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Equation of State for Fluids Containing Chain-like Molecules

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ABSTRACT

An equation of state for chain fluids has been derived through the r -particle cavity-correlation function (CCF) for chains obtained from sticky spheres; here r is the chain length. The r -particle CCF is approximated by a product of effective two-particle CCFs, accounting for nearest-neighbor correlations and next-to-nearest-neighbor correlations. For hard-sphere chain fluids (HSCF), the density dependence for nearest-neighbor effective two-particle CCFs is determined by the equation of Tildesley-Streett for hard-sphere dumbbells and that for next-to-nearest-neighbor effective two-particle CCFs by computer-simulation results for hard-sphere trimers. The final equation of state has a simple form which gives compressibility factors and second virial coefficients for homonuclear HSCFs covering a wide range of chain length (up to $r=201$) in excellent agreement with computer simulations. Satisfactory comparisons are also obtained between predicted and computer-simulation results for homonuclear HSCF mixtures, HSCFs containing side-chains and rings, and heteronuclear HSCFs (copolymers).

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I. INTRODUCTION

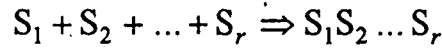
In recent years, much attention has been given toward development of an equation of state for an assembly of chain-like molecules. Numerous studies are based on modifications of the lattice theory¹ (e.g. Sanchez and Lacombe, Kleintjens and Koningsveld, Hu, Ying, Wu and Prausnitz), but most recent efforts are of the free-space (off-lattice) forms; they tend to be based on the perturbation theory and the integral theory of fluids (e.g. Wertheim², Chapman, Gubbins, Jackson and Radosz³, Chang and Sandler⁴, Phan, Kierlik, Rosinberg, Yu and Stell⁵, Walsh and Gubbins⁶, Amos and Jackson⁷, Johnson, Mueller and Gubbins⁸, Ghonasgi and Chapman⁹, Chiew¹⁰, Song, Lambert and Prausnitz¹¹), or on generalized Flory theory coupled with the concept of insertion probability (e.g. Dickman and Hall¹², Bokis, Donohue and Hall¹³, Yethiraj and Hall¹⁴).

The equation of state derived here follows from ideas that are somewhat different from those typically found in the literature. We do not use lattice theory, nor the perturbation theory and the integral theory of fluids, nor insertion probabilities. Instead, similar to Zhou and Stell¹⁵, we define an r -particle cavity-correlation function (CCF) for chains formed by sticky spheres; here r is the chain length. In terms of r -particle CCF, we obtain expressions for the Helmholtz function and the equation of state. To make progress, we require information concerning the density dependence of the r -particle CCF. We establish that information in two steps. First, we use an idea similar to Kirkwood's superposition approximation wherein we retain nearest-

neighbor and next-to-nearest neighbor correlations. Second, we establish those correlations using the dumbbell equation of Tildesley and Streett¹⁶ for nearest-neighbor correlations and computer-simulation results for hard-sphere trimers for next-to-nearest-neighbor correlations.

II. THERMODYNAMIC PROPERTIES FROM THE r-PARTICLE CAVITY CORRELATION FUNCTION

We consider a multicomponent system composed of r different species S_i , where $i=1, 2, 3, \dots, r$. These species can form an r -mer by the reaction



The configuration of the r -mer is shown in Figure 1, where n is the number of segments in the main chain; s is the number of segments in the side chain which starts from the f th segment in the main chain; $n+s=r$. For each nearest-neighbor pair S_i - S_j , there are m_{ij} different interaction configurations; each configuration is characterized by an inter-segment distance vector $L_{ij,k}$, where $k=1, 2, 3, \dots, m_{ij}$. These vectors originate from a definite number of interaction sites on each segment. The corresponding magnitude is L_{ij} , irrespective of k .

By adopting the sticky-point model of Cummings and Stell¹⁷ for each nearest-neighbor pair, the Mayer function for a group of r segments can be expressed as:

$$f_{S_1 S_2 \dots S_r}^{(r)} = -1 + \prod_{j=i+1}^{r-1} \left(L_{ij} \sum_{k=1}^{m_{ij}} \delta(\mathbf{r}_{ij} - \mathbf{L}_{ij,k}) / 12\tau_{ij} \right), \quad r_{ij} < \sigma_{ij} \quad (1)$$

$$= -1 + \exp(-\beta \epsilon_{S_1 S_2 \dots S_r}^{(r)}), \quad r_{ij} > \sigma_{ij}$$

where the product covers all possible nearest-neighbor segment pairs. For example, for an r -mer shown in Figure 1, when $i=n$, n should be changed to f and $j=n+1$. Variables \mathbf{r}_{ij} and r_{ij} are the inter-segment distance vector and the corresponding magnitude, respectively. Symbol δ is a Kronecker delta; σ_{ij} is the collision diameter; τ_{ij}^{-1} is the stickiness parameter; and $\varepsilon_{S_1 S_2 \dots S_r}$ is the attractive energy at distances beyond the collision diameter; $\varepsilon_{S_1 S_2 \dots S_r}$ is not a constant but a function of \mathbf{r}_{ij} . When $r_{ij} < \sigma_{ij}$, the corresponding r -particle total correlation function can be written as :

$$h_{S_1 S_2 \dots S_r}^{(r)} = -1 + \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(\lambda_{ij} L_{ij} \sum_{k=1}^{m_{ij}} \delta(\mathbf{r}_{ij} - \mathbf{L}_{ij,k}) / 12 \right), \quad r_{ij} < \sigma_{ij} \quad (2)$$

where λ_{ij} is a distribution parameter related to τ_{ij}^{-1} .

To form chains, we start with a mixture of monomers. (The monomers comprising a chain are not necessarily identical.) In general, an r -mer may contain r different monomers. Our initial mixture of monomers contains r species. All chains formed from this mixture of monomers have the same chain length r . For complete aggregation, the mole fractions of all different monomers must be the same; the number density for each species, associated or unassociated, equals a constant:

$$\rho_{0S_1} = \rho_{0S_2} = \dots = \rho_{0S_r} = \rho_0 \quad (3)$$

It is convenient to define α , the degree of association, by

$$\alpha \equiv \rho_{S_1 S_2 \dots S_r} / \rho_0 = \rho_0^{r-1} \int_{L_-}^{L_+} g_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{r-1,r}) d\mathbf{r}_{12} d\mathbf{r}_{23} \dots d\mathbf{r}_{r-1,r} \quad (4)$$

where $g_{S_1 S_2 \dots S_r}^{(r)}$ is the r -particle radial distribution function; $h_{S_1 S_2 \dots S_r}^{(r)} = g_{S_1 S_2 \dots S_r}^{(r)} - 1$.

The integration should cover all possible configurations of an r -mer. Substitution of eq.(2) into eq.(4) yields

$$\alpha = \omega \rho_0^{r-1} \prod_{j=i+1}^{r-1} [(\lambda_{ij} L_{ij} / 12)(4\pi L_{ij}^2)] = \omega \rho_0^{r-1} \prod_{j=i+1}^{r-1} (\lambda_{ij} \pi L_{ij}^2 / 3) \quad (5)$$

where ω , the number of possible configurations for an r -mer, is a constant that cancels out in the final results. The association ratio K is defined by

$$K \equiv \rho_{S_1 S_2 \dots S_r} / \prod_{i=1}^r \rho_{S_i} = \frac{\alpha}{\rho_0^{r-1} (1 - \alpha)^r} \quad (6)$$

When all number densities approach zero, K approaches K_0 which is determined by the Mayer function:

$$K_0 = \int_{L_-}^{L_+} \exp(-\beta \epsilon_{S_1 S_2 \dots S_r}^{(r)}) d\mathbf{r}_{12} d\mathbf{r}_{23} \dots d\mathbf{r}_{r-1,r} = \int_{L_-}^{L_+} (1 + f_{S_1 S_2 \dots S_r}^{(r)}) d\mathbf{r}_{12} d\mathbf{r}_{23} \dots d\mathbf{r}_{r-1,r} \quad (7)$$

Substitution of eq.(1) yields

$$K_0 = \omega \prod_{i=1}^{r-1} \left[(L_{ij} / 12\tau_{ij})(4\pi L_{ij}^2) \right] = \omega \prod_{i=1}^{r-1} (\pi L_{ij}^3 / 3\tau_{ij}) \quad (8)$$

We are now able to define the r-particle cavity correlation function (CCF):

$$y_{S_1 S_2 \dots S_r}^{(r)} \equiv \exp(\beta \varepsilon_{S_1 S_2 \dots S_r}^{(r)}) g_{S_1 S_2 \dots S_r}^{(r)} \quad (9)$$

When $r_{ij} = L_{ij,k}$, ($k = 1, 2, 3, \dots, m_{ij}$), the assembly of r particles becomes an r-mer. By substituting eqs.(1),(2),(5),(6) and (8) into eq.(9), we have a useful expression for the r-particle CCF for an r-mer associate:

$$y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) = \prod_{i=1}^{r-1} (\tau_{ij} \lambda_{ij}) = \frac{K}{K_0} (1 - \alpha)^r \quad (10)$$

where \mathbf{L} represents a set of $L_{ij,k}$.

To obtain the Helmholtz function, we use its functional derivative with respect to the Mayer function for an r-particle group, which is related to the r-particle CCF by

$$\frac{\partial(\beta A / V)}{\partial f_{S_1 S_2 \dots S_r}^{(r)}} = - \prod_{i=1}^r \rho_{0S_i} \times y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{r-1,r}) \quad (11)$$

From eq.(1) we have

$$\partial f_{S_1 S_2 \dots S_r}^{(r)} = \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(L_{ij} \sum_{k=1}^{m_{ij}} \delta(\mathbf{r}_{ij} - \mathbf{L}_{ij,k}) / 12 \right) \partial \tau_{ij}^{-1} \quad (12)$$

Substituting eq.(12) into eq.(11), integrating twice, first from \mathbf{L}_{ij,k^-} to \mathbf{L}_{ij,k^+} and then from 0 to τ_{ij}^{-1} , we have

$$\frac{\beta[A(\alpha) - A(\alpha = 0)]}{N_0} = -\frac{\omega}{r} \prod_{\substack{i=1 \\ j=i+1}}^{r-1} (\pi \rho_0 L_{ij} / 3) \int \dots \int_0^{\tau_{ij}^{-1}} y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) d\tau_{12}^{-1} d\tau_{23}^{-1} \dots d\tau_{r-1,r}^{-1} \quad (13)$$

Here N_0 is the total number of monomers prior to association. From eqs.(5) and (10),

$$\prod_{\substack{i=1 \\ j=i+1}}^{r-1} d\tau_{ij}^{-1} = d \left(\prod_{\substack{i=1 \\ j=i+1}}^{r-1} \lambda_{ij} / y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) \right) = \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \omega^{-1} (\pi \rho_0 L_{ij} / 3)^{-1} d \frac{\alpha}{y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L})} \quad (14)$$

Substitution into eq.(13) yields

$$\begin{aligned} \frac{\beta[A(\alpha) - A(\alpha = 0)]}{N_0} &= -\frac{1}{r} \int y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) d[\alpha / y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L})] \\ &= -\frac{1}{r} \left[\int_0^\alpha d\alpha - \int_{\alpha=0}^{\alpha=\alpha} \alpha d \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) \right] = -\frac{1}{r} \left[\alpha - \int_{\alpha=0}^{\alpha=\alpha} \alpha d \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) \right] \end{aligned} \quad (15)$$

To obtain the equation of state, we use the thermodynamic relation:

$$p = (r\rho_0)^2 \left(\frac{\partial(A/N_0)}{\partial(r\rho_0)} \right)_{T, \tau^{-1}} = r\rho_0^2 \left(\frac{\partial(A/N_0)}{\partial\rho_0} \right)_{T, \tau^{-1}} \quad (16)$$

Substitution of eqs.(5),(10) and (13) into eq.(16) yields

$$\begin{aligned} \frac{\beta[p(\alpha) - p(\alpha = 0)]}{r\rho_0} = & -\frac{1}{r}[(r-1)\alpha - (r-1)] \int_{\alpha=0}^{\alpha=\alpha} \alpha d \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) \\ & + \rho_0 \int_0^\alpha (\partial \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) / \partial \rho_0) d\alpha \\ & - \rho_0 \int_{\alpha=0}^{\alpha=\alpha} \alpha (\partial \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) / \partial \rho_0) d \ln y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) \end{aligned} \quad (17)$$

Eq. (15) gives the generalized Helmholtz function and eq.(17) gives the generalized equation of state for an equimolar mixture of original monomers where some monomers have associated into r-mers. When the degree of association α equals unity, eqs.(15) and (17) are generalized equations for a chain fluid. Because neither the sizes of monomers nor the configurations of a chain have been restricted, those equations can be applied to homonuclear chain fluids with or without side chains and rings, as well as to heteronuclear chain fluids such as random or block copolymers.

III. THE r-PARTICLE CAVITY CORRELATION FUNCTION

As shown in eqs.(15) and (17), the key to obtaining the Helmholtz function and the equation of state is provided by information on the r-particle CCF for an r-mer chain with a particular configuration. In principle, the r-particle CCF could be determined by the inter-segment potential function or the Mayer function. In effect,

Cummings and Stell¹⁷ have done so using the Percus-Yevick approximation for dimers. However, at present it is not possible to use a similar approach for polymers.

Zhou and Stell¹⁵ adopted a linear approximation and simplified the r-particle CCF by using the nearest-neighbor two-particle CCF raised to an empirical power. Following Zhou and Stell, and inspired by Kirkwood's superposition approximation, we propose to calculate the r-particle CCF as the product of two contributions: a chemical contribution $(1 - \alpha)^r$ dependent on the degree of association, and a physical contribution expressed by the product of nearest-neighbor effective two-particle CCFs $y_{S_i S_{i+1}}^{(2e)}$ and the product of next-to-nearest-neighbor effective two-particle CCFs $y_{S_i S_{i+2}}^{(2e)}$. The chemical term $(1 - \alpha)^r$ satisfies the boundary condition that when all number densities approach zero, $y_{S_1, S_2, \dots, S_r}^{(r)}(\mathbf{L}) = (1 - \alpha)^r$ according to eq.(10) while the physical contribution to CCF is reduced to unity. As for the physical term, this procedure retains the most essential part of the r-particle CCF. It provides a reasonable approximation because it makes a first-order attempt to include higher correlations between segments in a chain; it neglects only correlations between two segments that are separated by more than one segment.

$$y_{S_1 S_2 \dots S_r}^{(r)}(\mathbf{L}) = (1 - \alpha)^r \prod_{i=1}^{r-1} y_{S_i S_{i+1}}^{(2e)} \prod_{i=1}^{r-2} y_{S_i S_{i+2}}^{(2e)} \quad (18)$$

In this equation, the first product covers all possible nearest-neighbor segment pairs; the second product covers all possible next-to-nearest-neighbor segment pairs. The generalized Helmholtz function becomes

$$\beta[A(\alpha) - A(\alpha = 0)] / N_0 = \ln(1 - \alpha) + \alpha(r - 1) / r \quad (19)$$

However, this equation is of no use when $\alpha=1$. We obtain a useful equation for the residual Helmholtz function later.

The generalized equation of state is

$$\frac{\beta[p(\alpha) - p(\alpha = 0)]}{r\rho_0} = -\frac{\alpha}{r} \left[r - 1 + \rho_0 \sum_{i=1}^{r-1} \frac{\partial \ln y_{S_i S_{i+1}}^{(2e)}}{\partial \rho_0} + \rho_0 \sum_{i=1}^{r-2} \frac{\partial \ln y_{S_i S_{i+2}}^{(2e)}}{\partial \rho_0} \right] \quad (20)$$

To obtain a useful result, we require the density dependences of nearest-neighbor and next-to-nearest-neighbor effective two-particle CCFs and an equation of state for monomers.

IV. EQUATION OF STATE FOR HOMONUCLEAR HARD-SPHERE-CHAIN FLUIDS AND FLUID MIXTURES

Pure Homonuclear Hard-Sphere-Chain Fluids

For a homonuclear chain, we designate the total number of nearest-neighbor segment pairs by $r_{S_i S_{i+1}}$; neglecting end effects, all segment pairs have approximately the same effective two-particle CCF. We designate the total number of next-to-

nearest-neighbor segment pairs by $r_{S_i S_{i+2}}$ and again we do not distinguish between different homonuclear pairs. Eqs (19) and (20) can be further simplified. For a pure homonuclear HSCF, $\alpha = 1$; the equation of state and the residual Helmholtz function are :

$$Z \equiv \frac{\beta p}{\rho_0} = rZ(\alpha = 0) - [(r-1) + r_{S_i S_{i+1}} \eta \frac{d \ln y_{S_i S_{i+1}}^{(2e)}}{d\eta} + r_{S_i S_{i+2}} \eta \frac{d \ln y_{S_i S_{i+2}}^{(2e)}}{d\eta}] \quad (21)$$

$$\frac{\beta A^r}{N} = r \frac{\beta A^r(\alpha = 0)}{rN} - r_{S_i S_{i+1}} \ln y_{S_i S_{i+1}}^{(2e)} - r_{S_i S_{i+2}} \ln y_{S_i S_{i+2}}^{(2e)} \quad (22)$$

where $r_{S_i S_{i+1}} = r-1$; $r_{S_i S_{i+2}} = r-2$; A^r is the residual Helmholtz function; η is the reduced density; $\eta = \pi r \rho_0 \sigma^3 / 6$; and N is the total number of chain molecules. Eq.(21) comes directly from eq.(20). Eq.(22) is obtained by integration of eq.(16) with the pressure substituted by eq.(21). The corresponding monomer system is a hard-sphere fluid. Therefore, for $\alpha=0$, we use the well-known Carnahan-Starling equation.

$$Z(\alpha = 0) = \frac{\beta p}{r \rho_0} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (23)$$

$$\frac{\beta A^r(\alpha = 0)}{rN} = \frac{3\eta - 1}{(1 - \eta)} + \frac{1}{(1 - \eta)^2} \quad (24)$$

The density dependence of the effective two-particle CCF $y_{S_i S_{i+1}}^{(2e)}$ for the nearest-neighbor pair can be derived from the Tildesley-Streett equation¹⁶ for hard dumbbells. The result is.

$$\ln y_{S_i S_{i+1}}^{(2e)} = \frac{(3 + a_{20})\eta - (1 + b_{20})}{2(1 - \eta)} + \frac{1 + b_{20}}{2(1 - \eta)^2} - (c_{20} + 1)\ln(1 - \eta) \quad (25)$$

$$a_{20} = -a_2 + b_2 - 3c_2 \quad , \quad b_{20} = -a_2 - b_2 + c_2 \quad , \quad c_{20} = c_2 \quad (26)$$

$$a_2 = 0.45696 \quad , \quad b_2 = 2.10386 \quad , \quad c_2 = 1.75503 \quad (27)$$

To obtain the density dependence of the effective two-particle CCF $y_{S_i S_{i+2}}^{(2e)}$ for the next-to-nearest-neighbor pair, we assume a similar expression.

$$\ln y_{S_i S_{i+2}}^{(2e)} = \frac{(r-1)}{r} \left[\frac{a_{30}\eta - b_{30}}{2(1 - \eta)} + \frac{b_{30}}{2(1 - \eta)^2} - c_{30}\ln(1 - \eta) \right] \quad (28)$$

where parameters a_{30} , b_{30} , c_{30} are obtained by fitting computer-simulation data for compressibility factors for linear homonuclear hard-sphere trimers (Amos and Jackson¹⁸; Muller and Gubbins¹⁹).

$$a_{30} = -a_3 + b_3 - 3c_3 \quad , \quad b_{30} = -a_3 - b_3 + c_3 \quad , \quad c_{30} = c_3 \quad (29)$$

$$a_3 = -0.74745 \quad , \quad b_3 = 3.49695 \quad , \quad c_3 = 4.83207 \quad (30)$$

For homonuclear HSCFs, the final equation of state and excess Helmholtz function are given by remarkably simple forms:

$$\frac{\beta p}{\rho_0} = \frac{1+a\eta+b\eta^2-c\eta^3}{(1-\eta)^3} \quad (31)$$

$$\frac{\beta A^r}{N} = \frac{(3+a-b+3c)\eta-(1+a+b-c)}{2(1-\eta)} + \frac{1+a+b-c}{2(1-\eta)^2} + (c-1)\ln(1-\eta) \quad (32)$$

where a , b and c are functions of chain length r only:

$$a = r \left(1 + \frac{r-1}{r} a_2 + \frac{r-1}{r} \frac{r-2}{r} a_3 \right) \quad (33)$$

$$b = r \left(1 + \frac{r-1}{r} b_2 + \frac{r-1}{r} \frac{r-2}{r} b_3 \right) \quad (34)$$

$$c = r \left(1 + \frac{r-1}{r} c_2 + \frac{r-1}{r} \frac{r-2}{r} c_3 \right) \quad (35)$$

To test the reliability of the above equations, we compare predicted results with computer-simulation data. Figures 2, 3 and 4 compare calculated compressibility factors for homonuclear HSCFs (with chain length $r = 16, 51, 201$) with those from computer-simulation data (Denlinger and Hall²⁰; Dickman and Hall¹²; Gao and Weiner²¹; Yethiraj and Hall¹⁴;) Also shown are calculated results by TPT1(Wertheim⁵), GFD (Yethiraj and Hall¹⁴) and PY-CS of Chiew¹⁰.

Compressibility factors predicted by eq.(31) are in nearly perfect agreement with simulations, over a wide range of chain length.

From eq.(31), the reduced second virial coefficient for homonuclear HSCFs is

$$B_{2R} = \frac{B_2}{\sigma^3} = \frac{\pi}{6} r (3+a) \quad (36)$$

Figure 5 compares second virial coefficients predicted by this work to those obtained by TPT1 (Wertheim²), Zhou-Stell¹⁵, GFD (Honnell and Hall²²) with MC data (Yethiraj et al.²³).

Homonuclear Hard-Sphere-Chain Fluid Mixtures

For hard-sphere-chain fluid mixtures, eqs.(21) and (22) can be extended. For a K -component mixture,

$$Z = \tilde{r} Z(\alpha = 0) - \left[\tilde{r} - 1 + \sum_{i=1}^K x_i r_{S_j S_{j+1}(i)} \eta \frac{d \ln y_{S_j S_{j+1}(i)}^{(2e)}}{d\eta} + \sum_{i=1}^K x_i r_{S_j S_{j+2}(i)} \eta \frac{d \ln y_{S_j S_{j+2}(i)}^{(2e)}}{d\eta} \right] \quad (37)$$

$$\frac{\beta A^r}{N} = \tilde{r} \frac{\beta A^r(\alpha = 0)}{\tilde{r} N} - \sum_{i=1}^K x_i r_{S_j S_{j+1}(i)} \ln y_{S_j S_{j+1}(i)}^{(2e)} - \sum_{i=1}^K x_i r_{S_j S_{j+2}(i)} \ln y_{S_j S_{j+2}(i)}^{(2e)} \quad (38)$$

where r_i and x_i are the chain length and the mole fraction of component i respectively; $x_i = N_i / N$; N_i and N are numbers of molecules for component i and the whole system, respectively; $\bar{r} = \sum_{i=1}^K x_i r_i$ is the average chain length; $y_{S_j S_{j+1}}^{(2e)}$ and $y_{S_j S_{j+2}}^{(2e)}$ are two-particle CCFs for component i which can be calculated from eqs.(25) and (28). Because monomers for different components may have different sizes, instead of the Carnahan-Starling equation, $Z(\alpha=0)$ and $A'(\alpha=0)$ are now calculated from the Mansoori-Carnahan-Starling-Leland equation²⁴.

$$Z(\alpha=0) = 1 + \eta \left[\frac{1 + 3 \frac{BE}{F} - \frac{E^3}{F^2}}{1 - \eta} + \frac{3 \frac{BE}{F} \eta - \frac{E^3}{F^2}}{(1 - \eta)^2} + \frac{2 \frac{E^3}{F^2}}{(1 - \eta)^3} \right] \quad (39)$$

$$\frac{\beta A'(\alpha=0)}{\sum_i^K r_i N_i} = \frac{3 \frac{BE}{F} \eta - \frac{E^3}{F^2}}{1 - \eta} + \frac{\frac{E^3}{F^2}}{(1 - \eta)^2} + \left(\frac{E^3}{F^2} - 1 \right) \ln(1 - \eta) \quad (40)$$

where

$$B = \frac{\sum_{i=1}^K N_i r_i \sigma_i}{\sum_{i=1}^K N_i r_i}, \quad E = \frac{\sum_{i=1}^K N_i r_i \sigma_i^2}{\sum_{i=1}^K N_i r_i}, \quad F = \frac{\sum_{i=1}^K N_i r_i \sigma_i^3}{\sum_{i=1}^K N_i r_i}, \quad \eta = \frac{\pi}{6} \sum_{i=1}^K r_i \rho_i \sigma_i^3 \quad (41)$$

Figures 6 and 7 show comparisons between predicted compressibility factors of homonuclear HSCF mixtures and corresponding MC data (Honnell and Hall²⁵). The prediction is nearly perfect.

Homonuclear Hard-Sphere-Chain Fluids With Side Chains

We consider a homonuclear chain molecule with side chains. Of the total r segments, there are r_1 segments in the main chain which are bonded to one side-chain (single branch), and r_2 segments in the main chain which are bonded to two side-chains (double branch). If we ignore the steric hindrance between different side-chains, similarly, all CCFs for nearest-neighbor segment pairs are then equal to each other, all CCFs for next-to-nearest-neighbor segment pairs are equal to each other. The total number of nearest-neighbor segment pairs is the same as that in a linear homonuclear chain with the same number of segments. However, the total number of next-to-nearest-neighbor segment pairs is different from that of the corresponding linear chain. Each single branch has one more next-to-nearest-neighbor segment pair, each double branch has three more pairs, in comparison with the corresponding linear chain with the same number of segments. Eqs.(21) and (22) can then be used for the equation of state and the residual Helmholtz function as a reasonable approximation for homonuclear HSCFs with side chains, while $r_{S_i S_{i+1}} = r - 1$ and $r_{S_i S_{i+2}} = r - 2 + r_1 + 3r_2$.

To test the reliability of the proposed equations, we compare predicted results with computer-simulation data. Muller and Gubbins¹⁹ have reported simulation compressibility factors for homonuclear planar branched Y-type tetratomic and T-type tetratomic molecules. Comparisons of results predicted by this work and those by computer simulation, shown in Figure 8, indicates good agreement.

Hard-Sphere-Chain Fluids With Rings

We consider a ring molecule composed of r hard spheres. There are r nearest-neighbor and r next-to-nearest-neighbor segment pairs. Eqs.(21) and (22) are again used with $r_{s_i s_{i+1}} = r$ and $r_{s_i s_{i+2}} = r$. However, for ring trimers, there is no next-to-nearest-neighbor segment pair, i.e., $r_{s_i s_{i+2}} = 0$. For ring tetramers, the number of next-to-nearest-neighbor segment pairs is 2, i.e., $r_{s_i s_{i+2}} = 2$.

Sear and Jackson²⁶ have reported MC compressibility factors for equilateral triangle trimer, planar-square and tetrahedral tetramer and planar pentamer hard-sphere ring molecules. Figure 9, comparing predicted results with computer-simulation data, indicates good agreement.

V. EQUATION OF STATE FOR HETERONUCLEAR HARD-SPHERE-CHAIN FLUIDS AND FLUID MIXTURES

Next we consider a more general case. We consider a K -component mixture of hard-sphere-chains. Each component i contains N_i molecules; each chain is composed of r_i tangent hard spheres with different diameters. The total number of chains is denoted by $N = \sum_i^K N_i$. Altogether there are M different hard-sphere species in the mixture with different diameter $\sigma_j, j=1, 2, 3, \dots, M$. The number of hard spheres j in a molecule of component i is denoted by $r_{j(i)}$. Let $r_{jk(i)}$ and $r_{jkl(i)}$ represent the number of nearest-neighbor segment pairs of hard sphere j and hard sphere k , and the number of next-to-nearest-neighbor segment pair of hard-sphere j and hard sphere l with hard sphere k in between for a molecule of component i , respectively. We have

$$\sum_{j=1}^M r_{j(i)} = r_i \quad , \quad \sum_{j=1}^M \sum_{k=j}^M r_{jk(i)} = r_i - 1 \quad , \quad \sum_{j=1}^M \sum_{k=1}^M \sum_{l=j}^M r_{jkl(i)} = r_i - 2 \quad , \quad i=1, \dots, K. \quad (42)$$

Eqs.(21) and (22) for the equation of state and the residual Helmholtz function are then extended as follows:

$$Z = \frac{\beta p}{\rho_0} = \tilde{r} Z(\alpha=0) - [(\tilde{r} - 1) + \sum_{i=1}^K \sum_{j=1}^M \sum_{k=j}^M x_i r_{jk(i)} \eta \frac{d \ln y_{S_j S_k(i)}^{(2e)}}{d\eta} + \sum_{i=1}^K \sum_{j=1}^M \sum_{k=1}^M \sum_{l=j}^M x_i r_{jkl(i)} \eta \frac{d \ln y_{S_j S_k S_l(i)}^{(2e)}}{d\eta}] \quad (43)$$

$$\frac{\beta A^r}{\sum_i^K N_i} = \tilde{r} \frac{\beta A^r(\alpha=0)}{\sum_i^K r_i N_i} - \sum_{i=1}^K \sum_{j=1}^M \sum_{k=j}^M x_i r_{jk(i)} \ln y_{S_j S_k(i)}^{(2e)} - \sum_{i=1}^K \sum_{j=1}^M \sum_{k=1}^M \sum_{l=j}^M x_i r_{jkl(i)} \ln y_{S_j S_k S_l(i)}^{(2e)} \quad (44)$$

where $Z(\alpha=0)$ and $A'(\alpha=0)$ are calculated by the Mansoori-Carnahan-Starling-Leland equation, i.e., eqs.(39,40), while B , E and F in those equations are calculated from

$$B = \frac{\sum_{i=1}^K \sum_{j=1}^M N_i r_{j(i)} \sigma_j}{\sum_{i=1}^K N_i r_i}, \quad E = \frac{\sum_{i=1}^K \sum_{j=1}^M N_i r_{j(i)} \sigma_j^2}{\sum_{i=1}^K N_i r_i}, \quad F = \frac{\sum_{i=1}^K \sum_{j=1}^M N_i r_{j(i)} \sigma_j^3}{\sum_{i=1}^K N_i r_i}, \quad \eta = \frac{\pi}{6} \sum_{i=1}^K \sum_{j=1}^M r_{j(i)} \rho_i \sigma_j^3. \quad (45)$$

Considering the difference between the Carnahan-Starling equation, i.e., eqs.(23,24), and the Mansoori-Carnahan-Starling-Leland equation, we can revise the effective two particle CCF for a nearest-neighbor segment pair and a next-to-nearest-neighbor segment pair, eqs.(25) and (28) for a homonuclear chain molecule, for application to heteronuclear chains:

$$\ln y_{S_j S_k}^{(2e)} = \frac{(3 + a_{20}) \frac{B_2 E_2}{F_2} \eta - (1 + b_{20}) \frac{E_2^3}{F_2^2}}{2(1 - \eta)} + \frac{(1 + b_{20}) \frac{E_2^3}{F_2^2}}{2(1 - \eta)^2} - (1 + c_{20}) \frac{E_2^3}{F_2^2} \ln(1 - \eta) \quad (46)$$

$$\ln y_{S_j S_k S_l}^{(2e)} = \left(\frac{r_i - 1}{r_i} \right) \left[\frac{a_{30} \frac{B_3 E_3}{F_3} \eta - b_{30} \frac{E_3^3}{F_3^2}}{2(1 - \eta)} + \frac{b_{30} \frac{E_3^3}{F_3^2}}{2(1 - \eta)^2} - c_{30} \frac{E_3^3}{F_3^2} \ln(1 - \eta) \right] \quad (47)$$

where

$$B_2 = (\sigma_j + \sigma_k) / 2, \quad E_2 = (\sigma_j^2 + \sigma_k^2) / 2, \quad F_2 = (\sigma_j^3 + \sigma_k^3) / 2 \quad (48)$$

$$B_3 = (\sigma_j + \sigma_k + \sigma_l) / 3, \quad E_3 = (\sigma_j^2 + \sigma_k^2 + \sigma_l^2) / 3, \quad F_3 = (\sigma_j^3 + \sigma_k^3 + \sigma_l^3) / 3 \quad (49)$$

Pure Hard-Sphere Copolymers

We consider a fluid of pure hard-sphere copolymers which consist of two monomers A and B with different sizes. Under different polymerization conditions, three common types, i.e., alternating, block and random copolymers, can be obtained. In those copolymers, there are three different nearest-neighbor segment pairs: A-A, B-B and A-B. The numbers of these in a molecule are r_{AA} , r_{BB} and r_{AB} , respectively. There are six different next-to-nearest-neighbor segment pairs: A-A-A, A-A-B, A-B-A, B-B-A, B-A-B and B-B-B; the numbers of these in a molecule are r_{AAA} , r_{AAB} , r_{ABA} , r_{BBA} , r_{BAB} and r_{BBB} , respectively. Assuming there are r_A monomer A and r_B monomer B in a linear copolymer molecule, the following constraints must be obeyed:

$$r_A + r_B = r \quad , \quad \sum_{\alpha, \beta} r_{\alpha\beta} = r - 1 \quad , \quad \sum_{\alpha, \beta, \gamma} r_{\alpha\beta\gamma} = r - 2 \quad , \quad (\alpha, \beta, \gamma = A, B) \quad . \quad (50)$$

The equation of state and the residual Helmholtz function for those copolymers can then be written as:

$$\begin{aligned}
Z = rZ(\alpha = 0) - [& r - 1 + r_{AA}\eta \frac{d \ln y_{AA}^{(2e)}}{d\eta} + r_{AB}\eta \frac{d \ln y_{AB}^{(2e)}}{d\eta} + r_{BB}\eta \frac{d \ln y_{BB}^{(2e)}}{d\eta} \\
& + r_{AAA}\eta \frac{d \ln y_{AAA}^{(2e)}}{d\eta} + r_{AAB}\eta \frac{d \ln y_{AAB}^{(2e)}}{d\eta} + r_{ABA}\eta \frac{d \ln y_{ABA}^{(2e)}}{d\eta} \\
& + r_{BBA}\eta \frac{d \ln y_{BBA}^{(2e)}}{d\eta} + r_{BAB}\eta \frac{d \ln y_{BAB}^{(2e)}}{d\eta} + r_{BBB}\eta \frac{d \ln y_{BBB}^{(2e)}}{d\eta}]
\end{aligned} \quad (51)$$

$$\begin{aligned}
\frac{\beta A^r}{N} = r \frac{\beta A^r(\alpha = 0)}{rN} - [& r_{AA} \ln y_{AA}^{(2e)} + r_{AB} \ln y_{AB}^{(2e)} + r_{BB} \ln y_{BB}^{(2e)} + r_{AAA} \ln y_{AAA}^{(2e)} \\
& + r_{AAB} \ln y_{AAB}^{(2e)} + r_{ABA} \ln y_{ABA}^{(2e)} + r_{BBA} \ln y_{BBA}^{(2e)} + r_{BAB} \ln y_{BAB}^{(2e)} + r_{BBB} \ln y_{BBB}^{(2e)}]
\end{aligned} \quad (52)$$

For an alternating copolymer, the only nearest-neighbor segment pair is $A-B$. The only two different next-to-nearest-neighbor segment pairs are $A-B-A$ and $B-A-B$. The numbers of different segment pairs in a molecule are:

$$r_{AA} = 0, \quad r_{AB} = r - 1, \quad r_{BB} = 0 \quad (53)$$

$$r_{AAA} = 0, \quad r_{AAB} = 0, \quad r_{ABA} = r_A - 1, \quad r_{BBA} = 0, \quad r_{BAB} = r_B - 1, \quad r_{BBB} = 0 \quad (54)$$

For a block copolymer, the numbers of different segment pairs in a molecule are :

$$r_{AA} = r_A - 1, \quad r_{AB} = 1, \quad r_{BB} = r_B - 1 \quad (55)$$

$$r_{AAA} = r_A - 2, \quad r_{AAB} = 1, \quad r_{ABA} = 0, \quad r_{BBA} = 1, \quad r_{BAB} = 0, \quad r_{BBB} = r_B - 2 \quad (56)$$

For a random copolymer, the sequence is determined in a statistical sense. If the copolymer is completely random, the number of A-B nearest-neighbor segment pairs

is proportional to the product of X_A , the probability of finding a segment A, and X_B , the probability of finding a segment B in the copolymer. These probabilities are given by

$$X_A = r_A / r \quad , \quad X_B = 1 - X_A = r_B / r \quad (57)$$

Therefore, the numbers of different nearest-neighbor segment pairs in a molecule are:

$$r_{AA} = (r-1)X_A^2 \quad , \quad r_{BB} = (r-1)X_B^2 \quad , \quad r_{AB} = 2(r-1)X_A X_B \quad (58)$$

Similarly, $X_\alpha X_\beta X_\gamma$ ($\alpha, \beta, \gamma = A, B$) is the probability of finding segments α, β and γ . The numbers of different next-to-nearest-neighbour segment pairs in a molecule are:

$$\begin{aligned} r_{AAA} &= (r-2)X_A^3 \quad , & r_{AAB} &= 2(r-2)X_A^2 X_B \quad , & r_{ABA} &= (r-2)X_A^2 X_B \\ r_{BBA} &= 2(r-2)X_A X_B^2 \quad , & r_{BAB} &= (r-2)X_A X_B^2 \quad , & r_{BBB} &= (r-2)X_B^3 \end{aligned} \quad (59)$$

For any other type of copolymer, the numbers of different nearest-neighbor and next-to-nearest-neighbor segment pairs can be determined if the sequence is known.

Figure 10 compares predicted compressibility factors of a heteronuclear hard-sphere dumbbell fluid with Archer and Jackson's computer simulation results²⁷. Figures 11 and 12 show comparisons for heteronuclear linear triatomic hard-spheres. Computer-simulation results are from Amos and Jackson¹⁸. The prediction is satisfactory.

VI. DISCUSSION AND CONCLUSION

Recent molecular-thermodynamic methods are characterized by two steps. We use statistical mechanics to derive analytical expressions as a first step. However, even for a simple hard-sphere fluid, analytical expressions cannot be obtained without introducing mathematical simplifications. To avoid mathematical problems, the common procedure is to introduce a reasonable model. The final expression obtained may then include some unknown coefficients which must be determined. In this work, we adopt a sticky-point model and approximate the r -particle cavity-correlation function by a product of nearest-neighbor and next-to-nearest-neighbor effective two-particle cavity-correlation functions. The density dependences of those two-particle cavity correlation functions are unknown. Therefore, as a second step, we use computer-simulation results to determine those dependences.

In this work, to obtain the unknown density dependence of CCFs, we use the Tildesley-Streett equation for hard-sphere dumbbells and computer-simulation

results for hard-sphere trimers. Our final molecular-thermodynamic model has predictive value as indicated by satisfactory comparisons with computer-simulation results for homonuclear hard-sphere-chain fluids and fluid mixtures with or without side chains and rings as well as for heteronuclear hard-sphere-chain fluids.

The procedure in this work can be extended to chain fluids with attractive potentials. For example, for square-well chain fluids, we can use Alder's work²⁸ for square-well spheres as a reference. We can then use some computer-simulation results to determine the density dependence of effective two-particle cavity-correlation functions for square-well chain fluids.

The present work can be used as a basis for developing practical equation of state for polymer solutions and polymer blends.

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FIGURE CAPTIONS

Fig. 1 r-mer with a side chain.

Fig. 2. Compressibility factors of 16-mer HSCF.

Fig. 3. Compressibility factors of 51-mer HSCF.

Fig. 4. Compressibility factors of 201-mer HSCF.

Fig. 5. Second virial coefficients of HSCF.

Fig. 6. Compressibility factors of homonuclear HSCF mixture.

Fig. 7. Compressibility factors of homonuclear HSCF mixture.

Fig. 8. Compressibility factors of homonuclear planar Y-type and T-type tetratomic HSCF.

Fig. 9. Compressibility factors of 4-mer ring HSCF.

Fig. 10. Compressibility factors of heteronuclear 2-mer HSCF.

Fig. 11. Compressibility factors of heteronuclear 3-mer HSCF.

Fig. 12. Compressibility factors of heteronuclear 3-mer HSCF.

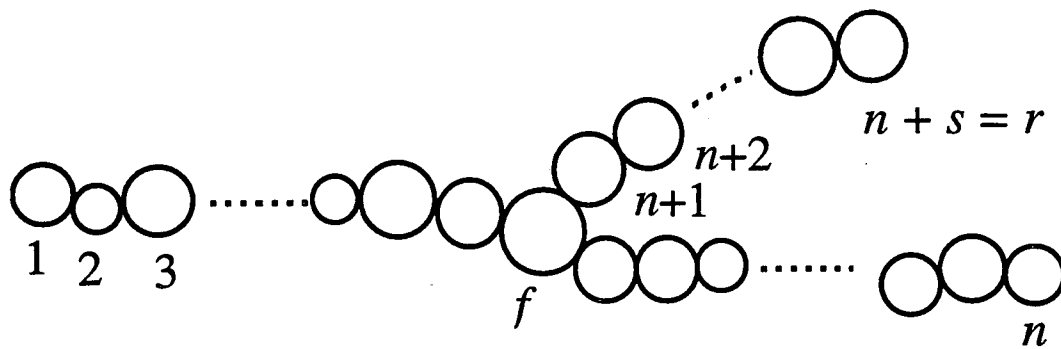


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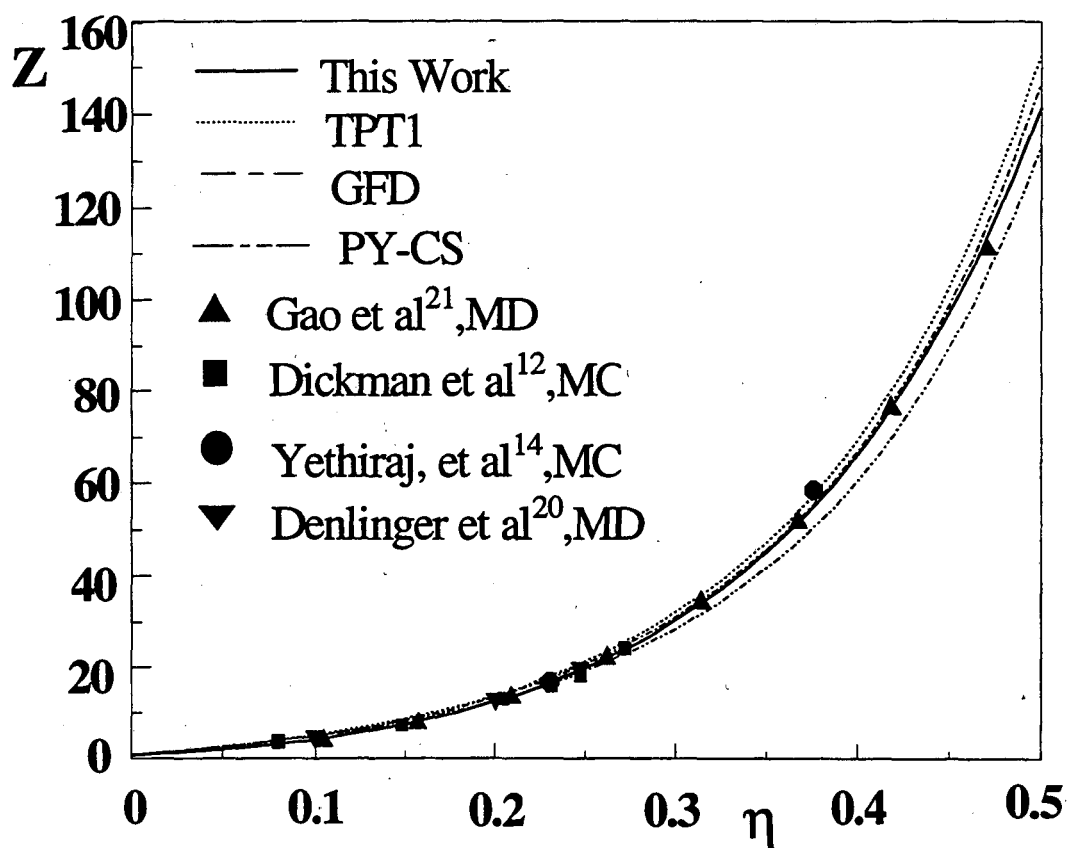


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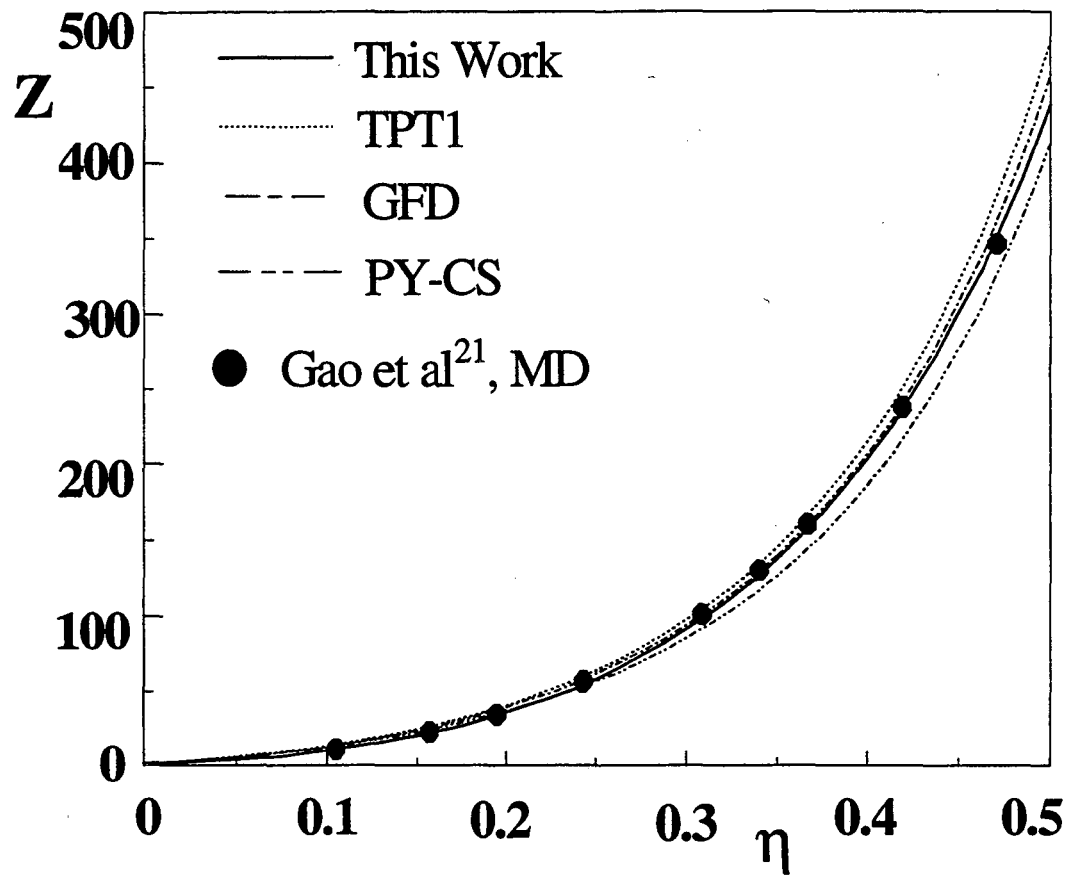


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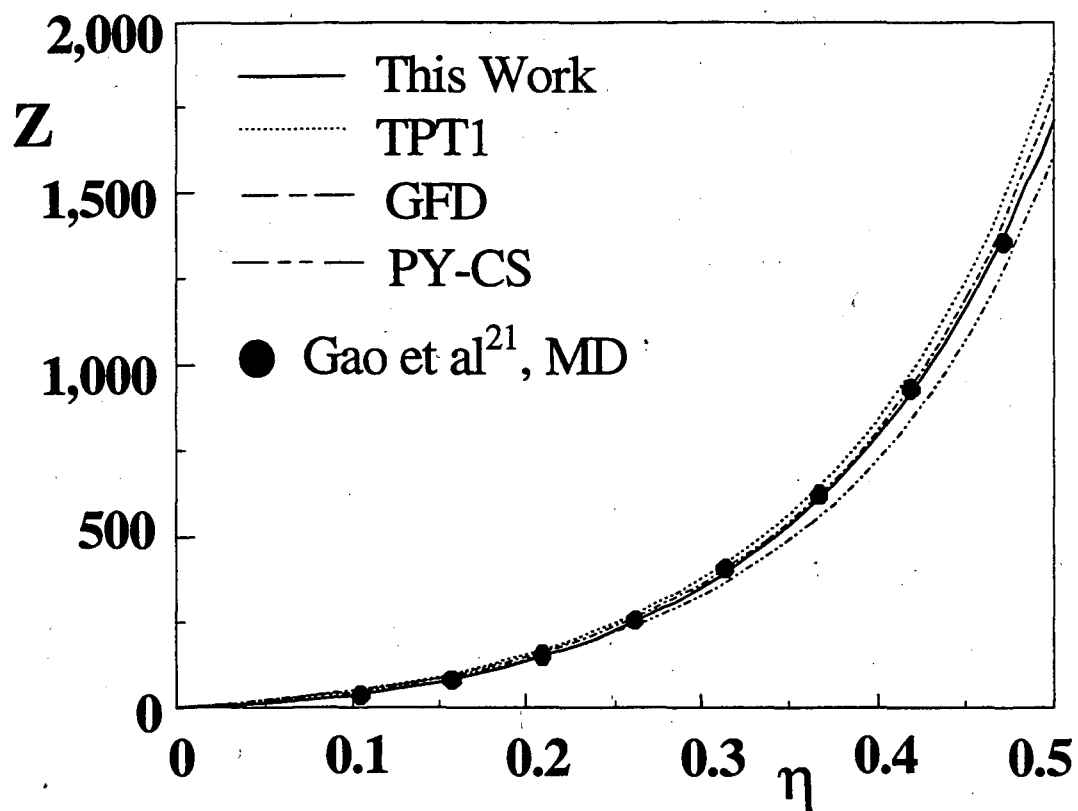


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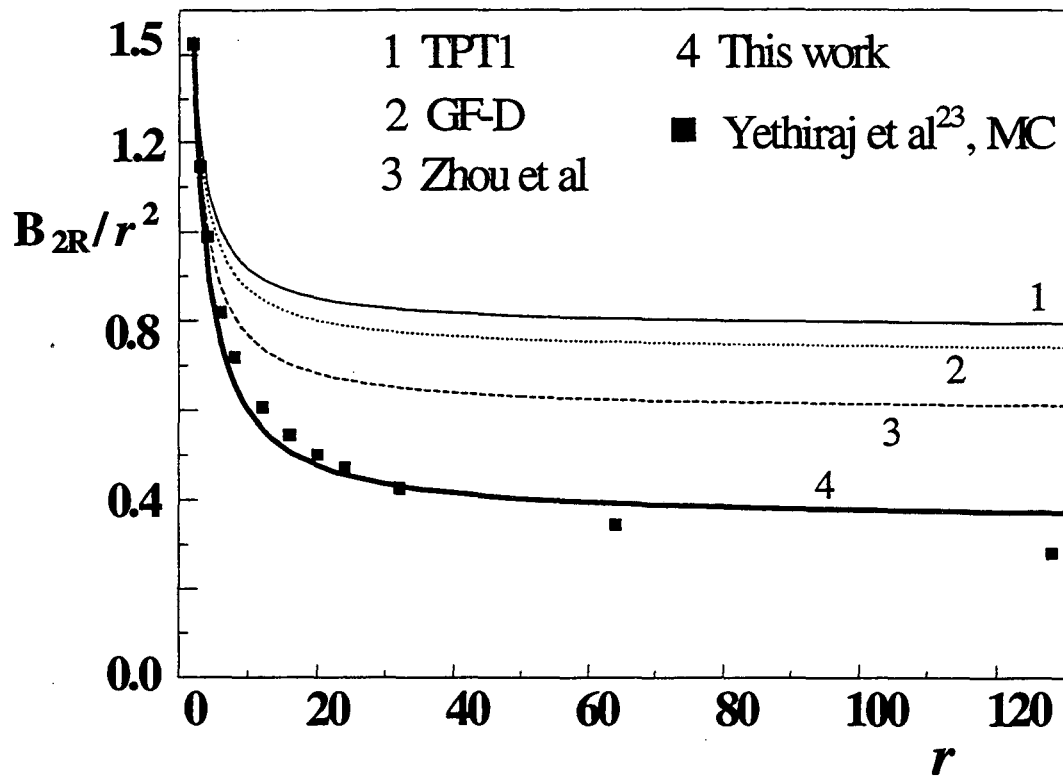


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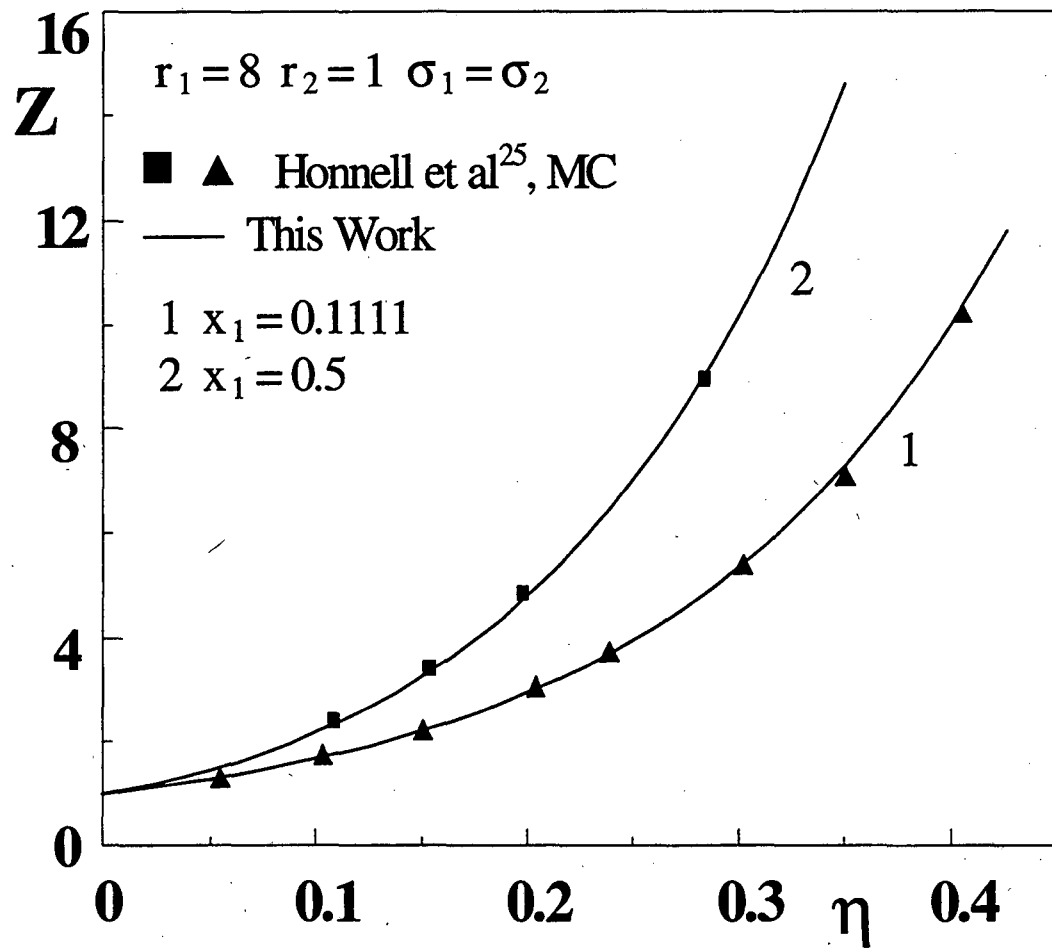


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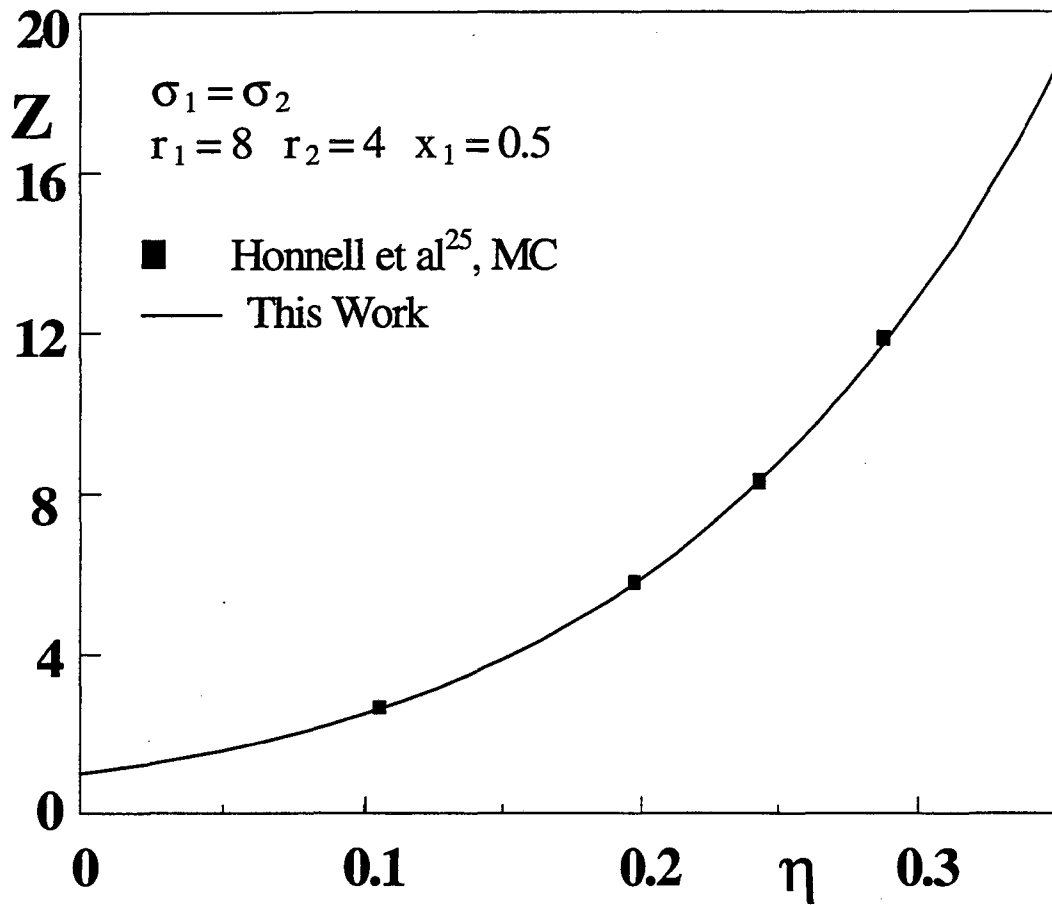


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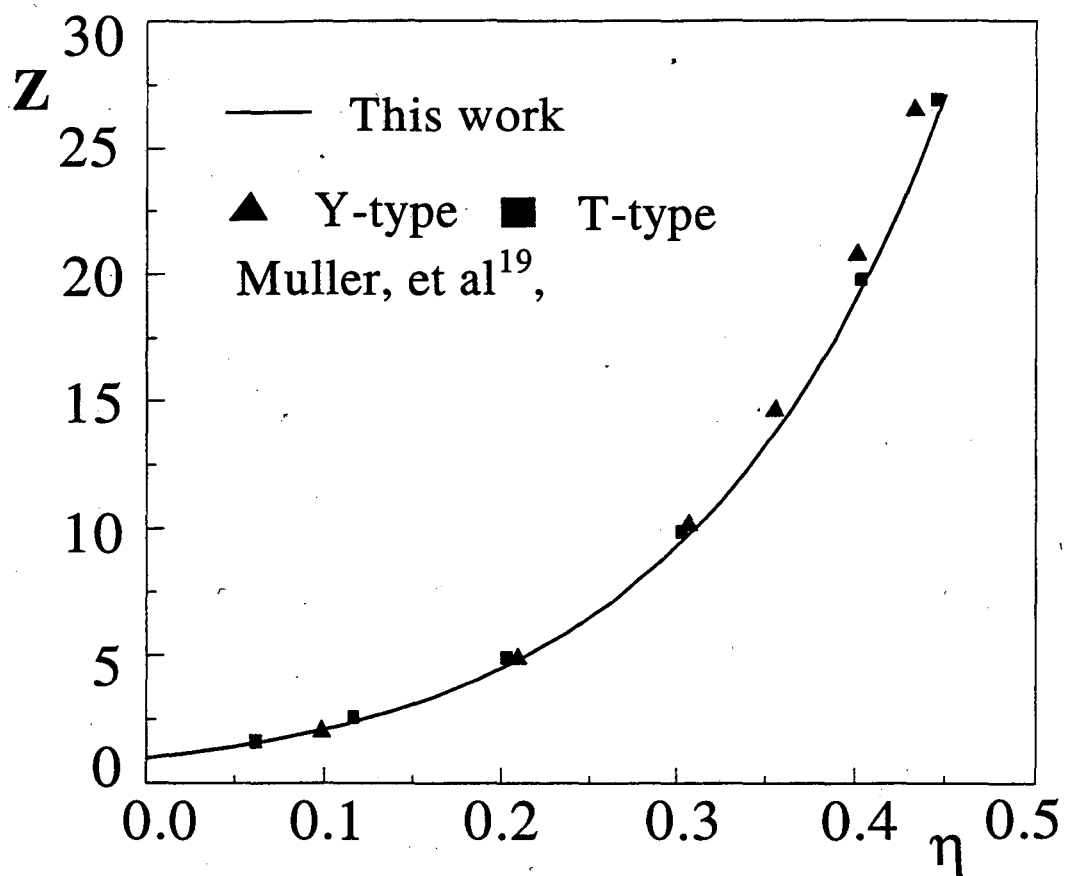


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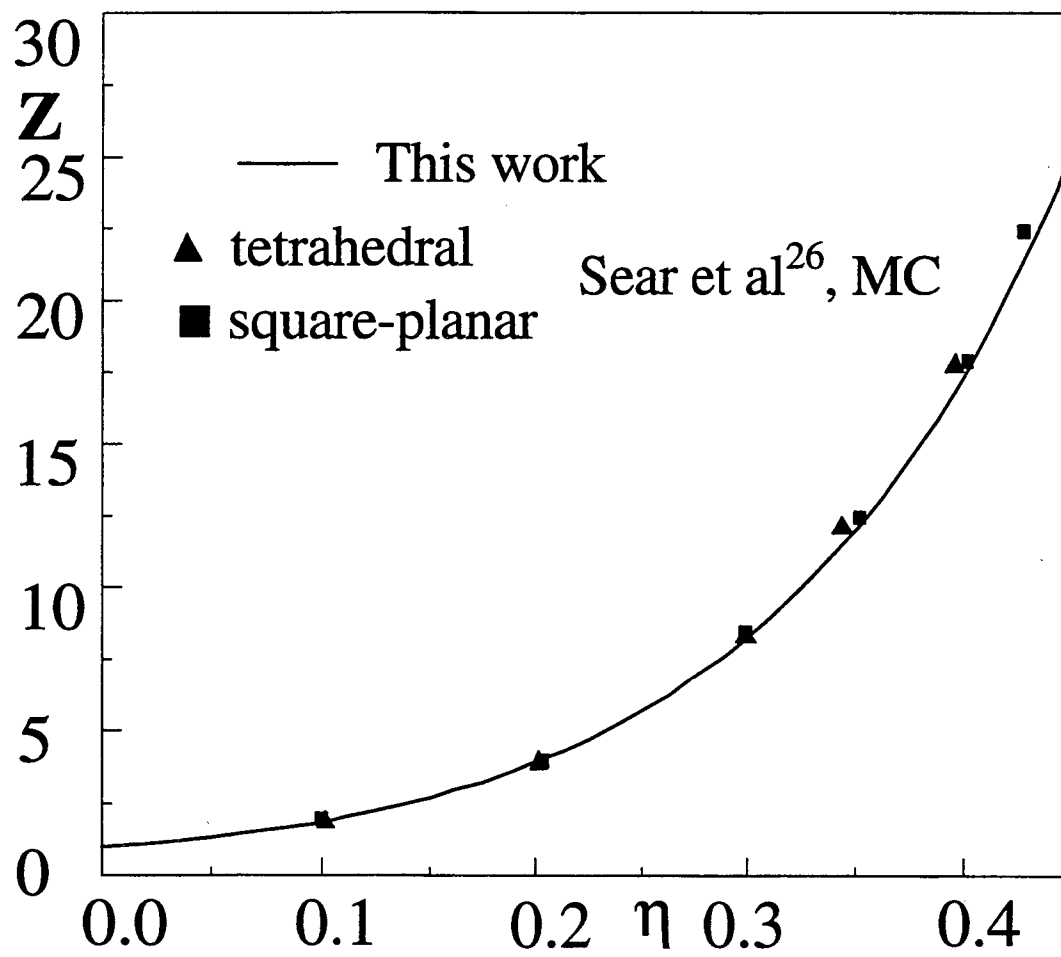


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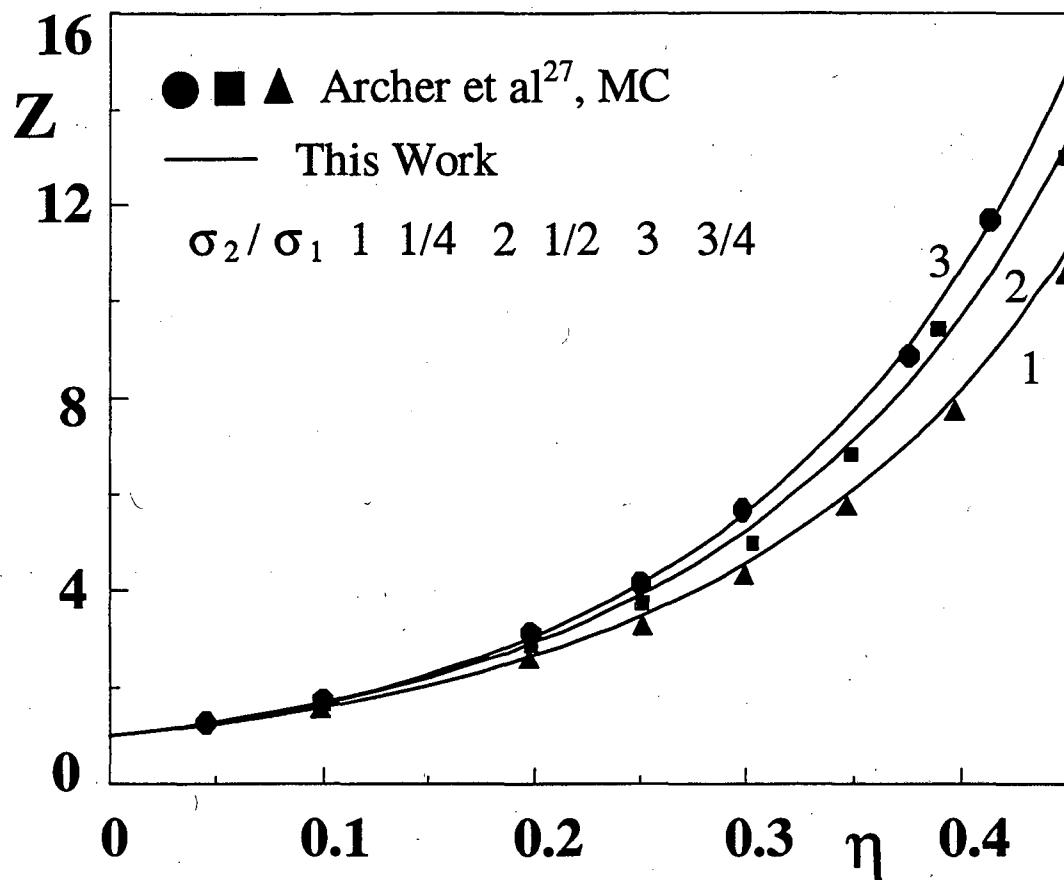


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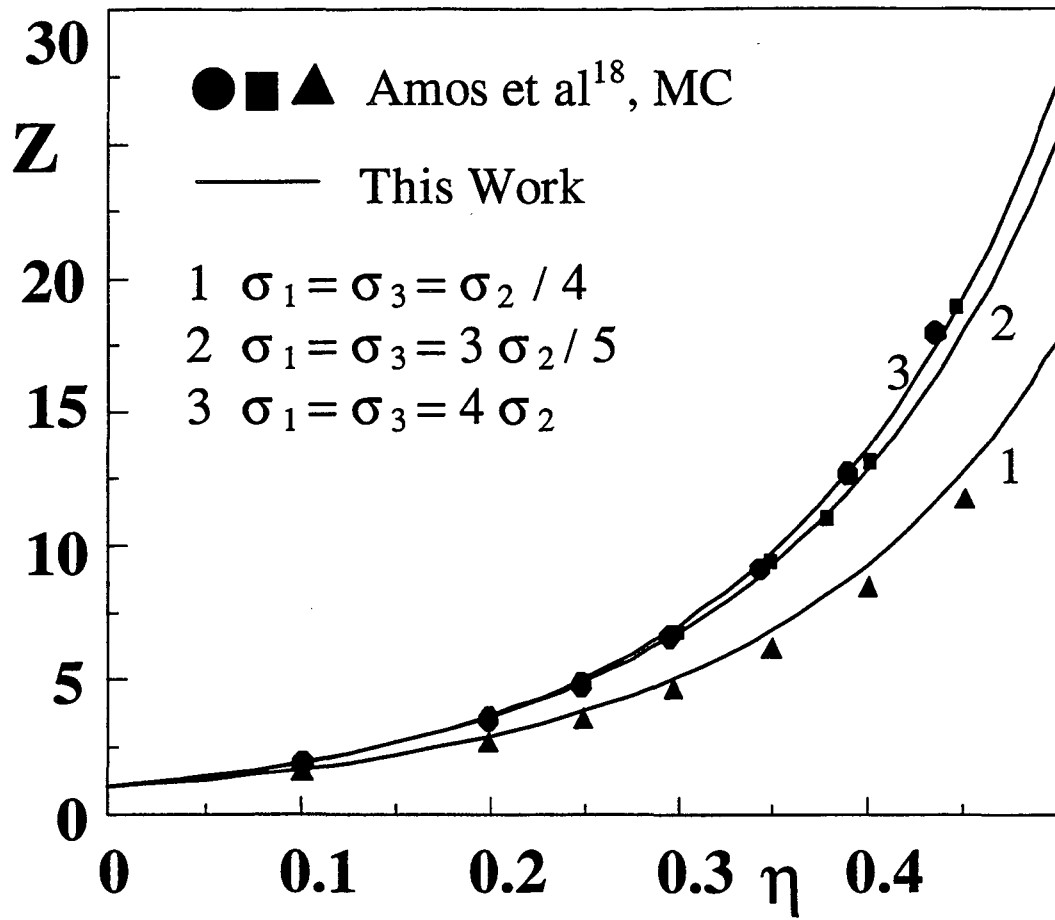


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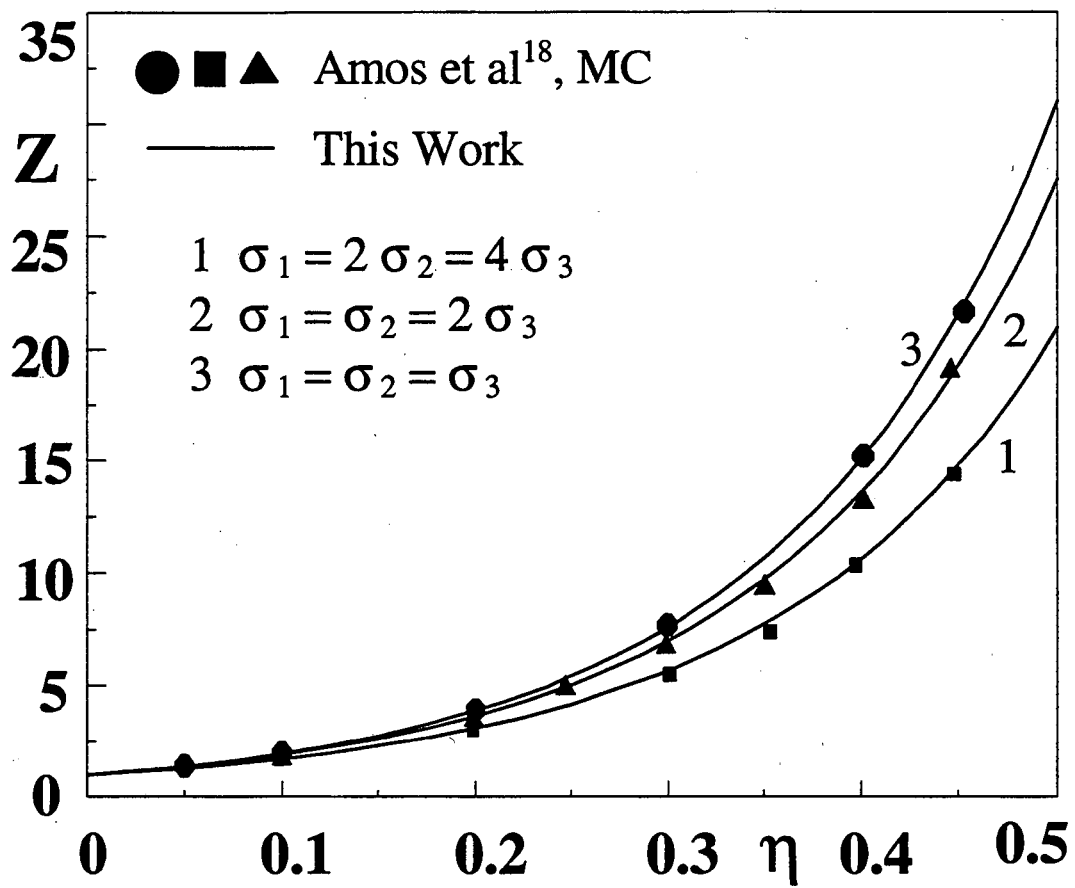


Fig.12, Hu, J. Chem. Phys.

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