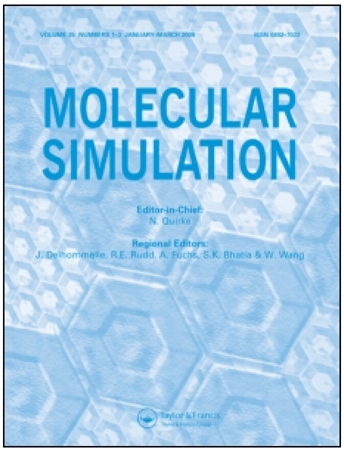

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Self-consistent Ornstein–Zernike Approach to Polymer Fluids

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In this work we study Flory–Huggins lattice polymers using a self-consistent Ornstein–Zernike approach. The results are compared with those derived from classical mean-field theory. A simple continuum-space (i.e. off-lattice) extension of the Flory–Huggins model is also proposed and studied.

Keywords: SCOZA; Ising model; Polymer fluids; Thermodynamics

INTRODUCTION

The self-consistent Ornstein–Zernike approach (SCOZA) was formulated some time ago [1,2], but quantitative SCOZA results for a wide variety of Hamiltonian models have only been obtained over the past few years [3–27]. Here we apply the SCOZA to the Flory–Huggins polymer model [28,29], which entails a reformulation of the original approximation that was initially used to define the SCOZA, as we discuss below.

In the Flory–Huggins lattice model, each polymer chain occupies n lattice sites. For simplicity a simple cubic lattice is used, and each lattice site is occupied by either a solvent molecule or part of a polymer chain. We use subscripts 1 and 2 to label quantities describing polymers and solvent molecules, respectively. Assuming nearest-neighbor site–site interactions, one immediately finds the Hamiltonian:

$$E = -v_1 N_{11} - v_2 N_{22} - v_{12} N_{12} \tag{1}$$

where N_{11}, N_{22} and N_{12} are the number of 1–1, 2–2 and 1–2 pairs on the lattice and v_1, v_2 and v_{12} are the corresponding negative interaction energies. Let N_1, N_2 be the number of sites occupied by polymers and solvents, respectively, N be the total number of sites, and q be the coordination number (for simple cubic lattice $q = 6$). Then one has the following relations for the lattice polymer system (via the ring polymer approximation in which end effects in chains are neglected):

$$\begin{aligned} (q-2)N_1 + qN_2 &= 2N_{11} + 2N_{12} + 2N_{22} \\ qN_2 &= 2N_{22} + N_{12} \\ N &= N_1 + N_2 \end{aligned} \tag{2}$$

so

$$\begin{aligned} N_{12} &= (q-2)N_1 - 2N_{11} \\ N_{22} &= \frac{1}{2}qN - (q-1)N_1 + N_{11} \end{aligned} \tag{3}$$

and

$$\begin{aligned} E = &-(v_1 + v_2 - 2v_{12})N_{11} - \\ &\big[(q-2)v_{12} - (q-1)v_2\big]N_1 - \frac{1}{2}qv_2 N \end{aligned} \tag{4}$$

where the last two terms in Eq. (4) can be dropped since they do not affect the thermodynamic behavior. So the resulting Hamiltonian is equivalent to that for a polymeric lattice–gas model with negative site–site interaction energy

$$v \equiv v_1 + v_2 - 2v_{12}. \tag{5}$$

In our calculations we define $v = 1/(q-2)$ for simplicity, which is analogous to setting $\int d^3\mathbf{r}\, v(\mathbf{r}) = 1$ in the continuum space.

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THEORY

SCOZA

SCOZA is based on the enforcement of thermodynamic consistency between different routes to thermodynamics. This imposes the following relation:

$$\frac{\partial \chi_{\text{red}}^{-1}}{\partial \beta} = \rho_m \frac{\partial^2(\rho_m u)}{\partial \rho_m^2}, \tag{6}$$

where $\beta = 1/(k_B T)$, a scaled inverse temperature, and ρ_m is the monomer bead density for the polymers. For a lattice polymer system ρ_m is the volume fraction. χ_{red} is the reduced isothermal compressibility computed via the fluctuation theorem:

$$\chi_{\text{red}}^{-1} \equiv \frac{\partial \beta p}{\partial \rho_m} = \frac{1}{1 + \rho_m \tilde{h}(0)}, \tag{7}$$

and u is the internal energy per particle calculated through the ensemble average over the Hamiltonian:

$$\begin{aligned}
\rho_m u &= -\frac{\rho_m^2}{2}\int_\sigma^\infty d^3\mathbf{r}\, g(\mathbf{r})v(\mathbf{r}) \\
&= -\frac{\rho_m^2}{2}\int_\sigma^\infty d^3\mathbf{r}\,(1 + h(\mathbf{r}))v(\mathbf{r}) \\
&= -\frac{\rho_m^2}{2} - \frac{\rho_m^2}{2(2\pi)^3}\int_0^\infty d^3\mathbf{k}\,\tilde{h}(\mathbf{k})\tilde{v}(\mathbf{k}) \\
&= -\frac{\rho_m^2}{2} - \frac{1}{2(2\pi)^3}\int_0^\infty d^3\mathbf{k}(\rho_m + \rho_m^2\tilde{h}(\mathbf{k}))\tilde{v}(\mathbf{k}).
\end{aligned} \tag{8}$$

Here $-v(\mathbf{r})$ is the pair potential outside its repulsive core region repulsion of diameter σ and $\tilde{v}(\mathbf{k})$ is the Fourier transform of $v(\mathbf{r})$. The $g(\mathbf{r}) \equiv h(\mathbf{r}) + 1$ is the pair distribution function and $\tilde{h}(\mathbf{k})$ is the Fourier transform of $h(\mathbf{r})$. For simplicity the pair potential is normalized such that

$$\tilde{v}(\mathbf{k} = 0) = \int_\sigma^\infty d^3\mathbf{r}\, v(\mathbf{r}) = 1. \tag{9}$$

For a lattice system the spatial integrations are replaced by summations, and the range of integration in Fourier space is reduced to a Brillouin Zone.

The above relations are exact. In order to proceed one has to use an approximate correlation function $\tilde{h}(\mathbf{k})$ as an input for Eqs. (7) and (8). In the SCOZA, $\tilde{h}(\mathbf{k})$ is obtained from the approximation that the Ornstein–Zernike direct correlation function $c(\mathbf{r})$ is proportional to the pair potential outside the potential-core region, in which $g(\mathbf{r}) \cong 0$ [1,2]. Here we shall find it convenient to reformulate the assumption in terms of a renormalized lowest-order Γ-ordered approximation (LOGA) [30]. In the LOGA, $c(\mathbf{r})/v(\mathbf{r}) = \beta$ outside the core region. In the SCOZA, the β is replaced by a renormalized parameter β_R that is adjusted to yield thermodynamic self consistency.

The Γ-ordering is a perturbation technique using expansions in the inverse range γ of the interaction potential $-v(\mathbf{r})$ that is added to the hard-core reference potential [30]. To the lowest order of the Γ-ordered expansion, one has the result

$$\rho_m + \rho_m^2\tilde{h}(\mathbf{k}) = \frac{\tilde{F}_0(\mathbf{k})}{1 - \tilde{F}_0(\mathbf{k})\tilde{\Phi}(\mathbf{k})}, \tag{10}$$

where

$$\tilde{F}_0(\mathbf{k}) \equiv \rho_m + \rho_m^2\tilde{h}_0(\mathbf{k}). \tag{11}$$

Here, $\tilde{h}_0(\mathbf{k})$ is the reference correlation function in Fourier space and $\tilde{\Phi}(\mathbf{k}) \equiv \beta\tilde{v}(\mathbf{k})$. By applying this to Eq. (8) one gets

$$\rho_m u = -\frac{\rho_m^2}{2} - \frac{1}{2\beta(2\pi)^3}\int d^3\mathbf{k}\frac{\tilde{F}_0(\mathbf{k})\tilde{\Phi}(\mathbf{k})}{1 - \tilde{F}_0(\mathbf{k})\tilde{\Phi}(\mathbf{k})}. \tag{12}$$

And by evaluating Eq. (10) at $\mathbf{k} = 0$ one can compute the inverse reduced compressibility:

$$\chi_{\text{red}}^{-1} = \rho_m\left(\frac{1}{F_0} - \tilde{\Phi}(0)\right) = \rho_m\left(\frac{1}{F_0} - \beta\right) \tag{13}$$

which is just the mean-field result (here $F_0 \equiv \tilde{F}_0(0)$). Putting the relations (12) and (13) into Eq. (6) one will immediately find a thermodynamic inconsistency. This inconsistency is due to the approximation made in representing the correlation function $\tilde{h}(\mathbf{k})$. This can be corrected by adding higher-order results. But instead of doing this, we shall use a simple renormalization scheme that restores thermodynamic consistency and yields accurate results.

The renormalizing process is carried out by introducing an extra degree of freedom into the analysis. Specifically, one replaces the inverse temperature β with a renormalized quantity $\beta_R(\beta, \rho_m)$, of which the functional dependence on β and ρ_m will be determined by solving the thermodynamic-consistency requirement using Eq. (6). One expects small differences between β and β_R unless the system is close to the critical region.

To implement this procedure, one can rewrite the inverse reduced compressibility in the renormalized scheme as

$$\frac{1}{\chi_{\text{red}}} = \rho_m\left(\frac{1}{F_0} - \beta_R\right) = \frac{\rho_m\epsilon^2}{F_0} \tag{14}$$

with

$$\epsilon^2 \equiv 1 - \beta_R F_0, \tag{15}$$

and the internal energy as

$$\rho_m u = -\frac{\rho_m^2}{2} - \frac{K}{2\beta_R}, \tag{16}$$

where

$$K \equiv \frac{1}{(2\pi)^3}\int d^3\mathbf{k}\,\frac{\tilde{F}_0(\mathbf{k})\tilde{\Phi}(\mathbf{k})}{1-\tilde{F}_0(\mathbf{k})\tilde{\Phi}(\mathbf{k})}. \tag{17}$$

The zeroth-order-Γ-ordered result given by Eq. (10) induces a first-order result for K that can be written in the critical region ($F_0\beta_R \cong 1$) simply as [31]

$$\frac{K}{\beta_R} \sim c\gamma^3(1-\epsilon)F_0, \tag{18}$$

where γ characterizes the inverse range of interaction for the system. This simple approximation was also applied by Borge and Høye to the Ising model using SCOZA [8]. For the polymer system, we will use here $\gamma = n^{-3/5}$, the inverse of which is the gyration radius for a polymer in the swollen phase [32], where n is the number of beads in the polymer. The proportional constant c is set to be

$$c \equiv \frac{1}{(2\pi)^3}\int d^3\mathbf{k}\,\frac{\tilde{v}(\mathbf{k})}{1-\tilde{v}(\mathbf{k})}. \tag{19}$$

For a simple cubic lattice $c = 0.516386\ldots$. Finally, by inserting Eqs. (14), (16) and (18) into the thermodynamic-consistency relation (6), one gets the SCOZA equation:

$$\frac{1}{F_0}\frac{\partial\epsilon^2}{\partial\beta} = -\left\{1+\frac{1}{2}\frac{\partial^2}{\partial\rho_m^2}\left[c\gamma_r^3(1-\epsilon)F_0\right]\right\}. \tag{20}$$

We note that the approximation so defined reduces to that for the lattice gas when $n = 1$.

The Reference System

In the Flory–Huggins lattice model for polymers the reference system is an athermal one, containing no interaction energies except exclusion of multiple occupations. This is equivalent to a system of self-avoiding random walks. In this paper, we utilize the approximate thermodynamic results derived in the original Flory–Huggins work [28,29]:

$$\frac{\Delta S_{\text{mix}}}{k_B V} = -\frac{\rho_m}{n}\log(\rho_m) - (1-\rho_m)\log(1-\rho_m) \tag{21}$$

$$\begin{aligned}\beta f &= 0 - \frac{\Delta S_{\text{mix}}}{k_B V}\\ &= \frac{\rho_m}{n}\log(\rho_m) + (1-\rho_m)\log(1-\rho_m)\end{aligned} \tag{22}$$

$$\begin{aligned}\beta p &= -\beta f + \rho_m\frac{\partial(\beta f)}{\partial\rho_m}\\ &= -\log(1-\rho_m) - \left(1-\frac{1}{n}\right)\rho_m\end{aligned} \tag{23}$$

$$\begin{aligned}\frac{1}{\rho_m}\frac{\partial(\beta p)}{\partial\rho_m} &= \frac{1}{\rho_m}\left[\frac{1}{\rho_m} - \left(1-\frac{1}{n}\right)\right] = \frac{1}{\rho_m + \rho_m^2\tilde{h}_0(0)}\\ &= \frac{1}{F_0}\end{aligned} \tag{24}$$

$$F_0 = \frac{n\rho_m(1-\rho_m)}{1+(n-1)\rho_m}, \tag{25}$$

where ΔS_{mix} is the mixing entropy, f is the Helmholtz free energy per unit volume (per lattice), p is the pressure, ρ_m is the bead density as well as

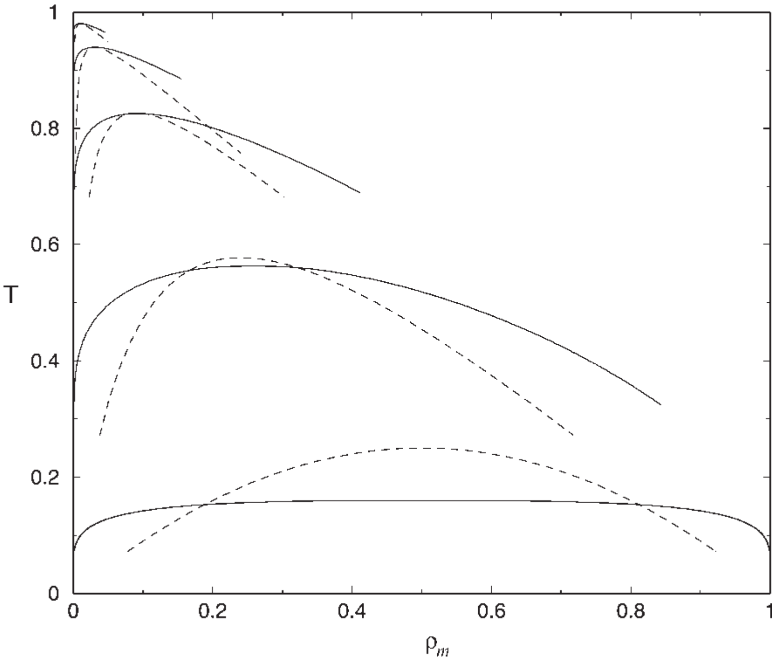

FIGURE 1 Spinodal curves of the lattice-polymer fluid for various values of n. The dash lines are the Flory–Huggins mean-field results, and the solid lines are the SCOZA results. From top to bottom, the curves correspond to $n = 10,000$, $n = 1000$, $n = 100$, $n = 10$ and $n = 1$, respectively.

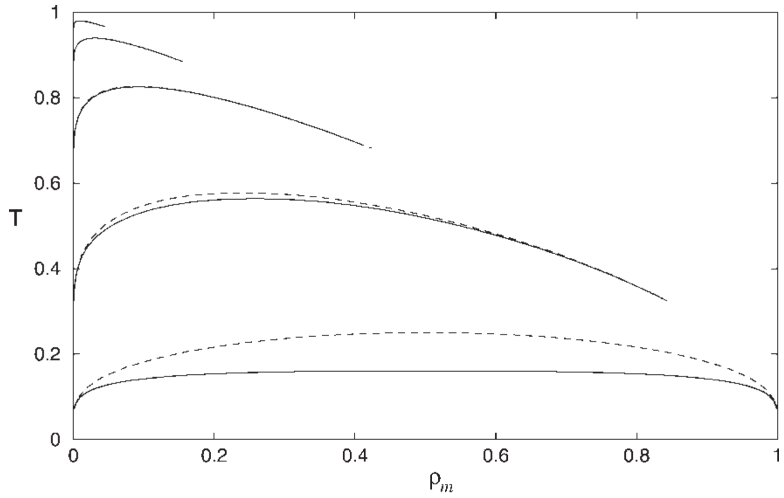

FIGURE 2 Coexistence curves of the lattice-polymer fluid. (Same labeling as in Fig. 1.)

the packing fraction in the lattice case, and n is the number of beads occupied by a single polymer chain.

RESULTS

In practice, we solve the SCOZA equation (20) numerically using a predictor–corrector method. The initial and boundary conditions are set as $\epsilon = 0$ for $\beta = 0$ and $\rho_m = 0, 1$. The numerical procedure is carried out on volume fraction grids with $\Delta\rho_m = 10^{-3} \sim 2 \times 10^{-4}$. Initially the inverse-temperature step is set as $\Delta\beta = 10^{-4}$, and this is gradually decreased when the system gets closer to the critical point. Below the critical temperature the coexistence curves are calculated by locating the density points which satisfy both the mechanical and chemical equilibrium.

Figure 1 shows our results for the spinodal curves compared with the Flory–Huggins mean-field theory for various n. We find that the spinodals we get are broader than the mean-field results. Furthermore, our data indicate a smaller critical temperature. However, these differences become smaller as the polymer length n increases.

TABLE I Critical parameters calculated from the SCOZA and the Flory–Huggins mean-field (MF) approach for various polymer length n

n	β_c(MF)	β_c(SCOZA)	ρ_c(MF)	ρ_c(SCOZA)
1	4.000000	6.255517	0.500000	0.5000
10	1.732456	1.775540	0.240253	0.2580
10^2	1.210000	1.211566	0.090909	0.0925
10^3	1.064246	1.064315	0.030653	0.0308
10^4	1.020100	1.020105	0.009901	0.0099
10^5	1.006335	1.006337	0.003152	0.0032

Our results for the coexistence curves are shown in Fig. 2. We see that our SCOZA coexistence curves exhibit only minor difference with the mean-field results as soon as n exceeds 10. In Table I, we list the values of β and ρ_m at their critical points. Comparing to the mean-field results, we observe that the SCOZA critical temperatures are smaller, and in general the critical densities are larger. And these differences gradually become indistinguishable as n increases.

In Fig. 3, we make the plot of β_c versus $1/\sqrt{n} + 1/(2n)$. The Shultz–Flory relationship is followed from the linear behavior of the curve at large n. In Fig. 4, we plot the critical volume fraction ρ_c versus n on logarithmic scales. The asymptotic scaling is also in good agreement with the Flory–Huggin mean-field theory. This mean-field-like nature of the SCOZA results also agrees well with recent simulation studies [33,34]. However, it should be noted that despite this apparent mean-field behavior for large n, the critical behavior is Ising-like as clearly shown by the $n = 1$ curve (Ising spins) in Fig. 2. This also follows from the analysis of SCOZA in the critical region by Høye *et al.* [35]. But instead of standard scaling they found that SCOZA yields a kind of generalized scaling which describes the critical region well.

EXTENSION TO A CONTINUOUS SYSTEM

By examining the pressure for the reference system (Eq. (23)) one notes that the first term represents the pressure for the monomer system without polymerization, and the second term is the reduction in ideal gas pressure due to polymerization of monomers. In analogy one can write down the approximate pressure for the reference system in

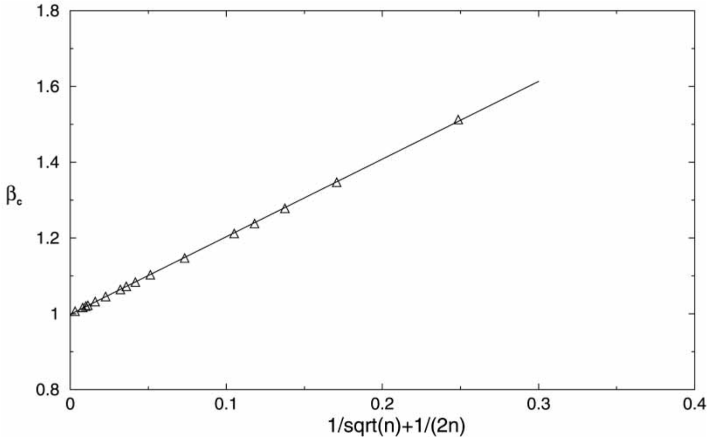

FIGURE 3 Inverse critical temperature β_c versus $1/\sqrt{n}+1/(2n)$. Error bars are too small to show. The data for $n \geq 20$ are fitted to a line with slope 2.0504.

a continuous polymer liquid:

$$\beta p = \beta p_h - \left(1 - \frac{1}{n}\right)\rho_m, \tag{26}$$

where ρ_m represents the monomer (bead) density in the continuous system. βp_h is the pressure for the hard-sphere system. For example, one can use the Carnahan–Starling equation as an approximation for βp_h:

$$\beta p_h = \rho_m \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}, \tag{27}$$

where $\eta = (\pi\rho_m)/6$ is the packing fraction for hard-sphere monomers with unit diameter. This ansatz for the pressure yields a sensible low-density result that becomes the ideal-gas relation for polymer molecules $\beta p \cong \rho_m/n$ as $\rho_m \rightarrow 0$. To get better results one can use more accurate expressions for the pressure in a system of freely-jointed hard-sphere chains.

From Eqs. (26) and (27) we have

$$\begin{aligned}\frac{1}{\rho_m}\frac{\partial(\beta p)}{\partial \rho_m} &= \frac{1}{\rho_m}\frac{\partial(\beta p_h)}{\partial \rho_m} - \left(1 - \frac{1}{n}\right)\frac{1}{\rho_m} \\ &= \frac{1}{\rho_m}\cdot\left[\frac{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}{(1-\eta)^4} - \left(1 - \frac{1}{n}\right)\right] \\ &= \frac{1}{F_0}.\end{aligned} \tag{28}$$

In the continuous case we shall simply plug this expression for F_0 into the SCOZA equation (20). In this example we use a hard-core Yukawa potential as the perturbing interaction:

$$v(r) = \begin{cases} 0 & \text{if } r \leq 1, \\ e^{-(r-1)}/(8\pi r) & \text{if } r > 1. \end{cases} \tag{29}$$

For simplicity we have set the hard-core diameter for the monomer bead to be equal to 1. In this example, the constant c that appears in Eqs. (19) and

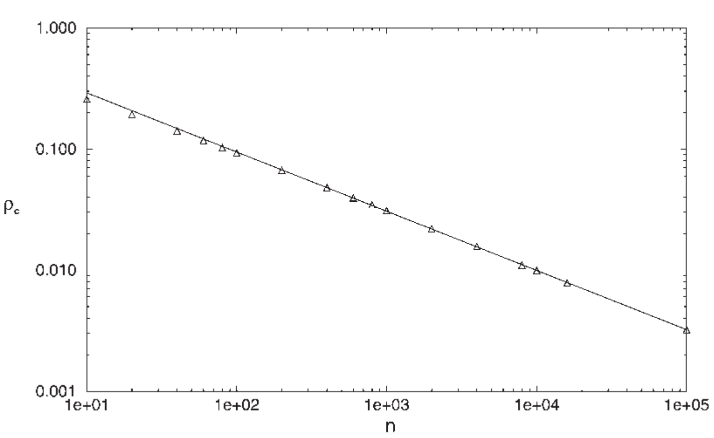

FIGURE 4 Scaling of critical volume fraction ρ_c versus n. Error bars are too small to show. For $n \geq 100$, the logarithmic plot follows well with a straight line with slope 0.4891.

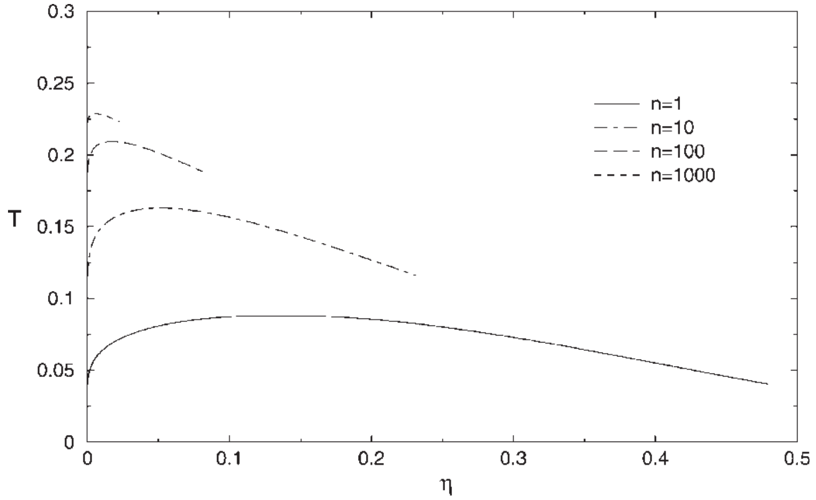

FIGURE 5 Coexistence curves calculated from SCOZA in the continuous case.

(20) is equal to 0.0152666…. Figure 5 shows the SCOZA coexistence curves for this continuum model. The horizontal axis $\eta \equiv (\pi\rho_m)/6$ is the volume packing fraction. Note that in the continuum case the asymmetry in the coexistence curve already exists for $n = 1$. As in the lattice-model case the results indicate only small deviations compared with those derived from the mean-field theory when $n > 10$. In the continuum case we obtain the latter directly from Eqs. (26) and (27), where the full pressure is given by the right-hand side of Eq. (26) minus $(\beta\rho_m^2)/2$.

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