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Thermodynamic perturbation theory: Sticky chains and square-well chains

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We extend Wertheim's first-order thermodynamic perturbation theory [J. Chem. Phys. **87**, 7323 (1987)] to sticky chains and square-well chains. The predicted compressibility factors for square-well chains are found to agree with Monte Carlo data. We demonstrate that the effect of chain connectivity is to reduce the attraction contributions to the compressibility factor and to the critical temperatures.

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INTRODUCTION

In the process of developing thermodynamic theories of polymer systems, large polymeric molecules are often approximated as homonuclear chains, that is, chains of equisized segments. For example, hard chains (HC) of Dickman and Hall [1], Honnell and Hall [2], Chiew [3], Boublik, Vega, and Diaz-Pena [4], and Schweizer and Curro [5,6], are composed of freely jointed hard-sphere (HS) segments. Such hard chains mimic covalently bonded hard spheres where the bond angles are not fixed and no attractive interactions are allowed. By contrast, attractive chains are composed of segments that can interact through attractive forces. For example, Yethiraj and Hall [7,8] proposed a theory for chains composed of freely jointed hard-sphere segments with square-well attraction.

Another approach to developing thermodynamic theories of attractive chains is based on Wertheim's first-order perturbation theory (TPT1) [9]. The advantage of using TPT1 to square-well chains is that TPT1 can be consistently extended to associating chain fluids. For example, in statistical associating-fluid theory (SAFT) [10–14], which applies to associating and nonassociating chain fluids, TPT1 was used to account for aggregation, i.e., association and chain formation, of HS segments. Specifically, TPT1 was used to calculate the thermodynamic properties of HS and HC reference fluids and contributions due to attraction (dispersion term) were treated as perturbation. However, the contributions due to attraction were approximated with models of nonbonded spherical segments, for example, Lennard-Jones (LJ) segments. Therefore the effect of chain connectivity on the dispersion term was not accounted for explicitly.

While such an approximation has been very effective in describing real systems [11–13] when combined with the temperature-dependent hard core diameter, we want to probe the effect of chain connectivity by allowing the reference fluid to be composed of attractive segments, rather than HS segments. Our specific objective is to quantify the effect of chain connectivity on those parts of the compressibility factor and critical temperature which are due to attraction. Our approach is to apply TPT1 to chains of freely jointed attractive spheres, such as chains of sticky spheres (SS), referred to as sticky chains (SC), and chains of square-well spheres (SWS), referred to as square-well chains (SWC).

GENERAL THEORY FOR CHAINS OF FREELY JOINTED ATTRACTIVE SEGMENTS

In TPT1 framework, the compressibility factor Z for chains composed of m spheres (segments) can be expressed as [10,14]

$$Z = mZ_{\text{ref}} + Z_{\text{chain}} \ , \tag{1}$$

where Z_{ref} is the compressibility factor of the reference fluid (nonbonded segments), and Z_{chain} is given by the equation

$$Z_{\text{chain}} = (1-m)\left[1 + \eta \frac{\partial}{\partial \eta} \ln g(\sigma,\eta)\right] , \tag{2}$$

In Eq. (2) $g(\sigma,\eta)$ is the contact value of the pair correlation function of the reference fluid, that is, for the separation $r=\sigma$, σ is the diameter of a spherical segment, and η is the reduced density defined as

$$\eta = \frac{\pi \rho \sigma^3}{6} , \tag{3}$$

where ρ is the number density of nonbonded segments, that is, the number of nonbonded segments per unit volume. In our notation, the subscript "ref" refers to the nonbonded reference fluid, whereas the subscript "chain" refers to the incremental change due to chain formation. Quantities without any subscripts are total. Superscripts, on the other hand, refer to specific model fluids, such as HS, HC, SS, SC, SWS, and SWC.

Equations (1) and (2) are general and can be applied to any spherical reference fluid. For example, for a HS reference fluid, the contact value of the pair correlation function can be approximated by the Carnahan-Starling expression [15], which is

$$g^{\mathrm{HS}}(\sigma,\eta)=\frac{1-\eta/2}{(1-\eta)^3}\ . \tag{4}$$

Therefore, for a HC fluid, the compressibility factor is

$$Z^{\mathrm{HC}}=mZ^{\mathrm{HS}}_{\mathrm{ref}}+Z^{\mathrm{HC}}_{\mathrm{chain}}\ , \tag{5}$$

where $Z^{\mathrm{HS}}_{\mathrm{ref}}$ is the HS compressibility factor in the Carnahan-Starling approximation:

$$Z^{\mathrm{HS}}_{\mathrm{ref}}=1+\frac{4\eta-2\eta^2}{(1-\eta)^3}\ . \tag{6}$$

For $Z^{\mathrm{HC}}_{\mathrm{chain}}$ Eq. (2) becomes

$$Z^{\mathrm{HC}}_{\mathrm{chain}}=(1-m)\left[1+\eta\frac{\partial}{\partial\eta}\ln g^{\mathrm{HS}}(\sigma,H)\right]\ . \tag{7}$$

Equation (5) agrees well with Monte Carlo (MC) simulation data for hard chains [10].

The compressibility factor for a reference HS fluid with attraction, on the other hand, can be written as a sum of the HS contribution $Z^{\mathrm{HS}}_{\mathrm{ref}}$ and a contribution due to attraction of nonbonded segments, $Z^{\mathrm{seg}}_{\mathrm{att}}$,

$$Z_{\mathrm{ref}}=Z^{\mathrm{HS}}_{\mathrm{ref}}+Z^{\mathrm{seg}}_{\mathrm{att}}\ , \tag{8}$$

where the superscript seg indicates that the corresponding contribution is due to nonbonded segments, and the subscript "att" indicates that the corresponding contribution is due to attraction. Therefore, after substituting Eq. (8) into Eq. (1), the compressibility factor for chains with attraction is

$$Z=mZ^{\mathrm{HS}}_{\mathrm{ref}}+mZ^{\mathrm{seg}}_{\mathrm{att}}+Z_{\mathrm{chain}}\ . \tag{9}$$

Furthermore, Z_{chain} can be separated into a hard chain contribution $Z^{\mathrm{HC}}_{\mathrm{chain}}$ and a corresponding contribution due to attraction, $\Delta Z_{\mathrm{chain}}$, as

$$Z_{\mathrm{chain}}=Z^{\mathrm{HC}}_{\mathrm{chain}}+\Delta Z_{\mathrm{chain}}\ . \tag{10}$$

Thus the total Z can be written as a sum of repulsive and attractive parts:

$$Z=Z^{\mathrm{seg}}_{\mathrm{att}}+Z^{\mathrm{HC}}\ , \tag{11}$$

where Z^{HC} is given by Eq. (5) and the attractive part is

$$Z_{\mathrm{att}}=\Delta Z_{\mathrm{chain}}+mZ^{\mathrm{seg}}_{\mathrm{att}}\ . \tag{12}$$

$\Delta Z_{\mathrm{chain}}$ is our measure of the attraction effect due to connectivity. For example, setting $\Delta Z_{\mathrm{chain}}$ equal to zero is equivalent to assuming that $Z^{\mathrm{seg}}_{\mathrm{att}}$ is equal to $mZ^{\mathrm{seg}}_{\mathrm{att}}$, and hence that Z_{att} is simply that for nonbonded segments. When $\Delta Z_{\mathrm{chain}}=0$, the corresponding expression for Z is

$$Z'=Z^{\mathrm{HC}}+mZ^{\mathrm{seg}}_{\mathrm{att}}\ , \tag{13}$$

where the prime means that $\Delta Z_{\mathrm{chain}}=0$.

For chains of attractive bonded segments, however, we expect Z_{att} to be smaller than Z_{att} for the nonbonded segments (Z') due to stronger excluded volume (repulsive) interactions. As a result, we expect $\Delta Z_{\mathrm{chain}}$ to be positive.

One way to account for $\Delta Z_{\mathrm{chain}}$ is to calculate the chain term Z_{chain} using $g(\sigma,\eta)$ in Eq. (2) for a reference fluid with attraction, rather than using $g^{\mathrm{HS}}(\sigma,\eta)$, and then to calculate Z from Eq. (9). This will consistently take into account the effect of chain connectivity on Z_{att}.

In this work we apply TPT1 to SC and SWC fluids because there are analytical solutions available for contact values of $g^{\mathrm{SS}}(r,\eta)$ and $g^{\mathrm{SWS}}(r,\eta)$, and there are MC data available for SWC fluids.

APPLICATION TO STICKY CHAINS

Properties of SS fluids have been extensively studied [16,17] and applied to adsorption [18], microemulsions [19], colloids and grafted polymers [20], and gelation of dispersions [21]. The two-body interaction energy $u^{\mathrm{SS}}(r)$ is such that the Boltzmann factor, $e(r)=\exp[-u^{\mathrm{SS}}/(kT)]$, is

$$e(r)=\frac{\sigma}{12\tau}\delta(r-\sigma^-)+\Theta(r-\sigma)\ , \tag{14}$$

where Θ is the standard Heaviside function, σ is the *SS* diameter, and τ is a dimensionless, temperature-related parameter. If τ goes to zero, T goes to zero, and when τ goes to infinity, T also goes to infinity.

In this section, we work within the framework of the Percus-Yevick (PY) approximation, using the compressibility pressure for calculating the compressibility factor of SC fluid. In order to calculate the compressibility factor for sticky chains from Eqs. (1) and (2), we need the reference compressibility $Z^{\mathrm{SS}}_{\mathrm{ref}}$ and the pair correlation function at contact of the reference fluid, $g^{\mathrm{SS}}(\sigma,\eta)$. Since the SS pair correlation function has its continuous and singular parts [16], it cannot be directly substituted into Eq. (2). We show, however, that instead of using $g^{\mathrm{SS}}(\sigma,\eta)$ in Eq. (2), one can use the contact value of a cavity function for sticky spheres, $y^{\mathrm{SS}}(\sigma,\eta)$, which agrees with the theory of Stell and Zhou [22].

Following Baxter [16,17], we list the expression for $Z^{\mathrm{SS}}_{\mathrm{ref}}$ and $y^{\mathrm{SS}}(\sigma,\eta)$:

$$Z^{\mathrm{SS}}_{\mathrm{zef}}=\frac{1+\eta+\eta^2-\mu(1+\eta/2)+(\mu^3\eta^{-1}/36)}{(1-\eta)^3}\ , \tag{15}$$

where $\mu=\lambda\eta(1-\eta)$, and

$$\lambda=\frac{6}{\eta}\left\{\tau+\frac{\eta}{1-\eta}-\left[\left[\tau+\frac{\eta}{1-\eta}\right]^2-\frac{\eta g^{\mathrm{PYHS}}(\sigma,\eta)}{3}\right]^{1/2}\right\}\ , \tag{16}$$

with $g^{\mathrm{PYHS}}(\sigma,\eta)=(1+\eta/2)/(1-\eta)^2$ and

$$y^{\mathrm{SS}}(\sigma,\eta)=g^{\mathrm{PYHS}}(\sigma,\eta)+\frac{\eta\lambda^2}{12}-\frac{\eta\lambda}{1-\eta}\ , \tag{17}$$

where $g^{\mathrm{PYHS}}(\sigma,\eta)$ is the PY contact value of the HS pair correlation function. Now Z^{SC} can be calculated from Eqs. (1) and (2),

$$Z^{\mathrm{SC}}=mZ^{\mathrm{SS}}_{\mathrm{ref}}+(1-m)\left[1+\eta\frac{\partial}{\partial\eta}\ln y^{\mathrm{SS}}(\sigma,\eta)\right], \quad (18)$$

and pressure P^{SC} from

$$\frac{P^{\mathrm{SC}}v^{00}}{kT}=\frac{\eta}{m}Z^{\mathrm{SC}}, \quad (19)$$

where $v^{00}=\pi\sigma^3/6$ is the segment volume. Similarly, for $\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}=0$,

$$Z^{\mathrm{SC}'}=mZ^{\mathrm{SS}}_{\mathrm{ref}}+(1-m)\left[1+\eta\frac{\partial}{\partial\eta}\ln g^{\mathrm{PYHS}}(\sigma,\eta)\right]. \quad (20)$$

For small η, that is, at low densities, we find the analytical form of Z^{SC}:

$$Z^{\mathrm{SC}}=1+\left[4\eta-\frac{1}{\tau}\right]\eta +(1-m)\left[1+\frac{5}{2}\eta+\left[\frac{1}{12\tau^2}-\frac{1}{\tau}\right]\eta\right]+o(\eta) \quad (21)$$

and the corresponding expressions for $Z^{\mathrm{SC}'}$ and $\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}$:

$$Z^{\mathrm{SC}'}=1+\left[4\eta-\frac{1}{\tau}\right]\eta+(1-m)[1+\tfrac{5}{2}\eta]+o[\eta], \quad (22)$$

$$\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}=(1-m)\left[\left[\frac{1}{12\tau^2}-\frac{1}{\tau}\right]\eta\right]+o[\eta]. \quad (23)$$

From these low density expansions, we can easily find that $\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}$ should be positive, for $\tau>\frac{1}{12}$ (which is well below the critical temperature), as expected. For a given density, we can also calculate both Z^{SC} and $\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}$ analytically, but the full expressions are lengthy, so that we do not present them here.

Figure 1 illustrates a significant difference between Z^{SC} and $Z^{\mathrm{SC}'}$;Z^{SC} is systematically and significantly greater than the corresponding $Z^{\mathrm{SC}'}$, which means that $\Delta Z^{\mathrm{SC}}_{\mathrm{chain}}$ is positive.

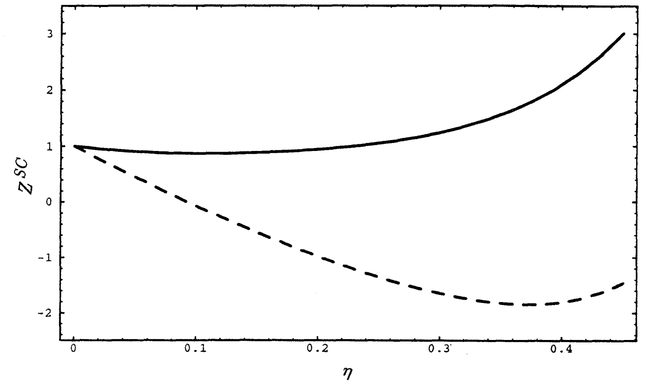

FIG. 1. Calculated values of the compressibility factor of 4-mer sticky chains based on Eqs. (18) [Z^{SC}—solid] and (20) [$Z^{\mathrm{SC}'}$—dashed].

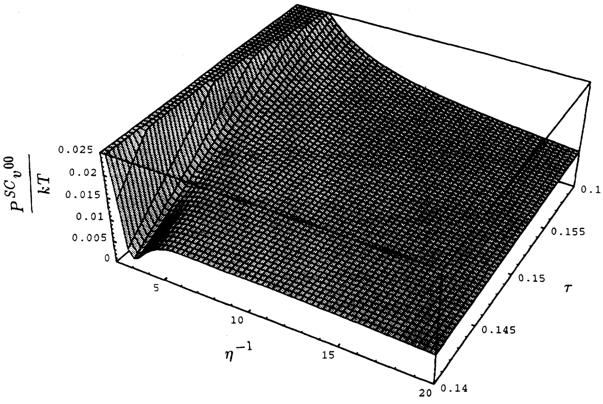

FIG. 2. Calculated values of the reduced pressure Pv^{00}/kT plotted as a function of inverse reduced density η^{-1} and dimensionless temperature τ for sticky chains with $m=4$.

We can also calculate pressure as an analytical function of τ, m, and η, which is an equation of state for sticky chains. For example, Fig. 2 shows a pressure surface for $m=4$ as a function of τ and η^{-1}. The critical temperature is found at $\tau_c=0.1465$ which, as expected, is much higher than that for sticky spheres ($\tau_c=0.0976$ [16,17]). We see, from Fig. 2, that for $\tau<\tau_c$ there is a two-phase region, and that the Maxwell construction can be performed to determine a coexistence curve. Similarly, we can determine τ_c for any chain length m. As expected, τ_c increases monotonically with increasing m, as shown in Fig. 3, for both Z^{SC} and $Z^{\mathrm{SC}'}$; for a given m, τ_c corresponding to $Z^{\mathrm{SC}'}$ is overestimated compared with τ_c corresponding to Z^{SC}.

APPLICATION TO SQUARE-WELL CHAINS

According to the perturbation theory of Barker and Henderson [23–26], the molar Helmholtz energy of SW fluid (with the well extended from $r=\sigma$ to $r=1.5\sigma$), $a^{\mathrm{SWS}}_{\mathrm{ref}}$, up to the second order, is

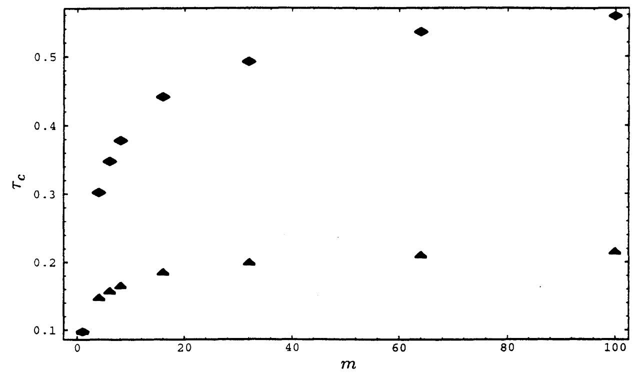

FIG. 3. Sticky chains: the critical temperature τ_c corresponding to Z^{SC} (triangles) and the critical temperature τ_c corresponding to $Z^{\mathrm{SC}'}$ (diamonds), as a function of chain length m.

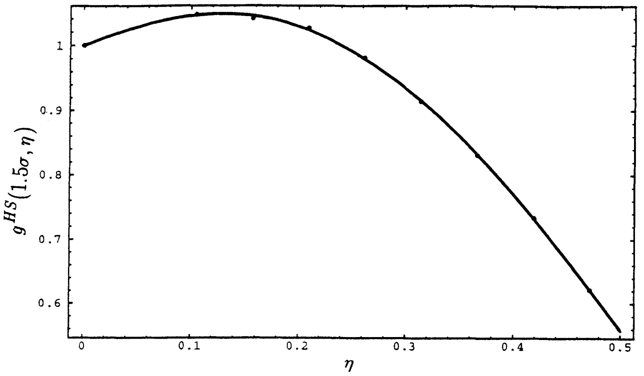

FIG. 4. Hard-sphere pair correlation function at $r=1.5\sigma$ versus reduced density η. Monte Carlo data shown as filled circles [28]. Solid curve is calculated from Eq. (32).

$$a_{\text{ref}}^{\text{SWS}}=a_{\text{ref}}^{\text{HS}}+\frac{1}{T^*}a^{(1)}+\frac{1}{T^{*2}}a^{(2)}\ , \qquad (24)$$

where T^* is the reduced temperature, $T^*=kT/u$, T is absolute temperature, u is the depth of the square well, K is Boltzmann's constant, $a_{\text{ref}}^{\text{HS}}$ is the molar Helmholtz energy of the reference HS fluid, and

$$\frac{a^{(1)}}{RT}=C_1\left[1-\exp\left[\frac{\alpha_1\rho^*}{\beta_1-\rho^*}\right]-\frac{\alpha_1}{\beta_1}\rho^*\right]+p_1\rho^*+q_1\rho^{*2}\ , \qquad (25)$$

$$\frac{a^{(2)}}{RT}=C_2\left[1-\exp\left[-\frac{\alpha_2\rho^*}{\beta_2-\rho^*}\right]-\frac{\alpha_2}{\beta_2}\rho^*\right]+p_2\rho^*+q_2\rho^{*2}\ , \qquad (26)$$

where

$$\rho^*=\frac{6}{\pi}\eta \qquad (27)$$

is the reduced number density, $\rho^*=\rho\sigma^3$, R is gas constant, and the coefficients C,α,β,p, and q are listed in the Appendix.

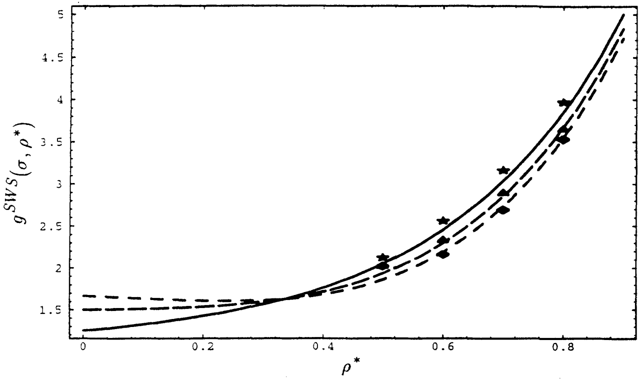

FIG. 5. Square-well sphere pair correlation function at contact, $g^{\text{SWS}}(\sigma,\rho^*)$, computed from Eq. (30) is plotted as a function of the reduced number density $\rho^*=\rho\sigma^3$ for well width $\lambda=1.5\sigma$. Curves are calculated from Eq. (30) and points are determined from computer simulation [29] at different reduced temperatures: star, $T^*=4.0$; triangle, $T^*=2.0$; diamonds, $T^*=1.5$.

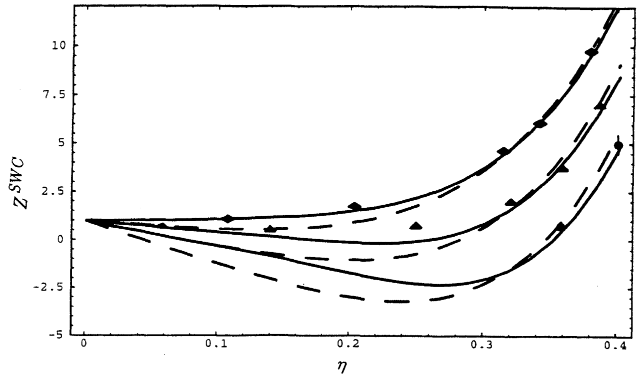

FIG. 6. Compressibility factor of 4-mer square-well chains, Z^{SWC}, plotted as a function of reduced density η. The solid and dashed curves represent values calculated from Eqs. (33) and (34), respectively. The symbols represent Monte Carlo data reported by Yethiraj and Hall [7,8], at $T^*=3.0$ (diamond), $T^*=2.0$ (triangle), and $T^*=1.5$ (circle).

We can calculate the compressibility factor of the reference fluid, $Z_{\text{ref}}^{\text{SWS}}$, from the thermodynamic relation [27]:

$$Z_{\text{ref}}^{\text{SWS}}=\eta\frac{\partial}{\partial\eta}\left[\frac{a_{\text{ref}}^{\text{SWS}}}{RT}\right]. \qquad (28)$$

Therefore, by substituting Eq. (24) into (28), we obtain

$$Z_{\text{ref}}^{\text{SWS}}=Z_{\text{ref}}^{\text{HS}}+\frac{1}{T^*}\eta\frac{\partial}{\partial\eta}\frac{a^{(1)}}{RT}+\frac{1}{T^{*2}}\eta\frac{\partial}{\partial\eta}\frac{a^{(2)}}{RT}\ . \qquad (29)$$

Let us also evaluate $g^{\text{SWS}}(\sigma,\eta)$, the contact value of the SWS pair correlation function, using the first-order perturbation theory of Henderson and Barker [25]:

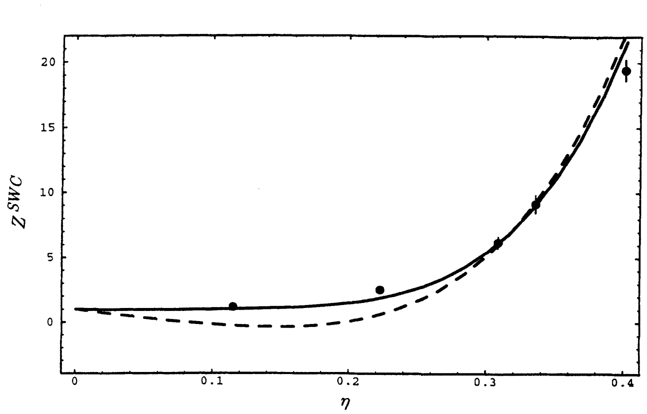

FIG. 7. Compressibility factor of 8-mer square-well chains, Z^{SWC}, plotted as a function of reduced density η. The solid and dashed curves represent values calculated from Eqs. (33) and (34), respectively. Circles represent Monte Carlo data reported by Yethiraj and Hall [7,8], at $T^*=3.0$.

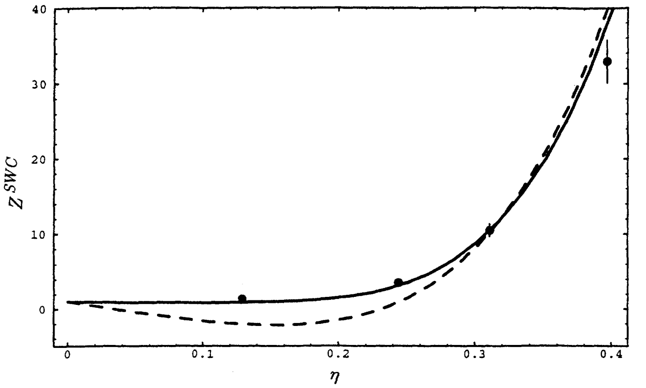

FIG. 8. Compressibility factor of 16-mer square-well chains, Z^{SWC}, plotted as a function of reduced density η. The solid and dashed curves represent values calculated from Eqs. (33) and (34), respectively. Circles represent Monte Carlo data reported by Yethiraj and Hall [7,8] at $T^*=3.0$.

$$g^{\mathrm{SWS}}(\sigma,\eta)=g^{\mathrm{HS}}(\sigma,\eta)+\frac{1}{T^*}(1.5)^3 g^{\mathrm{HS}}(1.5\sigma,\eta)+\frac{1}{T^*}\frac{1}{4\eta}\eta\frac{\partial}{\partial\eta}\frac{a^{(1)}}{RT}\,, \tag{30}$$

where $g^{\mathrm{HS}}(\sigma,\eta)$ is the contact value of the HS pair correlation function (reference for SWS), and $g^{\mathrm{HS}}(1.5\sigma,\eta)$ is the value of the HS pair correlation function at $r=1.5\sigma$. We approximate $g^{\mathrm{HS}}(\sigma,\eta)$ by the Carnahan-Starling expression

$$g^{\mathrm{HS}}(\sigma,\eta)\cong\frac{1-\eta/2}{(1-\eta)^3} \tag{31}$$

and we fit $g^{\mathrm{HS}}(1.5\sigma,\eta)$ to MC data interpolated for $r=1.5\sigma$ on the basis of Barker and Henderson's simulations [28]. The result is

$$g^{\mathrm{HS}}(1.5\sigma,\eta)=1+\gamma_1\eta+\gamma_2\eta^2+\gamma_3\eta^3+\gamma_4\eta^4\,, \tag{32}$$

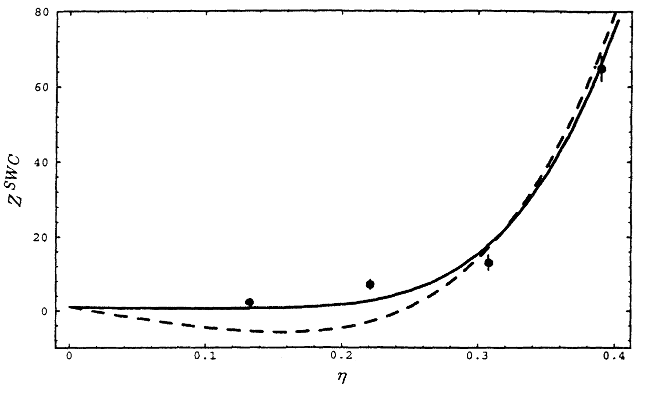

FIG. 9. Compressibility factor of 32-mer square-well chains, Z^{SWC}, plotted as a function of reduced density η. The solid and dashed curves represent values calculated from Eqs. (33) and (34), respectively. Circles represent Monte Carlo data reported by Hall, Yethiraj, and Wichert [30], at $T^*=3.0$.

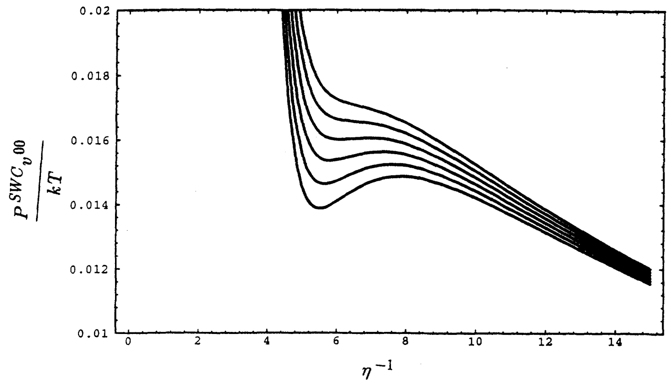

FIG. 10. Reduced pressure of SWC fluid is plotted as a function of reduced density η^{-1} for different values of the reduced temperature T^*. From bottom to top, $T^*=2.20$, 2.21, 2.22, 2.23, 2.24, and 2.25.

where $\gamma_1,\gamma_2,\gamma_3,\gamma_4$ are numerical coefficients listed in the Appendix. In Fig. 4, we show that our fit represents the MC data well. In Fig. 5, we show that the first-order perturbation theory for $g^{\mathrm{SWS}}(\sigma,\eta)$, Eq. (30), is reasonably accurate at different T^*'s [29], which means that we can use $g^{\mathrm{SWS}}(\sigma,\eta)$ for calculating Z^{SWC}.

Substituting Eqs. (29) and (30) into Eq. (1), we obtain the compressibility factor for square-well chains, Z^{SWC},

$$Z^{\mathrm{SWC}}=mZ_{\mathrm{ref}}^{\mathrm{SWS}}+(1-m)\left[1+\eta\frac{\partial}{\partial\eta}\ln g^{\mathrm{SWS}}(\sigma,\eta)\right] \tag{33}$$

and the corresponding $Z^{\mathrm{SWC}'}$ is

$$Z^{\mathrm{SWC}'}=mZ_{\mathrm{ref}}^{\mathrm{SWS}}+(1-m)\left[1+\eta\frac{\partial}{\partial\eta}\ln g^{\mathrm{HS}}(\sigma,\eta)\right]. \tag{34}$$

We calculate Z^{SWC} from Eqs. (33) and (34) for different m's and T^*'s as a function of η, and compare it with the MC data of Yethiraj and Hall, and Hall, Yethiraj, and Wichert [7,8,30]. The results are presented in Figs. 6–9. We demonstrate that Z^{SWC} calculated from Eq. (33) agrees with the MC data for different reduced tempera-

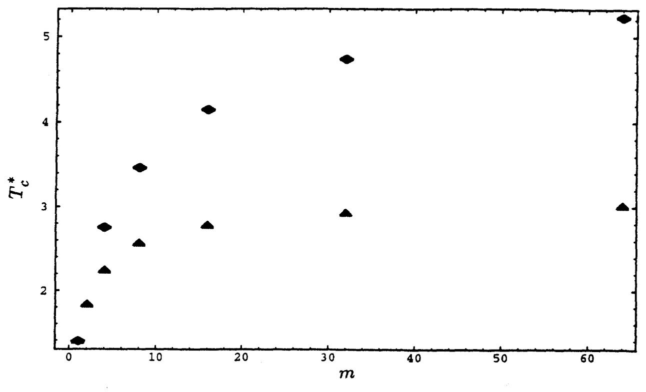

FIG. 11. Square-well chains: the critical temperature corresponding to Z^{SWC} (triangle) and the critical temperature corresponding to $Z^{\mathrm{SWC}'}$ (diamond), as a function of chain length m.

tures and chain lengths. However, this is not the case with $Z^{\mathrm{SWC}'}$ calculated from Eq. (34). The difference between Z^{SWC} and $Z^{\mathrm{SWC}'}$ can be considered a measure of the chain-connectivity effect on the attractive part of Z. As for the sticky chains, this difference is positive. At lower temperatures (e.g., at $T^*=2.0$ in Fig. 6) the agreement of Z^{SWC} with the corresponding MC data is not as good as that at higher temperatures. This is not surprising because the high temperature expansions [Eqs. (25), (26), and (30)] become less accurate at lower temperatures and in the vicinity of critical region.

Finally, we calculate the critical temperatures T_c^* for chains of different m's. The method is illustrated for $m=4$, by locating the critical isotherm in Fig. 10. The results for different m's are presented in Fig. 11; T_c^* monotonically increases as m is increased for both Z^{SWC} and $Z^{\mathrm{SWC}'}$. For a given m, T_c' corresponding to $Z^{\mathrm{SWC}'}$ is overestimated compared with T_c^* corresponding to Z^{SWC}. Again, we attribute this difference to the chain-connectivity effect on the attractive part of Z.

CONCLUSIONS

The compressibility factors derived from TPT1 agree well with Monte Carlo data for square-well chains. The chain connectivity is found to reduce the attraction contribution to the compressibility factor and to critical temperatures for both sticky chains and square-well chains. This is because the excluded-volume interactions for chains are greater than those for nonbonded segments. Also, the calculated critical temperatures monotonically increase with increasing m for both SWC and SC, as expected.

ACKNOWLEDGMENTS

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APPENDIX

The γ coefficients used in Eq. (32) are $\gamma_1=0.653\,305$, $\gamma_2=-1.381\,46$, $\gamma_3=-7.588\,44$, and $\gamma_4=8.401\,66$.

The coefficients for $a^{(1)}$ and $a^{(2)}$ in Eqs. (25) and (26) are $\alpha_1=4.5$, $\beta_1=\sqrt{2}$, $C_1=3.173\,136$, $p_1=-4.974\,192$, $q_1=5.134\,186$, $\alpha_2=9.75$, $\beta_2=\sqrt{2}$, $C_2=-0.384\,466$, $p_2=-2.487\,096$, and $q_2=-0.047\,652$.

[1] R. Dickman and C. K. Hall, J. Chem. Phys. **85**, 4108 (1986).

[2] K. G. Honnell and C. K. Hall, J. Chem. Phys. **90**, 1841 (1989).

[3] Y. C. Chiew, Mol. Phys. **70**, 129 (1990).

[4] T. Boublik, C. Vega, and M. Diaz-Pena, J. Chem. Phys. **93**, 730 (1990).

[5] K. S. Schweizer and J. G. Curro, J. Chem. Phys. **89**, 3342 (1988).

[6] K. S. Schweizer and J. G. Curro, J. Chem. Phys. **89**, 3350 (1988).

[7] A. Yethiraj and C. K. Hall, J. Chem. Phys. **95**, 1999 (1991).

[8] A. Yethiraj and C. K. Hall, J. Chem. Phys. **95**, 8484 (1991).

[9] M. Wertheim, J. Chem. Phys. **87**, 7323 (1987).

[10] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, Ind. Eng. Chem. Res. **29**, 1709 (1990).

[11] S. H. Huang and M. Radosz, Ind. Eng. Chem. Res. **29**, 2284 (1990).

[12] S. H. Huang and M. Radosz, Ind. Eng. Chem. Res. **30**, 1994 (1991).

[13] S. Chen and M. Radosz, Macromolecules **25**, 3089 (1992).

[14] W. G. Chapman, G. Jackson, and K. E. Gubbins, Phys. **65**, 1057 (1988).

[15] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[16] R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).

[17] R. J. Baxter, in *Physical Chemistry, An Advanced Treatise,* Vol. VIIIA, edited by D. Henderson (Academic, New York, 1971).

[18] J. W. Perram and E. R. Smith, Proc. R. Soc. London Ser. A **353**, 193 (1977).

[19] C. Robertus, W. H. Philipse, J. G. H. Joosten, and Y. K. Levine, J. Chem. Phys. **90**, 4482 (1989).

[20] P. W. Rouw, A. Vrij, and C. G. DeKruit, Colloids Surf. **31**, 299 (1991).

[21] Y. C. Chiew, J. Colloid Interface Sci. **143**, 397 (1991).

[22] G. Stell and Y. Zhou, Fluid Phase Equilbria **79**, 1 (1992).

[23] J. A. Barker and D. Henderson, Annu. Rev. Phys. Chem. **23**, 439 (1972).

[24] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[25] D. Henderson and J. A. Barker, in *Physical Chemistry, An Advanced Treatise* (Ref. [17]).

[26] W. R. Smith, D. Henderson, and J. A. Barker, J. Chem. Phys. **55**, 4027 (1971).

[27] L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980).

[28] J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).

[29] D. Henderson, W. G. Madden, and D. D. Fitts, J. Chem. Phys. **64**, 5026 (1976).

[30] C. K. Hall, A. Yethiraj, and J. M. Wichert, Fluid Phase Equilibria (to be published).