence curve fairly well for all these chain lengths.

For the case  $N = 100$  shown in Figure 3, the solid line corresponds to the RG transformation with  $\Lambda\sigma = 0.5$ ,



**Figure 3.** Vapor-liquid coexistence curve for linear chains composed of (1)  $N=4$  (circles), (2)  $N=8$  (triangles up), (3)  $N=16$  (squares), (4)  $N=32$  (triangles down), and (5)  $N=100$  (diamonds), Lennard-Jones atoms.

The symbols are Monte Carlo simulation data from Refs. 39 and 40, the dashed lines are the predictions of the TPT, and the solid and dotted lines are from the TPT with the RG corrections (see text).

$B\Lambda^2/(\beta\epsilon\sigma^3)=5$ , and  $\xi/\sigma=0$ , and the dotted line corresponds to the parameters  $\Lambda\sigma=0.5$ ,  $B\Lambda^2/(\beta\epsilon\sigma^3)=5$ , and  $\xi/\sigma=0.5$ . Based on these results, it appears that to get a good description of the phase behavior of chain molecules, the parameter  $\Lambda$  should decrease slightly with chain length.

## Conclusions

In this work, we have examined the application of a simple FRG method to provide fluctuation corrections for classical free energy models. This method can be readily applied to any model to better reproduce the nonanalytical behavior of the thermodynamic properties near the critical point.

In this work, we only illustrated the applicability of the FRG method to general classical free energy models that are commonly used by engineers to describe fluid thermodynamic properties. The quantities  $\Lambda$ ,  $B$ , and  $\xi$  appearing in the flow equation (see Eq. 25) have been left as adjustable parameters. This approach does, however, have a more rigorous molecular basis, and, in principle, the parameters can be linked more closely to the molecular features of the system.

More sophisticated approximations for the renormalizing free energy functional, beyond the simple gradient approximation,<sup>28</sup> can be used to obtain a more rigorous approach. However, this would come at a cost of increased complexity and computational burden.

The FRG method has been extended to account for the influence of intramolecular correlations which result from bonds between atoms within a molecule. These correlations tend to suppress the density fluctuations in the system and, as a consequence, shrink the critical region. The neglect of this effect when applying the renormalization group method to systems composed of large molecules has probably led to the calculation of vapor-liquid coexistence curves that are much too flat compared to that observed experimentally. By including intramolecular correlations, the FRG method is able to provide a good description of phase behavior of Lennard-Jones chain fluids, as compared to computer simulation results.

One of the key practical limitations of current RG corrections has been the practical difficulties in applying these methods to mixtures. While most of these methods can be straightforwardly generalized to account for multicomponent systems, such as the phase-space cell approximation and the FRG approach described here, they rapidly become impractical as the number of components in the system increases. This severely limits their usefulness in addressing real engineering problems. It is hoped that in presenting this different approach to implementing the renormalization group idea may stimulate new approximate methods to attacking multicomponent systems.

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