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ABSTRACT

Chiew's equation of state for mixtures of hard-sphere chains is generalized through the Carnahan-Starling radial distribution function for hard-sphere mixtures at contact for both the bonding and non-bonding terms. When compared with computer simulations of hard-sphere-chain mixtures, the new equation of state gives better agreement than the original equation of state. The new equation of state indicates the simplifying physical assumptions which are required to obtain the well-known Flory-Huggins athermal entropy of mixing. The generalization presented here is applied to mixtures of hard-sphere-chain copolymers, where the spherical segments of a given chain may have different diameters. Illustrative calculations are presented for three types of copolymers (alternating, block and random).

1. Introduction

Hard-sphere chains provide a simple model for assemblies of polymer molecules. Despite their simplicity, the properties of hard-sphere-chain models take into account some significant features of real polymer liquids, including excluded-volume effects and segment connectivity. More important, they provide a useful reference system in statistical-mechanical perturbation theories for chain-like molecular fluids, in a manner similar to the way that hard spheres provide a reference system in statistical-mechanical perturbation theories of simple fluids.[1] Therefore, several authors have given attention toward establishing accurate analytical equations of state for hard-sphere chains which can be tested with computer-generated simulation results. A number of methods have been developed, including the generalized Flory-Huggins theory[2,3] and the perturbation theory of polymerization.[4,5]

A particularly elegant, yet simple, method has been presented by Chiew[6] who studied mixtures of hard-sphere chains where a chain molecule is modeled by a series of r freely-jointed tangent spheres. Each sphere in a chain interacts with every other (non-bonded) sphere in the system through the hard-sphere potential. An analytical equation state for hard-sphere-chain mixtures was obtained based on the Percus-Yevick integral-equation theory coupled with chain connectivity. The pressure, p, consists of two parts; a non-bonding contribution (*i.e.*, hard-sphere mixtures prior to bonding to form chains) and a bonding contribution due to chain formation:

$$p = p_{hs} + p_{bond} \tag{1}$$

For the hard-sphere-mixture term, Chiew replaced the Percus-Yevick solution with the more successful Boublik-Mansoori[7,8] extension of the Carnahan-Starling equation. Chiew compared his result for hard-sphere chains with computer-simulation data for one-component systems. Agreement is good but deviations are evident at high densities.

Here we show that a significant modification to Chiew's result can be obtained for mixtures of hard-sphere chains. The key idea is a reformulation of the Percus-Yevick solution in terms of the radial distribution functions of hard-sphere mixtures at contact in *both* the non-bonding and bonding terms. By using radial distribution functions at contact from the Boublik-Mansoori-Carnahan-Starling (BMCS) equation for hard-sphere mixtures, the resulting equation of state for hard-sphere-chain mixtures is compared with recent simulation data for binary mixtures by Honnell and Hall.[9] In general, the new equation of state for chains, based on the BMCS equation for hard-sphere mixtures, is more accurate than the original equation of state for chains, based on the Percus-Yevick solution, especially at high densities.

Since the hard spheres in a chain need not all have the same diameter, the new equation of state, like Chiew's original equation of state, can also represent hard-sphere-chain copolymers and their mixtures where the spherical segments have different sizes. Overall, compared to the original equation of state, the new equation of state for hard-sphere-chain mixtures is expressed more succinctly and is more convenient for application.

Our goal is directed toward establishing a perturbed-hard-sphere chain equation of state for calculating phase equilibria in solutions containing solvents, polymers, and copolymers.

To achieve this goal, however, we must first establish an equation of state for mixtures of hard-sphere chains which can serve as a useful reference system.

2. Equation of state

At total volume V and temperature T, we consider an m-component mixture of hard-sphere chains containing N_i chains consisting of r_i tangent hard spheres of diameter d_i where component $i = 1, 2, \cdots, m$; the total number of chains is $N = \sum_i^m N_i$ and the total number of hard spheres is $N_r = \sum_i^m r_i N_i$. Chiew[6] gives details concerning the derivation of the equation of state for this system based on the Percus-Yevick integral theory coupled with chain connectivity; these details need not be presented here. We start from Chiew's result [Eq. (10) in Ref. 6] which is equivalent to

$$\begin{aligned}\frac{p}{\rho kT} &= \left(\frac{p}{\rho kT}\right)^{c}_{hs} + \left(\frac{p}{\rho kT}\right)^{PY}_{bond} \\ &= 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g^{c}_{ij}(d^{+}_{ij}) - \sum_{i}^{m} x_i (r_i - 1)\left[g^{PY}_{ii}(d^{+}_{ii}) - 1\right] \qquad (2)\end{aligned}$$

where p is the pressure, k is the Boltzmann constant, $\rho = N/V$ is the number density of chains, $x_i = N_i/N$ is the number fraction of component i, and b_{ij} is the second virial coefficient of hard-sphere mixtures prior to bonding to form chains, given by

$$b_{ij} = \frac{2}{3}\pi d_{ij}^3, \quad d_{ij} = \frac{d_i + d_j}{2}, \quad d_i = d_{ii} \qquad (3)$$

In Eq. (2) superscripts c stands for *compressbility* and PY for Percus-Yevick. Eq. (2) provides a clear and succinct expression of Chiew's result because the equation of state for mixtures of hard-sphere chains is written here only in terms of the radial distribution function of hard-sphere mixtures at contact in both the non-bonding and bonding terms. In Eq. (2), $g_{ij}^{c}(d_{ij}^{+})$ is the radial distribution function of hard-sphere mixtures at contact as calculated from the compressibility pressure equation of the Percus-Yevick solution,[10] and $g_{ij}^{PY}(d_{ij}^{+})$ is the Percus-Yevick radial distribution function of hard-sphere mixtures at contact.[10] If the Percus-Yevick theory were exact, both $g_{ij}^{c}(d_{ij}^{+})$ and $g_{ij}^{PY}(d_{ij}^{+})$ would be identical functions for a system of hard-sphere mixtures. The relation between $g_{ij}^{c}(d_{ij}^{+})$ and $g_{ij}^{PY}(d_{ij}^{+})$ is[10]

$$g_{ij}^{c}(d_{ij}^{+}) = g_{ij}^{PY}(d_{ij}^{+}) + \frac{3}{4}\frac{\xi_{ij}^{2}}{(1-\eta)^{3}} \tag{4}$$

$$g_{ij}^{PY}(d_{ij}^{+}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^{2}} \tag{5}$$

where η is the packing fraction of hard-sphere mixtures

$$\eta = \frac{\rho}{4}\sum_{i}^{m} x_i r_i b_i \tag{6}$$

$$\xi_{ij} = \frac{\rho}{4}\left(\frac{b_i b_j}{b_{ij}}\right)^{1/3}\sum_{i}^{m} x_i r_i b_i^{2/3} \tag{7}$$

For one-component systems and equal-monomer-size mixtures, $\xi_{ij} = \eta$.

Chiew replaced $(p/\rho kT)_{hs}$ in the non-bonding term of Eq. (2) by the more accurate BMCS result,[7,8] but did not utilize the Percus-Yevick radial distribution functions of hard-sphere mixtures prior to bonding to derive both the non-bonding and bonding terms in Eq. (2). Therefore we revise Chiew's result to obtain a general form of the equation of state for hard-sphere-chain mixtures.

The radial distribution function of hard-sphere mixtures at contact, $g_{ij}(d_{ij}^{+})$, is initially unspecified, in both the non-bonding and bonding terms of the Percus-Yevick solution in Eq. (2). We can rewrite Eq. (2) to give a more general form of the equation of state for hard-sphere-chain mixtures:

$$\frac{p}{\rho kT} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^{+}) - \sum_{i}^{m} x_i (r_i - 1) \Big[g_{ii}(d_{ii}^{+}) - 1 \Big] \tag{8}$$

Eq. (8) indicates that the radial distribution functions of hard-sphere mixtures at contact, $g_{ij}(d_{ij}^{+})$, prior to bonding to form chains, completely determine the equation of state for hard-sphere-chain mixtures. Moreover, Eq. (8) shows the connection between the non-bonding and bonding terms through $g_{ij}(d_{ij}^{+})$. Finally, Eq. (8) obeys the ideal-gas law in the limit $\rho \to 0$.

Although Eq. (8) is derived from the Percus-Yevick solution, we expect that better agreement with simulation results can be obtained if we use for $g_{ij}(d_{ij}^{+})$ a result better than the Percus-Yevick result. For example, we could use the computer-simulation results for $g_{ij}(d_{ij}^{+})$, which are available at least for binary mixtures of hard spheres.[11] On the other hand, although the (analytical) exact expression for $g_{ij}(d_{ij}^{+})$ is unknown, the Carnahan-Starling equation gives good results for one-component systems,[12] and the BMCS equation gives good results for mixtures.[13]

We approximate $g_{ij}(d_{ij}^{+})$ with the expression from the BMCS equation for hard-sphere mixtures:

$$g_{ij}(d_{ij}^{+}) \approx g_{ij}^{CS}(d_{ij}^{+}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3}. \tag{9}$$

3. Comparison with other results including simulation data

Honnell and Hall[9] have reported Monte Carlo computer simulations for binary mixtures of hard-sphere chains, including an 8-mer/monomer system and an 8-mer/4-mer system; in both mixtures, both components have the same hard-sphere diameters. The number fraction of each component is always one half. Figs. 1 and 2 show comparisons of Monte Carlo results with those based on Eqs. (8) and (9). We also compare our result with two other approximate equations of state for hard-sphere-chain mixtures: the Percus-Yevick solution, Eq. (2), and the result obtained by Chapman *et al.*,[5] based on the perturbation theory of polymerization of Wertheim,[4] which can be written as

$$\frac{p}{\rho kT} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^{+}) - \sum_{i}^{m} x_i (r_i - 1)\left[\rho \frac{\partial \ln g_{ii}(d_{ii}^{+})}{\partial \rho}\right] \tag{10}$$

Eqs. (8) and (10) differ only in the bonding term.

Figure 1 presents comparisons for the 8-mer/monomer mixture ($r_1 = 1$ and $r_2 = 8$). Compressibility factor $Z = p/\rho kT$, plotted against the hard-sphere packing fraction (reduced density), is shown for the entire fluid range of hard spheres to the freezing density, $\eta \approx 0.49$.[17] At low to moderate densities ($\eta < 0.2$), all three equations are almost indistinguishable from each other as well as from the simulation data. At higher densities, both the Percus-Yevick equation and the equation by Chapman *et al.*[5] overestimate the pressure; however, Eq. (8)

shows excellent agreement with the simulation data. These observations are not surprising, because it is known that the Percus-Yevick solution for hard spheres is accurate only at low to moderate densities, while the BMCS equation is superior to the Percus-Yevick solution, especially at high densities near the freezing density. The observed lower accuracy of Eq. (10) at high densities is probably due to truncation after the first-order perturbation contribution in the bonding term.

Figure 2 shows comparisons for the 8-mer/4-mer mixture ($r_1 = 4$ and $r_2 = 8$). At low to moderate densities, conclusions are similar to those that apply to Fig. 1; all three equations are accurate at $\eta < 0.2$. At higher densities, both Eqs. (2) and (10) again lead to overestimates of the pressure for the hard-sphere-chain mixtures. In contrast, Eq. (8) slightly underestimates the pressure but is in general more accurate than either Eq. (2) or Eq. (10) when compared to the simulation data.

4. Athermal entropy of mixing

We use Eqs. (8) and (9) to calculate the athermal entropy of mixing because we would like to understand the physical assumptions that are required to obtain the well-known athermal Flory-Huggins equation.[14]

The general definition for the entropy of mixing can be written:[15]

$$\begin{aligned}\Delta_{mix}S &= S_{mixture} - \sum_i^m S_i \\ &= \int_V^\infty \left[\frac{Nk}{V} - \left(\frac{\partial p}{\partial T}\right)_{V,N}\right] dV - \sum_i^m \int_{V_i}^\infty \left[\frac{N_i k}{V_i} - \left(\frac{\partial p_i}{\partial T}\right)_{V_i,N_i}\right] dV_i\end{aligned}$$

$$+ \quad Nk \sum_i^m x_i \ln\left(\frac{V}{V_i}\right). \tag{11}$$

For athermal hard-sphere chain mixtures, we have

$$\left(\frac{\partial p}{\partial T}\right)_{N,V} = \frac{p}{T} \tag{12}$$

We can then rewrite Eq. (11) as

$$\frac{\Delta_{mix}S}{Nk} = -\int_o^{\rho}\left(\frac{p}{\rho kT} - 1\right)\frac{d\rho}{\rho} + \sum_i^m x_i \int_o^{\rho_i}\left(\frac{p_i}{\rho_i kT} - 1\right)\frac{d\rho_i}{\rho_i} - \sum_i^m x_i \ln(x_i\rho/\rho_i) \tag{13}$$

The first integral refers to the mixture and the other integrals to the pure components. The quantity $\rho_i = N_i/V_i$ is the molecular number density of pure component i; pressure p_i is calculated from the equation of state for pure component i, which can be derived from Eq. (8) as

$$\frac{p_i}{\rho_i kT} = 1 + r_i^2 b_i \rho_i g_i(d_i^+) - (r_i - 1)\Big[g_i(d_i^+) - 1\Big] \tag{14}$$

where $g_i(d_i^+)$ is the radial distribution function of hard spheres at contact for pure component i, as calculated from the Carnahan-Starling equation,[16]

$$g_i(d_i^+) = \frac{1 - \eta_i/2}{(1 - \eta_i)^3}, \qquad \eta_i = \frac{r_i b_i \rho_i}{4} \tag{15}$$

We use the condition that the total volume is constant, that is,

$$V = \sum_i^m V_i, \qquad \text{or} \qquad \frac{1}{\rho} = \sum_i^m \frac{x_i}{\rho_i} \tag{16}$$

The final result for $\Delta_{mix}S$ is

$$\frac{\Delta_{mix}S}{Nk} = -\rho \sum_{ij}^m x_i x_j r_i r_j b_{ij} X_{ij} + \sum_i^m x_i (r_i - 1) Y_{ii} + \sum_i^m x_i H_i - \sum_i^m x_i \ln(x_i \rho/\rho_i) \tag{17}$$

where

$$
\begin{aligned}
X_{ij} &= \frac{1}{\rho}\int_o^{\rho} g_{ij}d\rho \\
&= -\frac{\ln(1-\eta)}{\eta} + \frac{3\xi_{ij}}{2\eta^2}\left[\frac{\eta}{1-\eta}+\ln(1-\eta)\right] - \frac{\xi_{ij}^2}{2\eta^3}\left[\ln(1-\eta)+\frac{\eta}{1-\eta}-\frac{1}{2}\frac{\eta^2}{(1-\eta)^2}\right]
\end{aligned}
\tag{18}
$$

$$
Y_{ij} = \int_o^{\rho}(g_{ij}-1)\frac{d\rho}{\rho} = -\ln(1-\eta)+\frac{3}{2}\frac{\xi_{ij}}{1-\eta}+\frac{1}{4}\frac{\xi_{ij}^2}{(1-\eta)^2} \tag{19}
$$

$$
\begin{aligned}
H_i &= \int_o^{\rho_i}\left(\frac{p_i}{\rho_i kT}-1\right)\frac{d\rho_i}{\rho_i} \\
&= r_i\left[\frac{4\eta_i}{1-\eta_i}+\frac{\eta_i^2}{(1-\eta_i)^2}\right]-(r_i-1)\left[-\ln(1-\eta_i)+\frac{3}{2}\frac{\eta_i}{1-\eta_i}+\frac{1}{4}\frac{\eta_i^2}{(1-\eta_i)^2}\right]
\end{aligned}
\tag{20}
$$

Eq. (17) consists of four terms; each has a particular significance. The first term represents the entropy of the (non-bonded) hard-sphere mixture. The second term takes into account the connectivity between tangent spheres in the mixture. The third term subtracts the entropy of pure components, including both the non-bonding and bonding contributions. All three terms come from the equation of state and represent *free-volume* effects. The last term is associated with the condition of mixing at constant total volume.

We now discuss the physical assumptions that are required to reduce Eq. (17) to the well-known athermal Flory-Huggins equation for the *incompressible lattice mixture*:[14]

$$
\frac{\Delta_{mix}S}{Nk} = -\sum_i^m x_i \ln\phi_i \tag{21}
$$

which is also equivalent to

$$
\frac{\Delta_{mix}S}{N_r k} = -\sum_i^m \frac{\phi_i}{r_i}\ln\phi_i \tag{22}
$$

where ϕ_i is the segment fraction of component i, defined as

$$\phi_i = \frac{r_i N_i}{N_r} = \frac{x_i r_i}{\sum_i^m x_i r_i} \tag{23}$$

The incompressible lattice model cannot respresent the effects of free volume; therefore, the key to reducing Eq. (17) to Eq. (21) or Eq. (22) is the elimination of the first three terms in Eq. (17).

Since all sites are of equal volume in the incompressible lattice model, the first physical condition is that all hard spheres in the mixtures must have the same diameter d:

$$b_{ii} = b_{jj} = b_{ij} = b = \frac{2}{3}\pi d^3 \tag{24}$$

This assumption alone, however, does not eliminate free-volume effects. To do so, a second condition requires equal packing fractions for all pure components before mixing:

$$\eta_1 = \eta_2 = \cdots = \eta_m \tag{25}$$

Presumably this packing fraction is at some high density; for example, it should be close to that at closest packing, but this detail is irrelevant for our purposes.

Under the above two conditions, we can show, from Eq. (16), that:

$$\frac{x_i \rho}{\rho_i} = \phi_i \tag{26}$$

which is also equivalent to

$$\eta = \eta_1 = \cdots = \eta_m \tag{27}$$

That is, the packing fraction for the mixture is the same as those for pure components.

Substituting Eqs. (24), (25), (26), and (27) into Eq. (17), we find that the first three terms together are zero and the last term is identical to the Flory-Huggins equation, Eq. (21), for the incompressible athermal lattice mixture.

However, even if mixing is performed at constant total volume and the packing fractions of pure components are equal, significant deviations from the Flory-Huggins entropy of mixing occur when components in the mixture have different hard-sphere diameters. These deviations are illustrated in Fig. 3 where the entropy of mixing is calculated for a monomer/100-mer mixture as a function of the segment fraction of 100-mer for different values of the ratio of segmental diameters. The packing fraction of the pure components is chosen to be that at closest packing. As the ratio of diameters increases, large deviations from the Flory-Huggins equation appear accompanied by a shift in the maximum to lower polymer concentrations. These effects of segment size cannot be rigorously included in lattice models of polymer mixtures.

5. Extension to copolymers

An important advantage of Chiew's model for hard-sphere-chain mixtures is that the spheres in a chain molecule need not all have the same diameter. Therefore, the model can be used to represent heteronuclear hard-sphere chains (*i.e.*, copolymers) and their mixtures where different spheres have different diameters. Extension of Eq. (2) to copolymer systems follows from a statistical-mechanical theory based on the Percus-Yevick approximation coupled with chain connectivity.[6] Here we use the generalized Eq. (8), rather than Eq. (2), for the extension to copolymer systems. The final results can also be expressed in terms of the radial distribution functions at contact for hard-sphere copolymers and mixtures. We generalize the radial distribution functions at contact from the BMCS equation [Eq. (15) for hard spheres and Eq. (9) for hard-sphere mixtures] to include copolymers and their mixtures. We first present the result for pure components.

A. Pure copolymers

Consider a pure copolymer system where each hard-sphere chain consists of r spheres (segments) but each sphere has a different diameter, indicated by $d(\alpha), \alpha = A, B, C, \cdots, r$. Following Chiew's work,[6] we represent this system as a hard-sphere mixture consisting of $N_r = rN$ different sized spheres (each sphere as a component), subject to connectivity constraints which lead to the formation of N chains. Under these conditions, Eq. (8) is generalized for the pure copolymer system:

$$\frac{p}{\rho kT} = 1 + \rho \sum_{\alpha\beta}^{r} b(\alpha\beta) g(\alpha\beta) - \sum_{\alpha}^{r-1} [g(\alpha, \alpha+1) - 1] \tag{28}$$

where $b(\alpha\beta)$ is the second virial coefficient,

$$b(\alpha\beta) = \frac{2}{3}\pi d^3(\alpha\beta), \qquad d(\alpha\beta) = \frac{1}{2}[d(\alpha) + d(\beta)], \qquad \alpha, \beta = A, B, C, \cdots, r \tag{29}$$

and $g(\alpha\beta)$ is the radial distribution function at contact between a sphere of diameter $d(\alpha)$ and a sphere of diameter $d(\beta)$.

To obtain an explicit equation of state for pure copolymers, however, a suitable mathematical form for $g(\alpha\beta)$ must be found. Toward that end, we generalize the radial distribution functions at contact from the BMCS equation to include hard-sphere copolymers. Since the copolymer system is modeled as a hard-sphere mixture with chain connectivity, the radial distribution function at contact, $g(\alpha\beta)$, must satisfy two conditions for a binary mixture. Only a binary mixture needs to be considered because all radial distribution functions for multcomponent hard-sphere mixtures are in terms of segment pairs.

Condition 1: When all spheres have the same diameter (*i.e.*, homopolymers), $g(\alpha\beta)$ must reduce to the Carnahan-Starling equation for one-component hard spheres,

$$g(\alpha = \beta) = \frac{1 - \eta/2}{(1 - \eta)^3} \tag{30}$$

where η is the packing fraction

$$\eta = \frac{\rho}{4} \sum_{\alpha}^{r} b(\alpha) \tag{31}$$

Condition 2: In the limit $d(\alpha) >> d(\beta)$, spheres of type β can be represented as point particles [*i.e.*, $d(\beta) \to 0$]. In this case, the configurational integral, Q, for a binary mixture factors into the product of the configurational integrals for each component,

$$Q = Q(\alpha)Q(\beta) \tag{32}$$

Eq. (32) says that type-β spheres (point particles) do not affect the configuration of type-α spheres, and type-α spheres (large particles) do not affect the configuration of type-β spheres except through inaccessible volume, $V(1-\eta)$. Consequently, the type α spheres behave like a pure hard-sphere system, so that the radial distribution function at contact for the like-pair, $g(\alpha\alpha)$, is the same as that in Eq. (30) for pure hard spheres:

$$g(\alpha\alpha) = \frac{1-\eta/2}{(1-\eta)^3} \tag{33}$$

For type-β spheres, since the only interaction with type-α spheres is through inaccessible volume, the radial distribution function at contact for the like-pair, $g(\beta\beta)$, and that for the unlike-pair, $g(\alpha\beta)$, must be the same,

$$g(\alpha\beta) = g(\beta\beta) \tag{34}$$

Since type-β spheres are point particles, the configurational integral $Q(\beta)$ can be computed as

$$Q(\beta) = \frac{[V(1-\eta)]^{N(\beta)}}{N(\beta)!} \tag{35}$$

where $N(\beta)$ is the number of type-β spheres. The pressure is related to the configurational integral by

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right) \tag{36}$$

In the limit $d(\beta) \to 0$, Eq. (36) reduces to

$$\begin{aligned} \frac{p}{kT} &= \left(\frac{\partial \ln Q(\alpha)}{\partial V}\right) + \left(\frac{\partial \ln Q(\beta)}{\partial V}\right) \\ &= \frac{p(\alpha)}{kT} + \frac{N(\beta)}{V}\frac{1}{1-\eta} \end{aligned} \tag{37}$$

where $p(\alpha)$ is the pressure calculated from the configurational integral of type-α spheres alone,

$$\frac{p(\alpha)}{kT} = \left(\frac{\partial \ln Q(\alpha)}{\partial V}\right) \tag{38}$$

Next, the pressure equation is expressed in terms of the radial distribution functions at contact for both pure hard spheres and binary mixtures which can be written, respectively, as

$$\frac{p(\alpha)}{\rho(\alpha)kT} = 1 + b(\alpha)\rho(\alpha)g(\alpha\alpha) \tag{39}$$

$$\frac{p}{\rho kT} = 1 + \rho[x^2(\alpha)b(\alpha)g(\alpha\alpha) + 2x(\alpha)x(\beta)b(\alpha\beta)g(\alpha\beta) + x^2(\beta)b(\beta)g(\beta\beta)] \tag{40}$$

where

$$\rho(\alpha) = \frac{N(\alpha)}{V}, \quad \text{and} \quad x(\alpha) = \frac{N(\alpha)}{N} \tag{41}$$

are the number density and fraction of type-α spheres, respectively. When $d(\beta) \to 0$, Eq. (40) reduces to

$$\frac{p}{\rho kT} = 1 + \rho[x^2(\alpha)b(\alpha)g(\alpha\alpha) + 2x(\alpha)x(\beta)b(\alpha\beta)g(\alpha\beta)], \quad \text{and} \quad b(\alpha\beta) = \frac{b(\alpha)}{8} \tag{42}$$

On combining Eqs (37) and (39), we obtain

$$\frac{p}{\rho kT} = 1 + \rho[x^2(\alpha)b(\alpha)g(\alpha\alpha) + 2x(\alpha)x(\beta)b(\alpha\beta)\frac{1}{1-\eta}]. \tag{43}$$

We then find from comparison with Eq. (42),

$$g(\alpha\beta) = g(\beta\beta) = \frac{1}{1-\eta}, \quad \text{as} \quad d(\beta) \to 0. \tag{44}$$

A generalization of the radial distribution function at contact from the Carnahan-Starling equation to the copolymer systems is found, by requiring that it satisfy the two conditions indicated above. The result is

$$g(\alpha\beta) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi(\alpha\beta)}{(1-\eta)^2} + \frac{1}{2}\frac{\xi^2(\alpha\beta)}{(1-\eta)^3} \tag{45}$$

where

$$\xi(\alpha\beta) = \frac{\rho}{4}\left[\frac{b(\alpha)b(\beta)}{b(\alpha\beta)}\right]^{1/3}\sum_{\gamma}^{r} b^{2/3}(\gamma) \tag{46}$$

For homopolymers, $\xi(\alpha\beta) = \eta$. In that case, Eq. (45) reduces to Eq. (30) for pure hard spheres. When $d(\beta) \rightarrow 0$, $\xi(\alpha\beta) \rightarrow 0$, Eq. (45) becomes Eq. (30) for $\alpha\alpha$ pairs, and Eq. (44) for $\alpha\beta$ and $\beta\beta$ pairs.

B. Mixtures of copolymers

Extension of Eq. (28) to mixtures of copolymers is straightforward. Here we present only the final result:

$$\frac{p}{\rho kT} = 1 + \rho\sum_{ij}^{m} x_i x_j\left[\sum_{\alpha}^{r_i}\sum_{\beta}^{r_j} b_{ij}(\alpha\beta)g_{ij}(\alpha\beta)\right] - \sum_{i}^{m} x_i \sum_{\alpha}^{r_i-1}[g_{ii}(\alpha,\alpha+1) - 1] \tag{47}$$

where $b_{ij}(\alpha\beta)$ is the second virial coefficient

$$\begin{aligned} b_{ij}(\alpha\beta) &= \frac{2}{3}\pi d_{ij}^{3}(\alpha\beta), \quad d_{ij}(\alpha\beta) = \frac{1}{2}[d_i(\alpha) + d_j(\beta)] \\ & \qquad i,j = 1,2,\cdots m; \quad \alpha = A,B,C,\cdots,r_i; \quad \beta = A,B,C,\cdots,r_j \end{aligned} \tag{48}$$

and $g_{ij}(\alpha\beta)$ is the radial distribution function at contact. Indices i and j, denoting components in the mixture, should not be confused with indices α and β, labeling species of spheres.

Once again, we need to find a suitable mathematical expression for $g_{ij}(\alpha\beta)$ so that we may use Eq. (47) for obtaining an equation of state for mixtures of copolymers. We extend

Eq. (45) to mixtures of copolymers with the result

$$g_{ij}(\alpha\beta) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}(\alpha\beta)}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2(\alpha\beta)}{(1-\eta)^3} \tag{49}$$

where

$$\eta = \frac{\rho}{4}\sum_i^m x_i \sum_\alpha^{r_i} b_i(\alpha) \tag{50}$$

$$\xi_{ij}(\alpha\beta) = \frac{\rho}{4}\left[\frac{b_i(\alpha)b_j(\beta)}{b_{ij}(\alpha\beta)}\right]^{1/3} \sum_l^m x_l \sum_\gamma^{r_l} b_l^{2/3}(\gamma) \tag{51}$$

C. Specific copolymer systems

To illustrate the usefulness of the equations derived above for copolymers, we now derive pertinent equations of state for specific copolymers. The discussion here is limited to pure hard-sphere copolymers which consist of only two segments that have different sizes (A and B). Extension to mixtures is straightforward and not included here. Three common types (illustrated in Fig. 4) are alternating, block, and random copolymers. Copolymer composition, X_i, is defined as

$$X_A = 1 - X_B = \frac{r(A)}{r} \tag{52}$$

With these simplifications Eq. (28) becomes

$$\begin{aligned} \frac{p}{\rho kT} &= 1 + r^2\rho\Big[X_A^2 b(AA)g(AA) + 2X_AX_B b(AB)g(AB) \\ &+ X_B^2 b(BB)g(BB)\Big] - \sum_\alpha^{r-1}[g(\alpha,\alpha+1) - 1] \end{aligned} \tag{53}$$

Eq. (53) has two important features. First, the properties of the copolymer are only a function of the pair distribution functions at contact for the unbonded hard-sphere mixture.

Second, the sequence of the copolymer need only be accounted for in the bonding term [the last term of Eq. (53)]

$$\sum_{\alpha}^{r-1}[g(\alpha,\alpha+1)-1] \tag{54}$$

The radial distribution function at contact in Eq. (54) is only for neighboring segments in the chain; therefore, for the case of a two-segment copolymer, Eq. (54) can be rewritten as

$$n(AA)[g(AA)-1]+n(AB)[g(AB)-1]+n(BB)[g(BB)-1] \tag{55}$$

where $n(\alpha\beta)$ is the number of $\alpha\beta$ nearest neighbors along the copolymer chain. All of the $n(\alpha\beta)$ are not independent; for a linear copolymer, they are constrained by

$$n(AA)+n(AB)+n(BB)=r-1 \tag{56}$$

For an alternating copolymer, $r(A) = r(B) = r/2$ which fixes $X_A = X_B = 1/2$. There are no AA or BB neighboring sequences; therefore, $n(AA) = n(BB) = 0$, and $n(AB) = r-1$. Eq. (55) reduces to

$$(r-1)[g(AB)-1] \tag{57}$$

For a block copolymer, there is only one AB pair and the number of AA and BB pairs depends on the length of each block; therefore, $n(AB) = 1$, $n(AA) = rX_A - 1$, $n(BB) = rX_B - 1$, and Eq. (55) reduces to

$$(rX_A-1)[g(AA)-1]+[g(AB)-1]+(rX_B-1)[g(BB)-1]. \tag{58}$$

For a random copolymer, the sequence is only known in a statistical sense. If the sequence is completely random and the total number of pairs is $r-1$, then the number of $\alpha\beta$

neighboring pairs is proportional to the product of the probabilities of finding a segment of type α and a segment of type β in the copolymer. The probability of finding a segment of type α is the fraction of α segments in the copolymer. The number of each type of pair can be approximated by

$$n(AA) = (r-1)X_A^2 \tag{59}$$

$$n(BB) = (r-1)X_B^2 \tag{60}$$

$$n(AB) = 2(r-1)X_A X_B. \tag{61}$$

The factor of two in Eq. (61) arises because there are two types of AB pairs, AB and BA. Substitution into Eq. (55) yields

$$(r-1)\{[X_A^2[g(AA)-1] + 2X_A X_B[g(AB)-1] + X_B^2[g(BB)-1]\}. \tag{62}$$

These equations can be used to calculate the effect of chain sequence on the thermodynamic properties of hard-sphere-chain copolymers. Figure 5, a sample calculation, shows the compressibility factor versus packing fraction for a copolymer consisting of 20 segments and composition $X_A = X_B = 1/2$. The ratio of diameters of the two types of spheres is $d_B/d_A = 3/2$. Calculations are performed for the three types of sequences described above. Also shown is a homopolymer with $r = 20$. (For a homopolymer the compressibility factor depends only upon the packing fraction and the polymer chain length.) There is a significant difference between the compressibility of the copolymer and that of the homopolymer; the block copolymer shows the largest difference, followed by the random copolymer and the alternating copolymer. The compressibilty factor for copolymers is always less than that for a homopolymer with the same number of segments. Additonal calculations show that the difference in compressbility factor due to chain architectures increases as the ratio of segment diameters increases, and decreases as the chain length rises.

Figure 6 shows the effects of copolymer composition and architecture on the compressibilty at a fixed packing fraction (at a high, liquid-like value of $\eta = 0.45$). The solid curve is for a 20-mer homopolymer blend where the ratio of segment diameters of the two components is 3/2. The composition of each homopolymer is adjusted so that the total number of spheres of one diameter is equal to the total number of spheres in the corresponding copolymer system. In other words, a 20-mer copolymer of composition $X_A = 0.5$ has a corresponding homopolymer blend having segment fraction of component 1, $\phi_1 = 0.5$. The dash curve represents the block copolymer and the dot-dash curve represents the random copolymer. (An alternating copolymer is not considered since its composition is fixed at 1/2.) The block copolymer gives the largest deviation from "blend" behavior. For the block copolymer, the compressiblity is not evaluated below (or above) compositions where less than one sphere is of type A or B since these would be unrealistic systems.

Sample calculations for binary copolymer blends having only two different size segments ($d_B/d_A = 3/2$) are shown in Figs. 7 (random copolymer blends) and 8 (block copolymer blends). Both copolymers in the blend have 20 segments. In each figure, the compressibility is plotted versus the fraction of copolymer 1 in the mixture for different compositions of the copolymers. For simplicity, symmetric copolymer compositions are chosen such that $X_{A1} = 1 - X_{A2}$ where X_{Ai} is the fraction of A segments in component i. Similar behavior is observed for both types of copolymers; however, all mixtures of block copolymers give the same compressibility when $x_1 = x_2 = 1/2$. The largest deviations from the compressibility of the pure copolymers is observed when the difference in copolymer compositions is the largest.

6. Conclusions

Following the ideas of Chiew, we have developed an equation of state for hard-sphere-chain mixtures in terms of the radial distribution function of hard-sphere mixtures at contact. Our derivation is based on the Percus-Yevick solution for hard-sphere-chain mixtures where our result is expressed in terms of the radial distribution function of hard-sphere mixtures at contact in both the non-bonding and bonding terms. The resulting equation of state for hard-sphere-chain mixtures [Eq. (8)] is reduced to practice using the Boublik-Mansoori-Carnahan-Starling equation of hard-sphere mixtures [Eq. (9)] for the radial distribution function at contact. The accuracy of Eq. (8) with Eq. (9) appears to be very good, insofar as it can be checked against available computer-simulation data for binary mixtures of hard-sphere chains.

We have also presented a generalization of the Boublik-Mansoori-Carnahan-Starling equation for hard spheres to hard-sphere chains and their mixtures where different single spheres have different diameters. With this result, we are able to establish equations of state for athermal pure copolymers [Eq. (28)] and for mixtures of athermal copolymers [Eq. (47)].

The results obtained in this work provide suitable reference equations of state for a perturbation theory for molecular fluid mixtures containing polymers, copolymers, and solvents.

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FIGURE CAPTIONS

Figure 1: Compressibility factor vs. hard-sphere packing fraction (reduced density) for an 8-mer/monomer hard-sphere chain mixture. Points are computer-simulation results. The solid curve is from Eq. (8) with Eq. (9) for $g_{ij}(d_{ij}^{+})$. The dash curve is from Eq. (2). The dotted curve is from Eq. (10) with Eq. (9) for $g_{ij}(d_{ij}^{+})$.

Figure 2: Same as Fig. 1, for an 8-mer/4-mer hard-sphere-chain mixture.

Figure 3: Athermal entropy of mixing for monomer/100-mer mixtures as a function of segment fraction of 100-mer. Mixing is performed such that the total volume is constant and the packing fractions of both pure components are equal to that at closest packing. Each curve represents a different ratio of segmental diameters, d_2/d_1. The Flory-Huggins result is recovered only when $d_1 = d_2$.

Figure 4: Three simple types of hard-sphere copolymer chain architecture: (a) alternating, (b) block, and (c) random (one possible sequence).

Figure 5: Compressibility factor vs. hard-sphere packing fraction for a homopolymer and for three different types of copolymer architecture: homopolymer (solid curve), block copolymer (dash curve), random copolymer (dot-dash curve), alternating copolymer (dotted curve). All polymers consist of 20 segments. The copolymers all have the same composition, $X_A = X_B = 1/2$ and ratio of segment sizes, $d_B/d_A = 3/2$.

Figure 6: The compressibilty of a pure block copolymer (dash curve) and pure random

copolymer (dot-dash curve) as a function of copolymer composition at a fixed packing fraction of $\eta = 0.45$. Both copolymers have 20 segments of type A and B and the ratio of sizes is $d_B/d_A = 3/2$. Also shown is the compressibility of a homopolymer blend (solid curve) having the same segment fraction of each type of sphere as that of the corresponding copolymer (*i.e.*, a copolymer with $X_A = 0.5$ corresponds with a homopolymer blend with segment fraction of component 1, $\phi_1 = 0.5$).

Figure 7: Compressibility of random copolymer blends as a function of the fraction of copolymer 1. Both copolymers have 20 segments and consist of segments of type A and B where the ratio of diameters, $d_B/d_A = 3/2$. The copolymer compositions are chosen such that $X_{A1} = 1 - X_{A2}$. X_{A1} is chosen as follows: $X_{A1} = 0.55$ (solid curve), $X_{A1} = 0.65$ (dotted curve), $X_{A1} = 0.75$ (short-dash curve), $X_{A1} = 0.85$ (long-dash curve), and $X_{A1} = 0.95$ (dot-dash curve).

Figure 8: Compressibility of block copolymer blends as a function of the fraction of copolymer 1. Both copolymers have 20 segments and consist of segments of type A and B where the ratio of diameters, $d_B/d_A = 3/2$. The copolymer compositions are chosen such that $X_{A1} = 1 - X_{A2}$. X_{A1} is chosen as follows: $X_{A1} = 0.55$ (solid curve), $X_{A1} = 0.65$ (dotted curve), $X_{A1} = 0.75$ (short-dash curve), $X_{A1} = 0.85$ (long-dash curve), and $X_{A1} = 0.95$ (dot-dash curve).

Figure 1

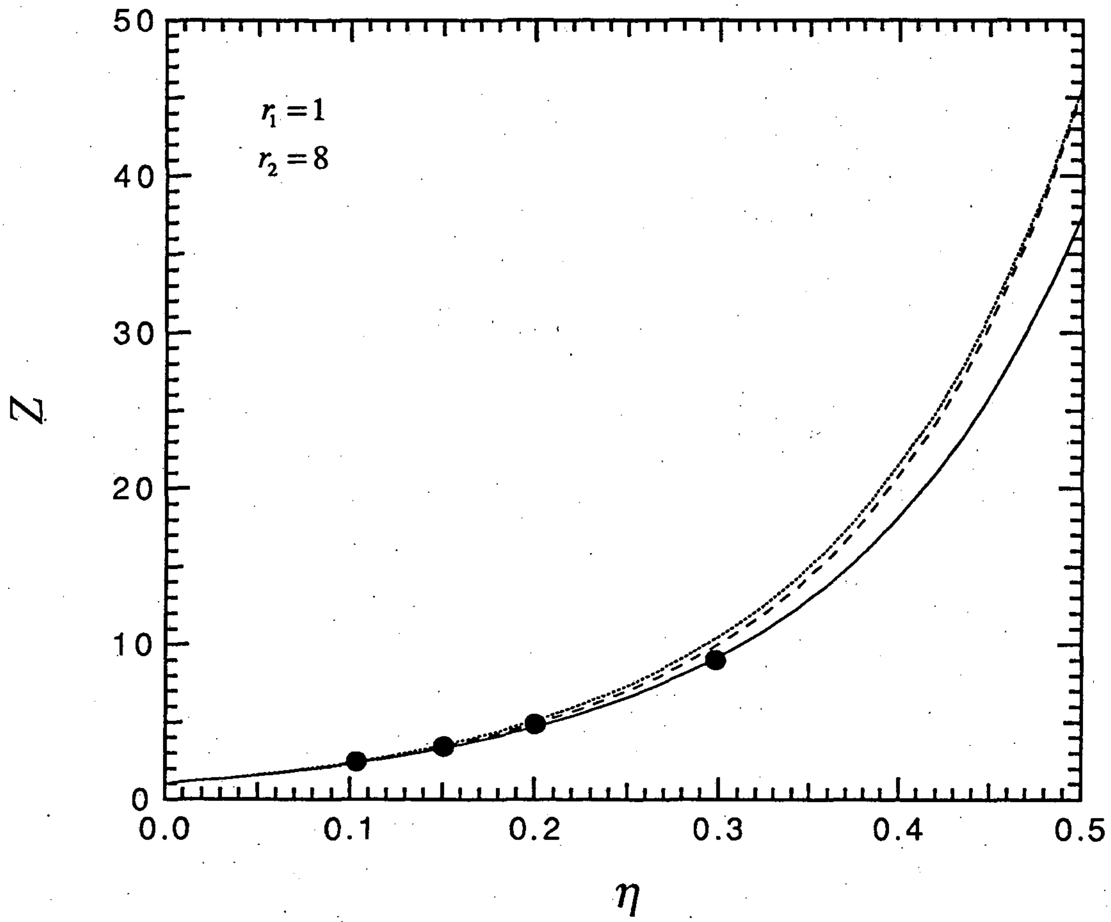
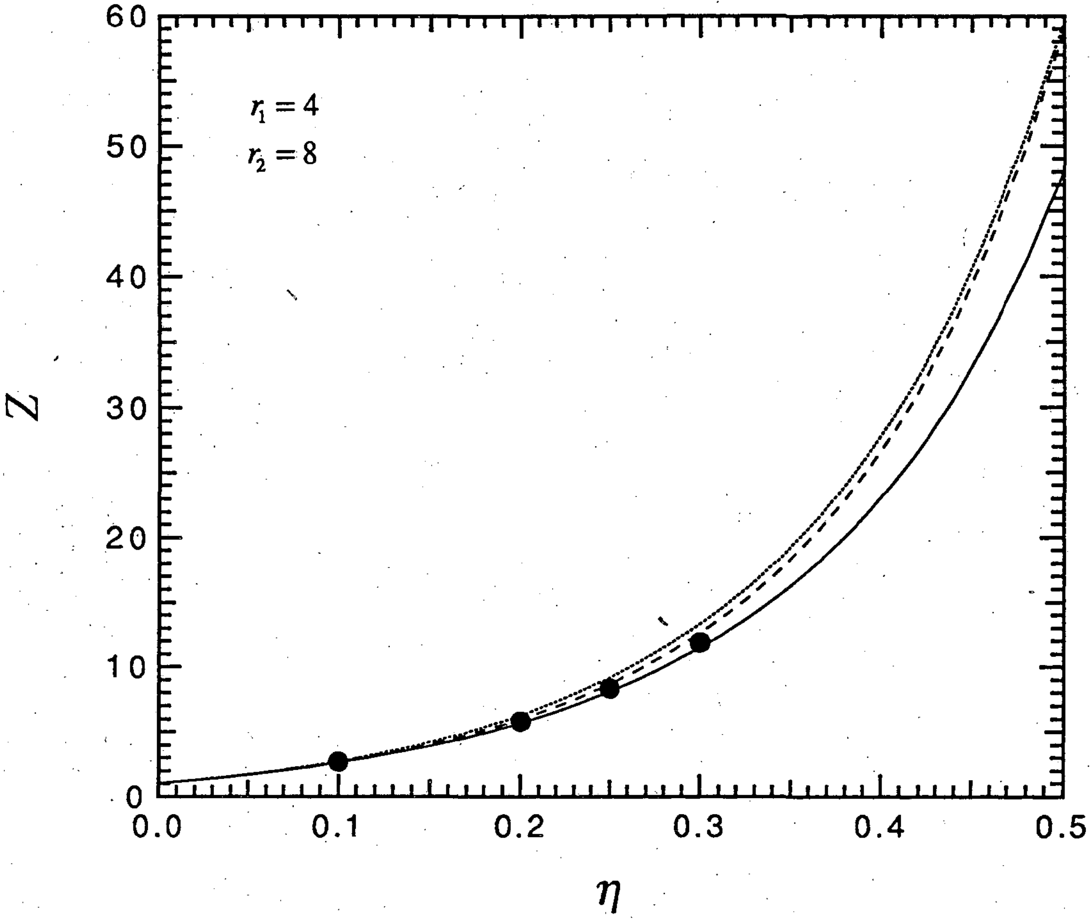


Figure 2



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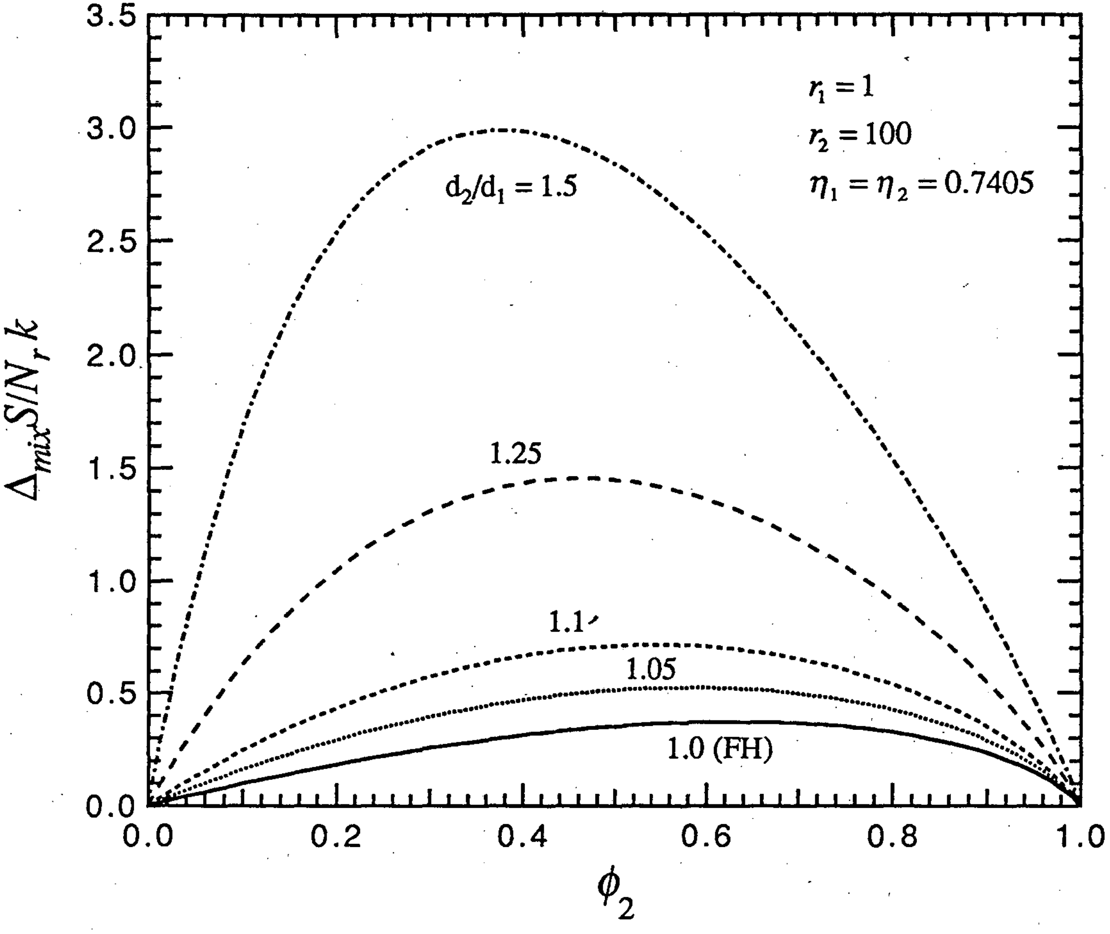
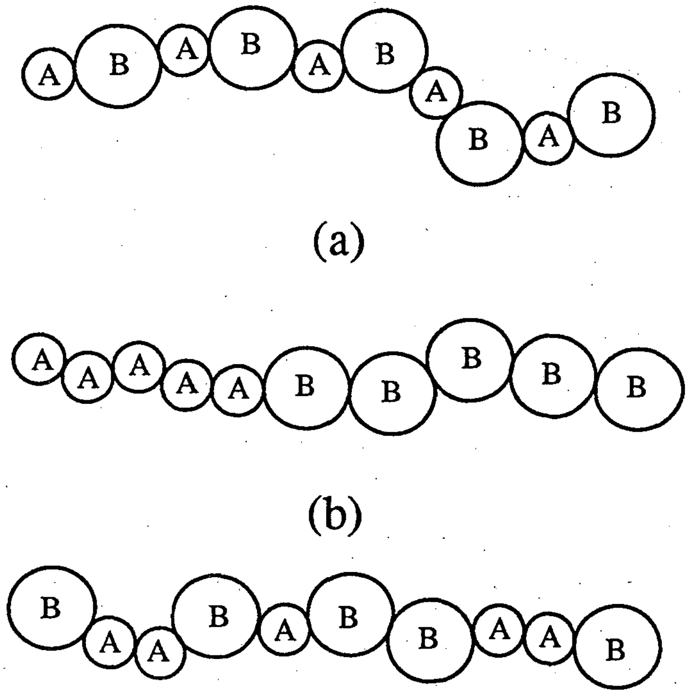

$r_1 = 1$
$r_2 = 100$
$\eta_1 = \eta_2 = 0.7405$
$d_2/d_1 = 1.5$
1.25
1.1
1.05
1.0 (FH)
$\Delta_{mix}S/N_r k$
ϕ_2
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0

Figure 4

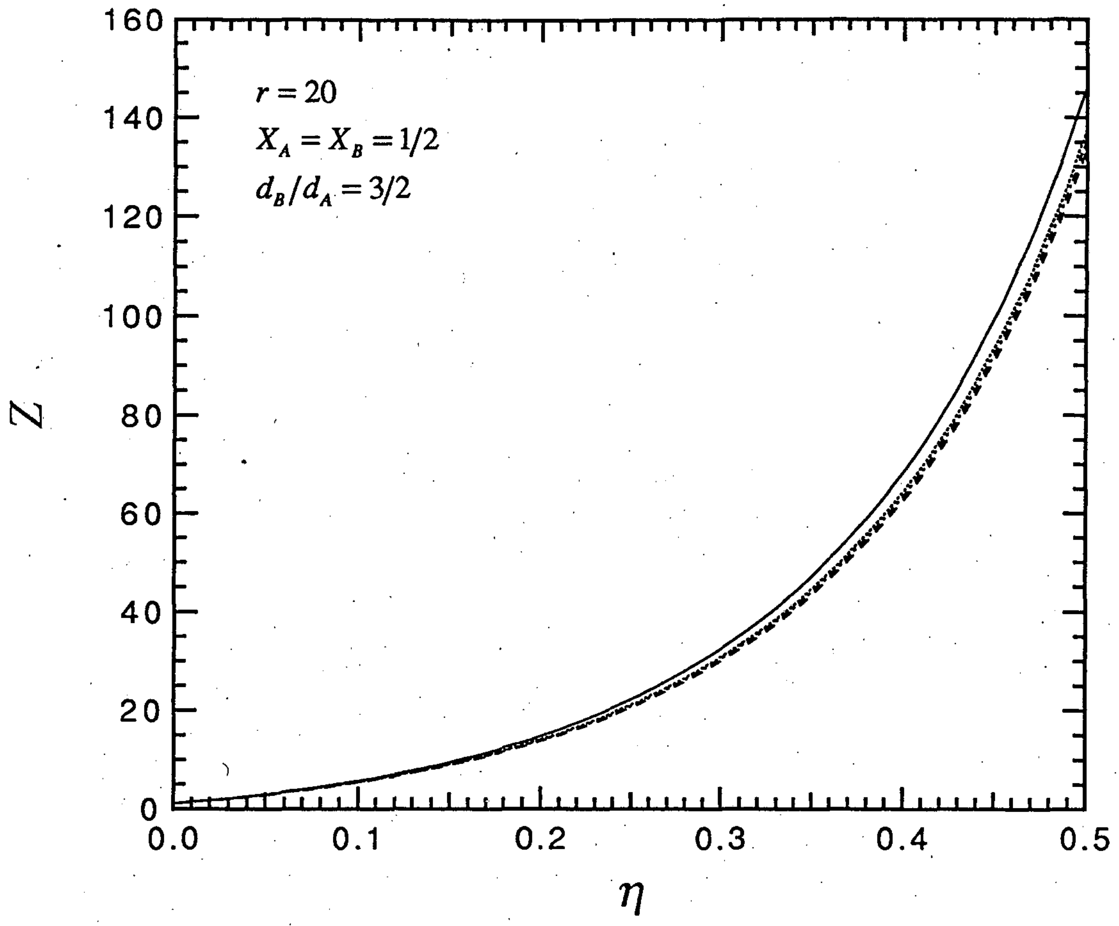


(a)

(b)

(c)

Figure 5



$r = 20$
$X_A = X_B = 1/2$
$d_B/d_A = 3/2$
Z
η
0
20
40
60
80
100
120
140
160
0.0
0.1
0.2
0.3
0.4
0.5

Figure 6

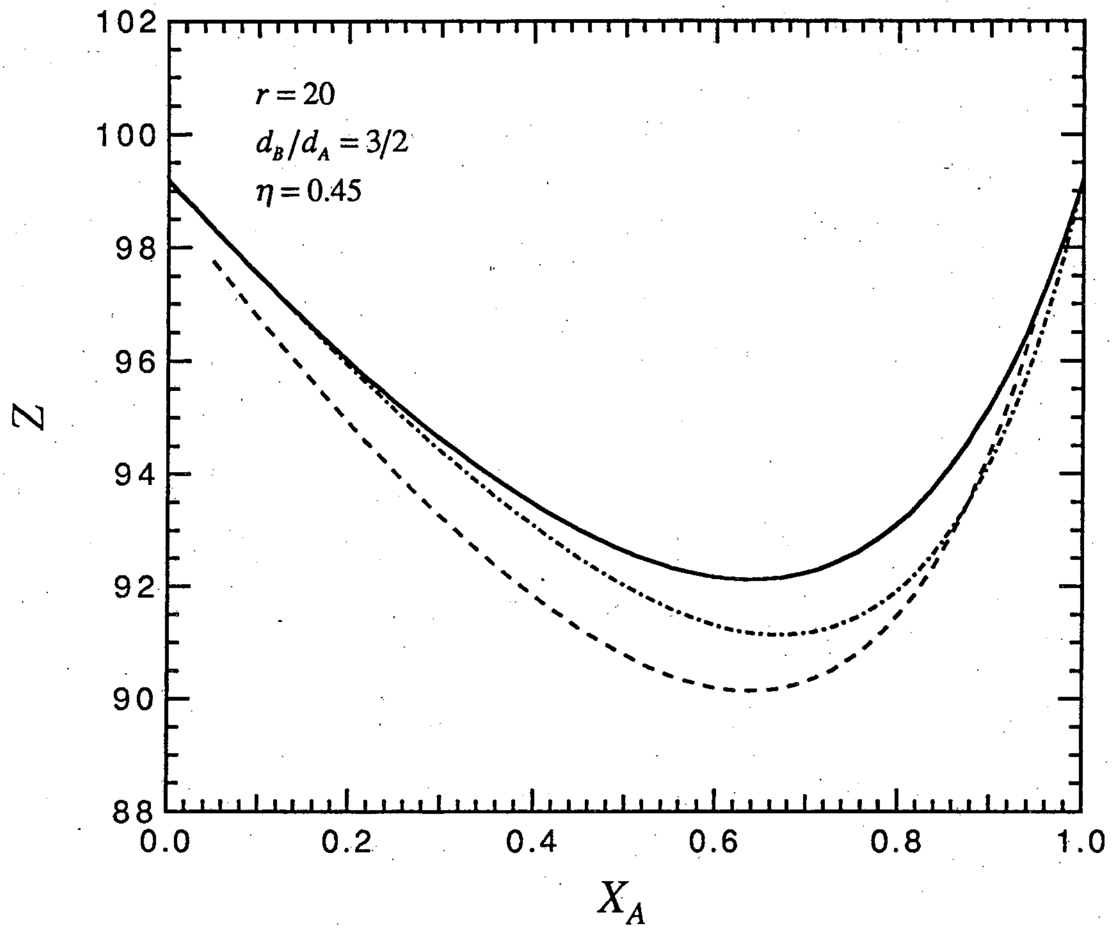


Figure 7

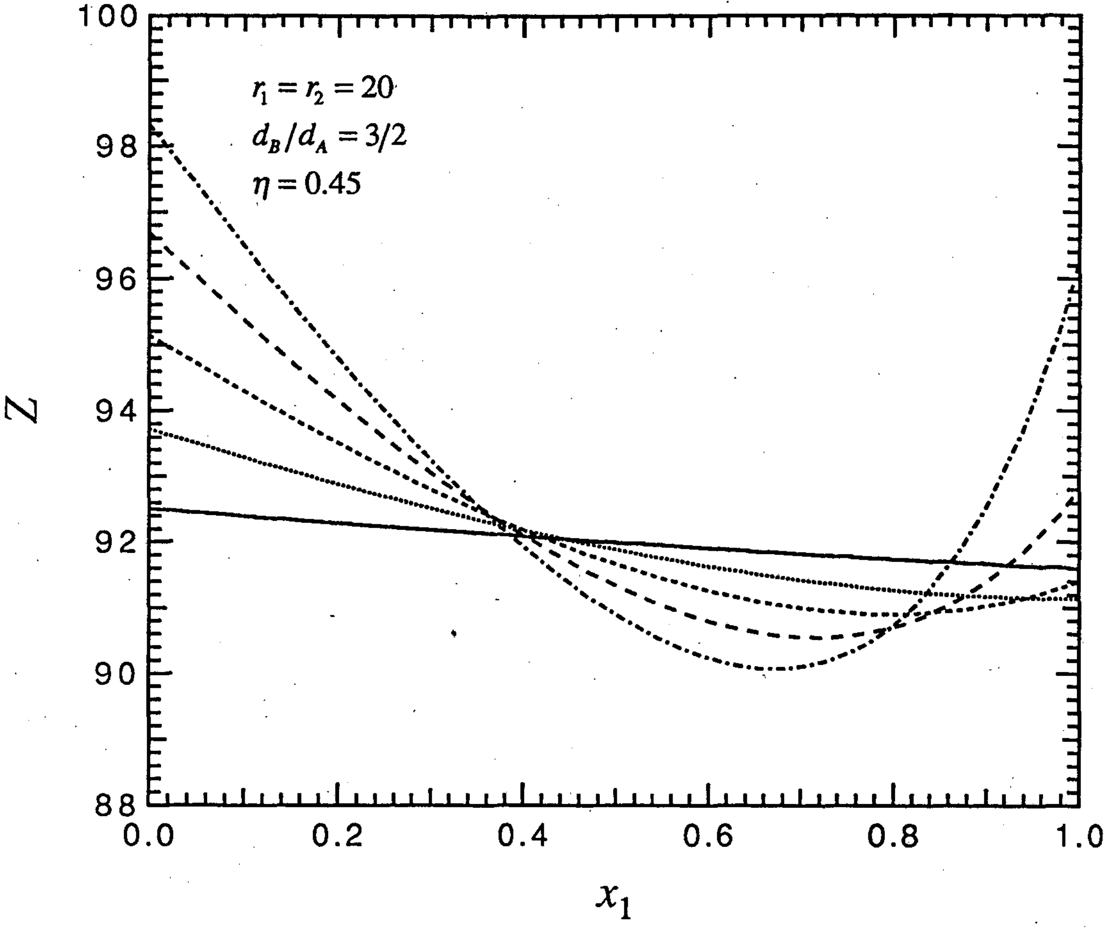
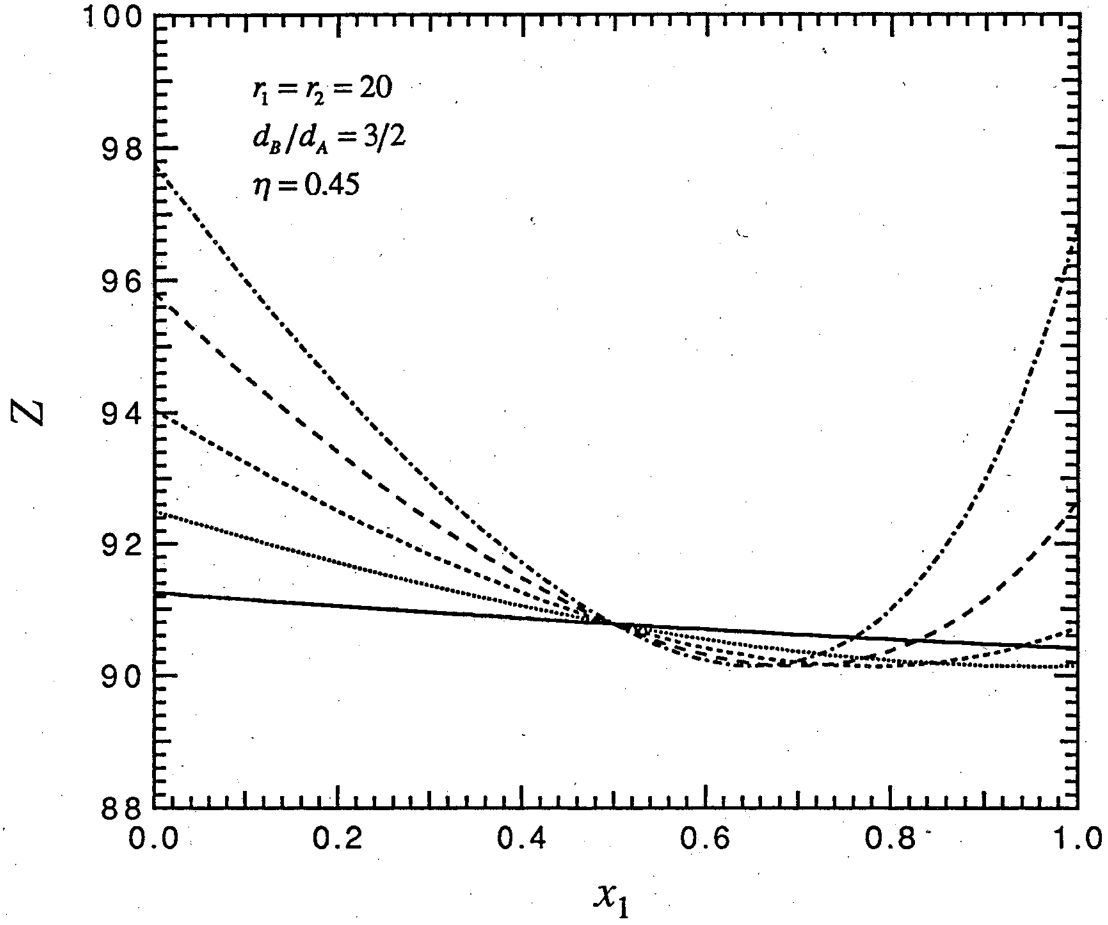


Figure 8



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