Shape Parameters and the Density Dependence of Hard-Chain Equations of State

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Equations of state that provide accurate representation for the properties of small spherical molecules are not accurate in describing the properties of chain molecules, including polymers. This happens because such molecules have rotational and vibrational motions, some of which depend on density and hence, affect the equation of state and other configurational properties. Prigogine et al. (1953, 1957) developed a corresponding states theory for polymers (n-mers), based on the concept that some rotational and vibrational motions are density-dependent. Therefore, they factored the rotational and vibrational contributions to the partition function into external and internal terms. Only the external term depends on density. Then, they introduced a shape parameter c, defined as the one-third the total number of external degrees of freedom; since there are three translational degrees of freedom, $3c-3$ are external rotational and vibrational motions. Flory (1965) developed a simple theory to describe polymer behavior based on Prigogine's ideas. His theory is similar to Prigogine's except that the expressions used to describe intermolecular interactions are taken from free-volume concepts, instead of lattice theory. Prigogine and Flory treat the density dependence of each of the $3c-3$ external degrees of freedom as equivalent to $V_f^{1/3}$ and arrived at similar expressions for the molecular repulsions. Pitzer and coworkers (1955) demonstrated that the compressibility factor and other thermodynamic functions of nonspherical molecules can be described adequately by a relation of the form:

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{1}$$

where $Z^{(0)}$ is the compressibility factor of a simple fluid and $Z^{(1)}$ is the deviation of the compressibility factor of the real from the ideal fluid. ω is a shape parameter called the *acentric factor*, and as originally proposed, it represented the acentricity or nonsphericity of a molecule. For monatomic molecules (argon, methane), ω is therefore essentially zero and ω increases with increasing chain length and/or polarity. At present, the acentric factor is very widely used as a measure of the complexity of a molecule in terms of both geometry and polarity (Reid et al., 1988). Boublik (1975, 1981) derived a hard, convex-body equation of state using scaled particle theory, which has the form:

$$Z^{HC} = \frac{1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3}{(1-\eta)^3} \tag{2}$$

where α is a shape parameter defined as $\alpha = R_m S_m / 3V_m$, where V_m and S_m are the volume and the surface area of the molecule, and R_m is the $(1/4\pi)$-multiple of the mean radius of curvature of the hard convex body. In the limiting case of hard spheres (with $\alpha = 1$), Eq. 2 is identical to the Carnahan-Starling (1972) equation.

In this work, we investigate the role of the shape parameters in different equations of state for hard-chain molecules and examine their correlation with density and chain length.

Review of Equations of State for Hard Chains

Several approaches are available for describing the contributions of the repulsive forces in the equation of state. In the perturbed-hard-chain theory (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978), the Carnahan-Starling (1972) expression for the free volume, V_f, is used, together with the parameter c, which accounts for the one-third of the external (density-dependent) degrees of freedom. Donohue and Prausnitz (1978) treated the nonidealities in the equation of state caused by each external rotational and vibrational degree of freedom as equivalent to the nonidealities caused by each translational degree of freedom. By making this assumption, the PHCT meets the ideal-gas limit at low densities, whereas Prigogine's and Flory's theories give a value of c, rather than unity, at zero density. The hard-chain compressibility factor in PHCT has therefore the form:

$$Z^{HC} = 1 + cZ^{\text{rep}} \tag{3}$$

where Z^{rep} is calculated by the Carnahan-Starling equation.

More recently, Dickman and Hall (1986) derived a continuous-space analogue of the Flory equation of state. They developed the generalized Flory (GF) equation of state for freely-jointed tangent hard chains, which can be written in the form:

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$$Z^{HC} = 1 + \alpha Z^{CS} \tag{4}$$

where α is the ratio of the excluded volume of the n-mer to the excluded volume of the monomer $[\alpha = v_e(n)/v_e(1)]$. It is interesting to note that Eq. 4 (GF) has the same form as Eq. 3 (PHCT). In PHCT, however, the parameter c is empirical and is determined by reduction of vapor pressure and liquid-density data, whereas in GF, α is calculated from molecular structure. In extending the GF theory, Honnell and Hall (1989) proposed a more sophisticated model for chain molecules, the generalized Flory-Dimer (GF-D) theory. This theory accounts for the connectivity of chains and relates the compressibility factor of an n-mer fluid to those of both monomer and dimer fluids, calculated at the same volume fraction, η. The GF-D equation has the form:

$$Z^{HC}(\eta,n) = Z(\eta,2) + Y_n[Z(\eta,2) - Z(\eta,1)] \tag{5}$$

where $Z(\eta,1)$ is the compressibility factor for monomers and is calculated with the Carnahan-Starling equation. The dimer term $Z(\eta,2)$ is calculated with the Tildesley-Streett (1980) equation of state. The parameter Y_n depends on excluded volumes and is given by:

$$Y_n = \frac{v_e(n) - v_e(2)}{v_e(2) - v_e(1)} \tag{6}$$

where $v_e(n)$, $v_e(2)$ and $v_e(1)$ are the excluded volumes of the n-mer, dimer and monomer, respectively.

Radosz and coworkers (Chapman et al., 1990; Huang and Radosz, 1990, 1991) proposed the statistical associating fluid theory (SAFT), which uses a reference term that incorporates both the chain length and molecular association, instead of the simple hard-sphere reference fluid. They developed their model using Wertheim's (1984, 1986) cluster-expansion theory. For nonassociating hard chains, the hard-chain compressibility factor calculated with SAFT is:

$$Z^{HC} = 1 + mZ^{CS} + (1-m)Z^{\text{chain}} \tag{7}$$

where m is the number of segments in the chain and $(1-m)Z^{\text{chain}}$ is the compressibility factor increment due to the formation of the chains.

Elliott et al. (1990) proposed a relatively simple equation:

$$Z^{HC} = 1 + \frac{4c\eta}{1 - 1.9\eta} \tag{8}$$

The ESD equation (Eq. 8) is a compromise between GF, PHCT and the simple van der Waals repulsive form, and gives the divergence of pressure as first-order, whereas other theories are third-order.

Figure 1 shows a comparison of the theories briefly described above, together with Monte Carlo simulation data (Dickman and Hall, 1988) for hard tangent 4-mers. As noted by Vimalchand and Donohue (1989), calculations using bond length, bond angles, and van der Waals radii show that a four-segment chain of tangent hard spheres has the same l/σ ratio as n-octane. Therefore in the calculations for PHCT and SAFT we used parameters fitted to experimental data for n-octane and for ESD the acentric factor of n-octane. In the same figure, calculations using the Sanchez-Lacombe (1976) equation (a model derived from lattice-fluid theory) and the equation proposed by Boublik (Eq. 2) also are included. It can be seen that the GF-D and the SAFT models give a very good representation of Z^{HC} over the whole density range, while the GF theory

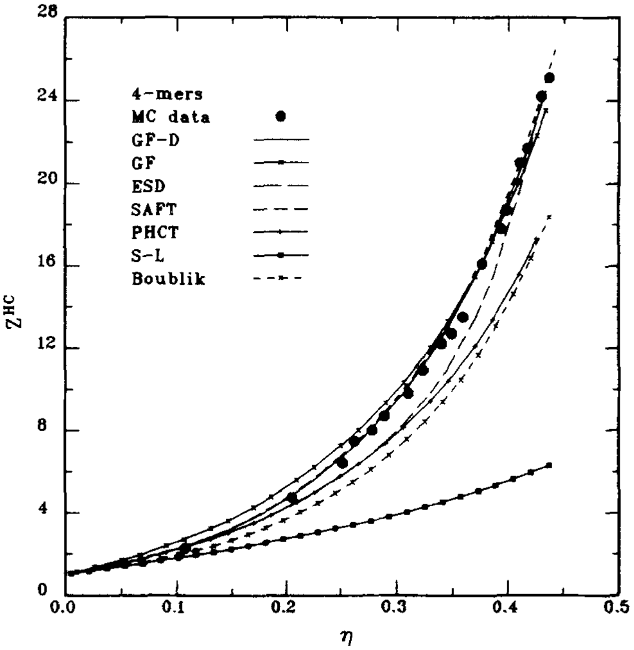

Figure 1. Compressibility factors for hard 4-mers obtained from various equations of state compared with computer simulation data.

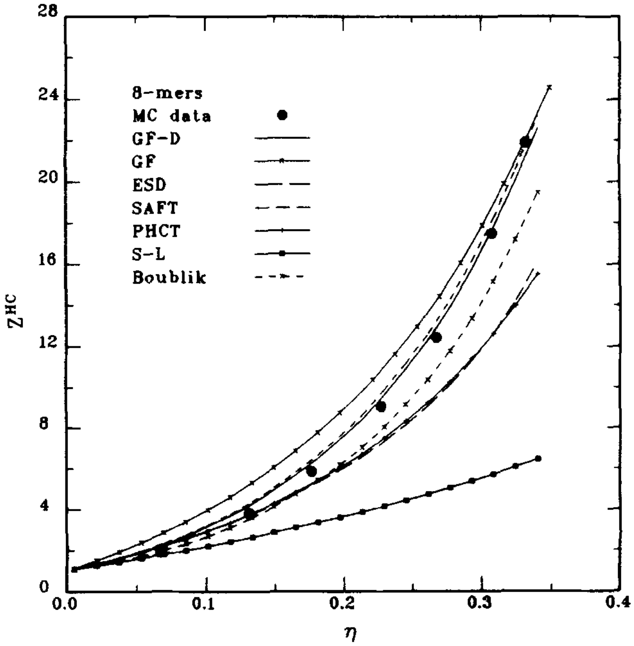

Figure 2. Compressibility factors for hard 8-mers obtained from various equations of state compared with computer simulation data.

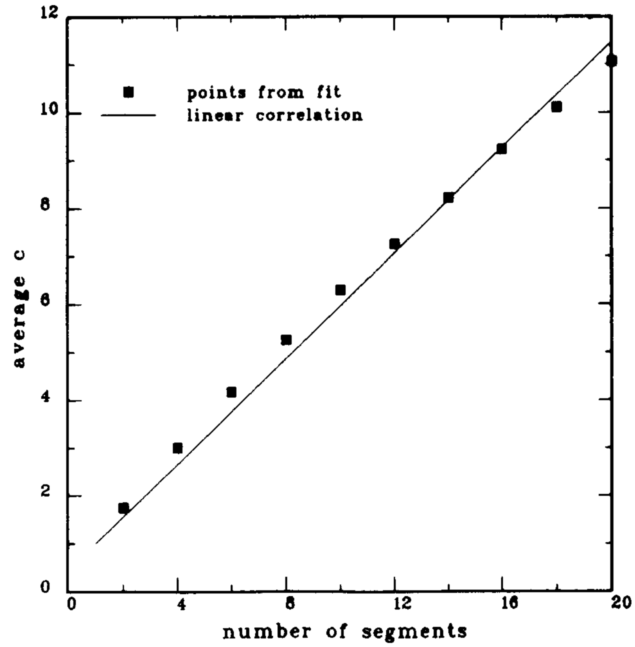

Figure 3. Average (density-independent) *c* parameter obtained by fitting PHCT to GF-D vs. the chain length and linear correlation.

overestimates the compressibility factor. ESD and PHC theories are reasonable at low densities, but underestimate the pressure at higher densities. The Sanchez-Lacombe and the Boublik equations underestimate the compressibility factor everywhere. Similar results are shown in Figure 2 that shows a comparison of the same theories with simulation data for tangent 8-mers using parameters for hexadecane.

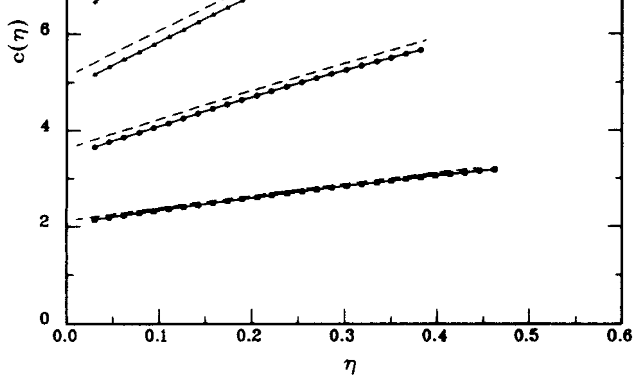

Figure 4. Density dependence of the shape parameter for various *n*-mers obtained by fitting PHCT to GF-D (———) and SAFT (- - - -).

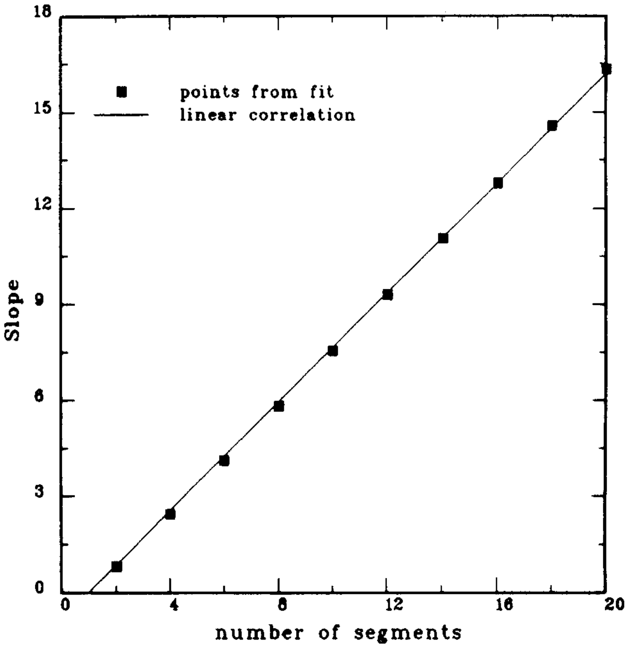

Figure 5. Linear correlation of the slope of the solid lines in Figure 4 (GF-D) with the chain length.

Shape Parameters

In the theories discussed above, the shape factors account for different things. In SAFT and Sanchez-Lacombe equations, m and r represent the number of segments in the molecule, respectively. In PHCT, the Prigogine c parameter accounts for one-third of the external degrees of freedom. In ESD, c is an empirical shape parameter and is correlated with the acentric factor according to a simple second-order polynomial. In the GF and GF-D theories, α and Y_n are ratios of excluded volumes. One question that arises is whether the accuracy of the GF-D equation can be mimicked by the simpler GF or PHCT equations. To examine this, we fitted Eq. 3 (PHCT or GF) to GF-D to obtain the optimal c (or α) value for each n-mer molecule. Results are shown in Figure 3. The variation of the parameter c with the chain length is almost linear with a slight curvature.

After simple algebra, the GF-D equation (Eq. 3) can be rewritten as:

$$Z^{HC} = 1 + \left[1 + (Y_n + 1)\left(\frac{Z^{TS}}{Z^{CS}} - 1\right) \right] Z^{CS} \qquad (9)$$

Equation 9 reduces to GF (and PHCT) if the quantity within the square brackets is independent of density. Figure 4 shows the variation of this quantity with the volume fraction. It also shows a plot of the corresponding quantity from the SAFT equation, if we rewrite it in a way similar to Eq. 9. For both GF-D and SAFT theories, the term in brackets is a linear function of density with both slope and intercept increasing as the number of segments in the chain increases. The slope of these lines (from Eq. 9) varies linearly with chain length, as shown in Figure 5. There is also a linear correlation between the slope and the intercept, as indicated in Figure 6. This suggests that it is not necessary to introduce any additional

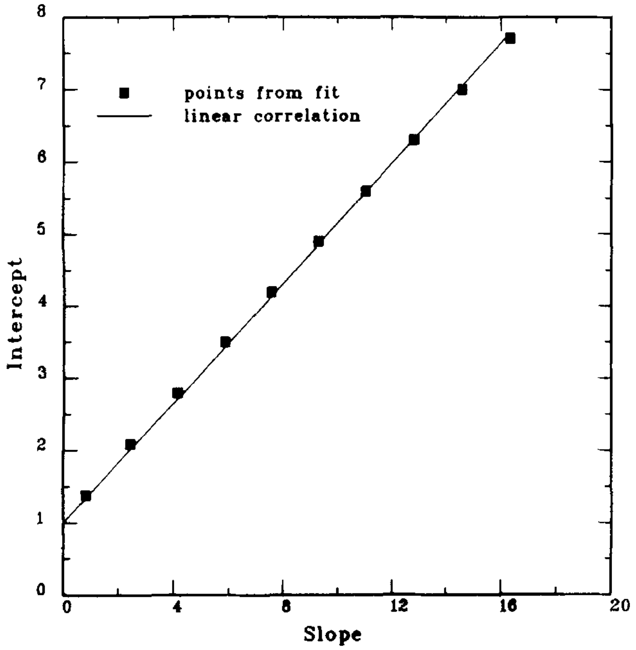

Figure 6. Linear correlation between the slope and intercept of solid lines in Figure 4 (GF-D).

parameters to obtain the GF-D behavior by using the GF (or PHCT) form (Eq. 3). After trivial linear regression, GF-D can be written as:

$$Z^{HC} = 1 + [1 + 0.852(0.415 + \eta)(n-1)]Z^{CS} \tag{10}$$

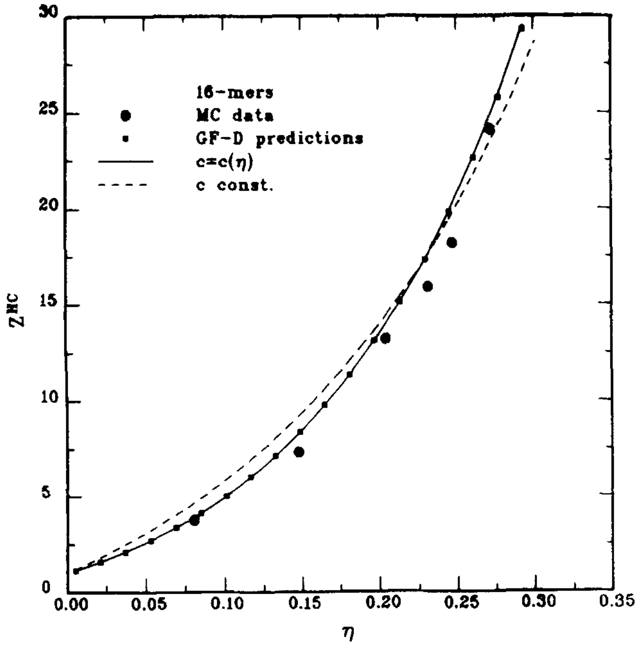

Figure 7. Compressibility factors for hard 16-mers obtained with density-dependent (——) and density-independent (- - - -) shape parameter; predictions of the GF-D theory and Monte Carlo simulations of Dickman and Hall (1988) are also shown.

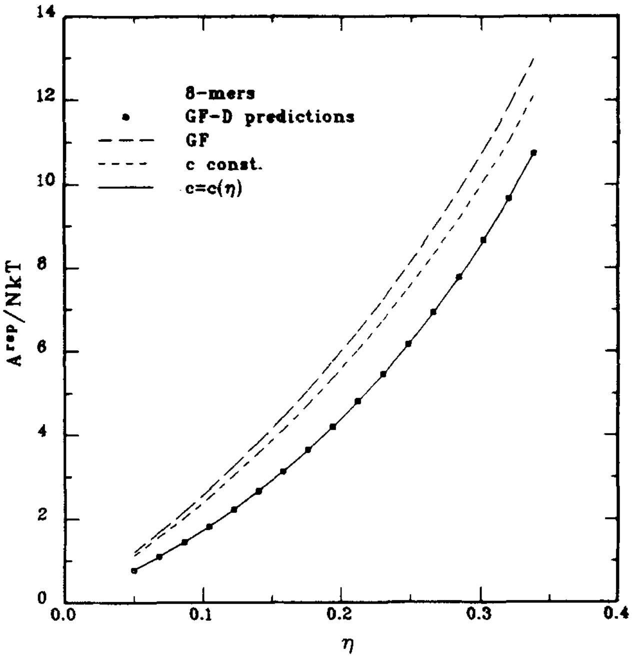

Figure 8. Repulsive contribution to the Helmholtz free energy for hard 8-mers obtained by using constant *c*, density-dependent *c*, and the GF and GF-D theories.

where n represents the number of segments in each chain molecule and is the only parameter in Eq. 10. In the limit of the chain that consists of one segment (hard-sphere), n is unity; hence, the shape factor in Eq. 9 becomes unity, as it is in PHCT, GF, and GF-D. Equation 10 is a compromise between PHCT and GF-D. It is somewhat more complicated than PHCT but simpler than GF-D, while it retains the accuracy of GF-D theory.

In Figure 7 we show a comparison of our results with GF-D theory, in terms of the hard-chain compressibility factor for 16-mers. Equation 10 is in excellent agreement with the GF-D predictions, whereas the PHCT with fitted, but density-independent, c goes from overestimating the pressure at low densities to underestimating it at high densities.

In Figure 8, we show a comparison of the theories discussed above in terms of predicting the repulsive contribution to the Helmholtz free energy for hard 8-mers. The equation that uses the density-dependent shape parameter (Eq. 10) agrees with the GF-D theory. The PHC theory with the parameter c fitted is not in agreement with the GF-D predictions.

Conclusions

All the equations in this work can be written in the form:

$$Z^{HC} = 1 + c(\eta)Z^{rep} \tag{11}$$

Their difference is that they use different expressions for describing the repulsive part, Z^{rep}, and that the shape parameter $c(\eta)$ has different physical meaning in each theory. In PHCT, c accounts for the external degrees of freedom, while in the GF theory, α represents the ratio of excluded volumes. In GF-D, as written in Eq. 9, the shape parameter takes into account the fact that the chain is composed of *connected* segments through the Tildesley-Streett dimer equation. We show that it is possible to obtain the GF-D behavior by using the PHCT formalism with a density-dependent c parameter. The model developed here (Eq. 10) uses a linear shape parameter and is in excellent agreement with GF-D in terms of predicting the repulsive contribution to the Helmholtz free energy and the equation of state, while it does not add much complexity to PHCT. However, when we tried to fit a density-independent c parameter to GF-D, we did not have much success, as Figures 7 and 8 demonstrate. This suggests that for an accurate representation of the repulsive part of the Helmholtz free energy and the pressure using a PHCT-type equation, a density-dependent shape parameter is necessary.

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Notation

c = shape parameter in Eqs. 3 and 8
m, n = number of segments
l = bond length
R_m = mean radius of curvature
S_m = surface area of the molecule
v_e = excluded volume
V_f = free volume
V_m = volume of the molecule
Y_n = ratio of excluded volumes
Z = compressibility factor

Greek letters

α = shape parameter in Eqs. 2 and 4
η = volume fraction
σ = hard-sphere diameter
ω = acentric factor

Superscripts

(0) = zeroth-order term in Eq. 1
(1) = first-order term in Eq. 2
CS = Carnahan-Starling
HC = hard chain
rep = repulsive
TS = Tildesley-Streett

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