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# Simulation and Model Development for the Equation of State of Self-Assembling Nonadditive Hard Chains

**Basel F. Abu-Sharkh and Esam Z. Hamad***

*Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

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ABSTRACT: Molecular dynamics simulations for short hard chains interacting with nonadditive size interactions were performed. Different densities and nonadditivities were used. Microphase separation was observed at high density and positive nonadditivity for diblock copolymers but not for alternating copolymers. The equation of state for these chains was also investigated, and a model was developed to predict the compressibility factor.

## Introduction

Nonadditive size interactions represent a simple model where phase separation is observed for hard spheres with positive nonadditivity parameter, $\Delta$. Spherical nonadditive size interaction is characterized by a cross collision diameter $\sigma_{ij}$ of the form

$$\sigma_{ij} = (1 + \Delta)(\sigma_{ii} + \sigma_{jj})/2 \qquad \Delta \geq -1 \tag{1}$$

Nonadditive interactions were used in describing liquid metals,[1,2] protein interactions,[3] and fluid−fluid phase separation at very high pressures[4−6] where repulsive interactions dominate.

The simplest molecules for which nonadditive interactions were studied are mixtures of hard spheres. Binary mixtures of equal-size components were studied by computer simulation,[7−11] integral equations,[11−13] and other analytical techniques.[7,8,11,12,14,15] Mixtures with unequal size components were recently studied by computer simulation,[16] and expressions for the contact pair correlation functions and equations of state were developed.[17] In addition, a general mixture theory, which accounts for nonadditive size interactions in spherical and nonspherical molecules, has been developed.[18,19]

An interesting question is whether phase separation will take place when nonadditive size interactions are part of a chain molecule, where only some of the segments interact by size nonadditivity. One would expect that a microphase separation becomes a possibility, depending on the magnitude and sign of the nonadditive interactions and on the composition, structure, and distribution of segments interacting with nonadditive interactions. In this work we use computer simulation to investigate the possibility of microphase separation in diblock and alternating hard chain copolymers where nonadditive interactions are present. We also develop a model for the equation of state of hard chains with nonadditive interactions. The model is used to predict the compressibility factor for diblock and alternating hard chain copolymers, and the results are compared to the simulation data.

There are very few studies in the literature that addressed nonadditive interactions in hard chains. In a study on liquid crystalline phases, nonadditive size interactions were used to form a stiff chain out of an 8-mer flexible chain.[20] In this study, the nonadditive interactions were limited to intramolecular interactions between the eight segments. In a more recent study a general method of representing chain stiffness, segment fusion, ring rigidity, and specific forces using nonadditive size interactions was suggested.[21]

## Molecular Dynamics

We consider chains consisting of two types of hard sphere segments in a volume $V$. The cross interaction between segments is governed by eq 1. The packing fraction of the chains is

$$y = \frac{\pi}{6}\frac{N}{V}\sum_i x_i {\sigma_{ii}}^3 \tag{2}$$

where $x_i$ is the mole fraction of spheres of type $i$. The total number of spheres, $N$, is fixed at 512. The chain model consists of $\nu$ freely jointed touching hard spheres where $\nu$ is equal to 2, 4, 8, and 16. The hard sphere potential between pairs of nonbonded atoms is approximated by a truncated Lennard-Jones (LJ) potential with purely repulsive character that has the form[22]

$$\begin{aligned} u_{\text{hs}}(r) &= 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon, \quad r < 2^{1/6}\sigma \\ &= 0, \quad r > 2^{1/6}\sigma \end{aligned} \tag{3}$$

where $r$ is the distance between any pair of interacting segments. All spherical segments in the system are assigned the same values of $\epsilon$ and $\sigma$.

We perform molecular dynamics simulations in a cubic box with periodic boundary conditions. We employ the DL_POLY 2.0 simulation program[23] in the NVT ensemble. The distances between bonded spheres are constrained using the shake algorithm. The value of $\epsilon/kT$ in eq 3 is fixed at 0.8. This value of $\epsilon/kT$ makes the parameter $\sigma$ of the Lennard-Jones potential equivalent to the hard sphere diameter.[22] Our compressibility factor results compare well with discontinuous molecular dynamics results for additive hard sphere chains of 8 and 16 spheres at a volume fraction of 0.45[24] (0.5% deviation) as shown in Table 1.

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* Corresponding author. E-mail: ezhamad@kfupm.edu.sa.

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**Table 1. Compressibility Factors for Nonadditive Hard Sphere Chains Composed of 16, 8, 4, and 2 Units at Different Packing Fractions and Size Ratios**

| | | 16-mer | | 8-mer | | 4-mer | | dumbbell |
|---|---|---|---|---|---|---|---|---|
| $\rho$ | $\Delta_{12}$ | $Z_{\text{alternating}}$ | $Z_{\text{block}}$ | $Z_{\text{alternating}}$ | $Z_{\text{block}}$ | $Z_{\text{alternating}}$ | $Z_{\text{block}}$ | $Z$ |
| 0.37 | −0.2 | 20.07 | 23.89 | 11.64 | 14.5 | 6.13 | 6.97 | 4.24 |
| | 0.0 | 48.94 | 48.94 | 29.11 | 27.47 | 14.37 | 14.37 | 8.523 |
| | 0.1 | 84.01 | 58.53 | 44.55 | 37.74 | 22.87 | 20.05 | 12.51 |
| 0.45 | −0.2 | 31.30 | 38.02 | 17.89 | 21.94 | 9.34 | 10.41 | 6.09 |
| | 0.0 | 97.00 | 97.00 | 50.74 | 50.74 | 26.00 | 26.00 | 14.59 |
| | | 97.4[a] | 97.4[a] | 50.5[a] | 50.5[a] | | | |
| | 0.1 | 207.6 | 112.40 | 88.54 | 67.09 | 42.05 | 35.86 | 21.93 |

[a] Compressibility factor data reported by S. W. Smith et al. (1996).

Each system is started from a cubic lattice of chains randomly placed. The initial velocities are generated according to the Maxwell−Boltzmann distribution. Each system is initially relaxed by performing a simulation of $4 \times 10^5$ molecular dynamics time steps. Compressibility factor data are then collected over $5 \times 10^4$ steps. Increasing the number of time steps to $10^6$ resulted in less than 0.1% change in the calculated average compressibility factor. The equation of motion is integrated using the Verlet algorithm as provided with the DL_POLY 2.0 program. The time step for the simulation is 0.5 fs. The simulations are carried out for two different packing fractions—$y = 0.37$ and 0.45—and three different nonadditivity ratios—$\Delta = -0.2$, 0.0, and 0.1. The cutoff radius for the Verlet neighborhood list is kept constant at $3\sigma_{11}$.

## Model Development

The presence of nonadditive size interaction excludes a lattice-based model. Therefore, we seek an off-lattice model that is general enough to allow nonadditive interactions between segments. In this work we will base our model on the first-order perturbation theory of associating fluids (TPT1), which was pioneered by Wertheim.[25−27] In this model, the chain is constructed by forming strong association bonds between two sites on each monomer (repeat unit). In the literature, the work done using this model was based on additive interactions. In general, the equation of state of $m$ repeat unit chains can be written as

$$Z = m(Z_{\text{units}} + Z_{\text{bond}}) \tag{4}$$

where the first term between the parentheses is the compressibility factor of the unbonded units, and the second term accounts for the change in $Z$ due to the presence of bonds between the units in a polymer chain. The general form of the bonding contribution $Z_{\text{bond}}$ for $M$ multicomponent mixtures and heteronuclear chains containing additive hard spherical units was given by Malakhov and Brun:[28]

$$Z_{\text{bond}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{c(k)}}{\rho}\left[1 + \rho\frac{\partial \ln g_{sk,(s+1)k}}{\partial\rho}\right] \tag{5}$$

where the subscript $k$ runs over chain type and the subscript $s$ runs over segments in each chain. In the above expression $N_k$ is the degree of polymerization, $\rho$ is the particle density, $\rho_{c(k)}$ is the density of chains of type $k$, and $g_{sk,(s+1)k}$ is the contact pair correlation function between consecutive segment types. Although eq 5 was derived for spherical segments interacting with *additive* size parameters, we will test its validity to modeling chains of tangent spheres, where the bond length between consecutive segments is equal to the collision diameter (whether additive or nonadditive).

In this work we will consider two types of segments and emphasize two polymer structures, diblock and alternating. These two structures represent the two limits of segregation of the different segments in the molecular structure. Diblock copolymers consist of two types of units arranged in two blocks. The blocks are chemically bonded together. If we allow nonadditive hard sphere (NAHS) interactions, then eqs 4 and 5 can be combined to give

$$Z = 1 + (m_a + m_b)(Z_{\text{NAHS}} - 1) - \rho\frac{\partial}{\partial\rho}[(m_a - 1)\ln g_{11} + (m_b - 1)\ln g_{22} + \ln g_{12}] \tag{6}$$

where $m_a$ and $m_b$ are the lengths of the two blocks, and the $g_{ij}$ are now for nonadditive hard spheres. In alternating copolymers two types of repeat units appear alternately. For this type of polymer, only the unalike pair correlation function appears in the bonding term, and we have

$$Z = 1 + m(Z_{\text{NAHS}} - 1) - (m - 1)\left[\rho\frac{\partial \ln g_{12}}{\partial\rho}\right] \tag{7}$$

where $m$ is the total number of segments in the chain.

To use eqs 6 and 7, we will need expressions for the compressibility factor and the contact values of NAHS fluid. Two forms are available for these quantities.[17] The more accurate form is complex and requires numerical integration. In this work, we will use the simpler, slightly less accurate form. The like pair contact value is given by[17]

$$g_{ii} = g_{ii}^{\text{add}}(\sigma_{jj} \rightarrow (2\sigma_{ij} - \sigma_{ii})) \qquad j \neq i,\ \sigma_{ij} \geq \sigma_{ii}/2 \tag{8}$$

$$g_{ii} = g_{ii}^{\text{add}}(\sigma_{jj} \rightarrow 0) \qquad \sigma_{ij} \leq \sigma_{ii}/2 \tag{9}$$

where the arrow implies replacing $\sigma_{jj}$ by the indicated quantity and $g_{ii}^{\text{add}}$ is any expression for the contact value of additive hard spheres. Here we use the Mansoori−Carnahan−Starling−Leland (MCSL) for $g_{ii}^{\text{add}}$.[29] The unalike contact value for NAHS is given by[17]

$$g_{ij} = \frac{1}{1-y} + \frac{3}{2}\frac{\frac{\pi}{6}\rho\sum x_k f_{ij,k}}{(1-y)^2} + \frac{1}{2}\frac{\left(\frac{\pi}{6}\rho\sum x_k f_{ij,k}\right)^2}{(1-y)^3} \tag{10}$$

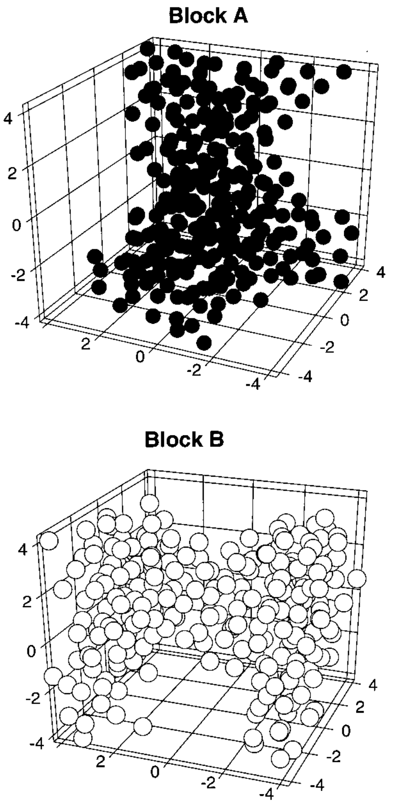


**Figure 1.** Simulation cell after 4.5 × $10^5$ time steps for 16-mer block copolymers at a reduced density of 0.45. Black and white circles represent segments of different blocks.

where for binary mixtures

$$f_{ij,k} = \sigma_{kk}{}^{3}(2\sigma_{ij} - \sigma_{kk})/\sigma_{ij} \qquad \sigma_{ij} \geq \sigma_{kk}/2 \tag{11}$$

$$f_{ij,k} = 0 \qquad \sigma_{ij} \leq \sigma_{kk}/2 \tag{12}$$

The compressibility factor for the nonbonded spheres is obtained from the virial equation of statistical mechanics:

$$Z_{\mathrm{NAHS}} = 1 + \frac{4\pi}{6}\rho\sum_{i}\sum_{j}x_i x_j \sigma_{ij}{}^{3} g_{ij} \tag{13}$$

The simulation and model results are presented in the following section.

## Results and Discussion

The presence of microphase separation for the chains under investigation can be checked by observing equilibrated chains at different times and checking for a stable segregation of segments of different types. Figure 1 shows the simulation cell after 4.5 × $10^5$ time steps for the 16-mer block copolymer at a reduced density of 0.45. Each block (type of segment) is shown in a separate plot to simplify the visual identification of any phase separation. The figure clearly shows a segregation of the two different blocks. The region, which is occupied by one type of block (top plot), is seen to be void of the other blocks (bottom plot) due to the positive nonadditive interactions between the segments of the two blocks. The phase separation is also observed at the lower density of 0.37 (Figure 2). However, it is not observed for chains with zero or negative nonadditive interactions. Phase separation is also observed for the 8-mer and 4-mer block copolymers. However, stronger phase separation is observed for longer chains and the higher density compared to shorter chains and the lower density. A clear phase separation could not be identified in the case of dumbbells.

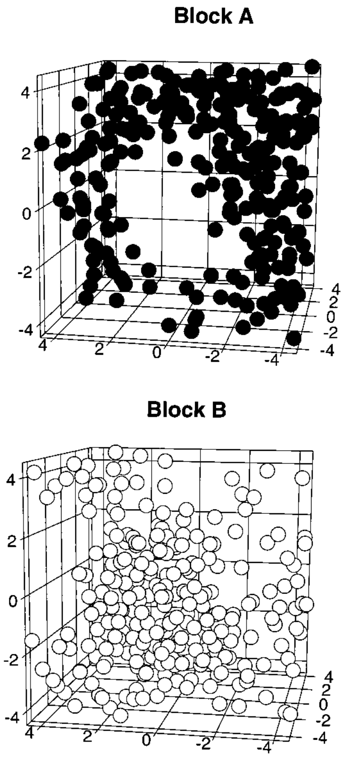


**Figure 2.** Simulation cell after 4.5 × $10^5$ time steps for 16-mer block copolymers at a reduced density of 0.37. Black and white circles represent segments of different blocks.

Another indicator of microphase separation is the site–site pair correlation function, $g_{ij}$. The site–site pair correlation functions for the like (A–A) and unalike (A–B) pairs are shown in Figure 3a–c for the 4-, 8-, and 16-mers at the reduced density of 0.37 and 0.45. The height of the first peak is proportional to the local concentration of the segments of type $i$ around a segment of type $j$. The height of the first peak for the like pair correlation function is almost twice the height of the peak for the unalike pair correlation function. This is a clear indication that segments of the same type tend to aggregate together, while segment of different types tend to stay away from each other. It can also be observed that the first peak of the like pair correlation function (A–A) is higher at the higher density for all chain lengths, indicating stronger aggregation. To study the influence of chain length on the level of segregation, the average number of (A) segments within a sphere of radius $r$ centered at another (A) is plotted in Figure 4 for the different chain lengths. It can be observed that the level of aggregation increases as the number of segments per chain increases from 4 to 16.

In block copolymers the two types of segments are chemically bonded only at one point in the chain, namely, between the two blocks. This bond will be located at the interface between the different microdomains. However, for alternating copolymers the situation is different. Each segment is chemically bonded to one of the other type. This arrangement is expected to prevent the physical separation of the segments into microdomains. This is what was observed in simulation of alternating copolymers. When the two types of

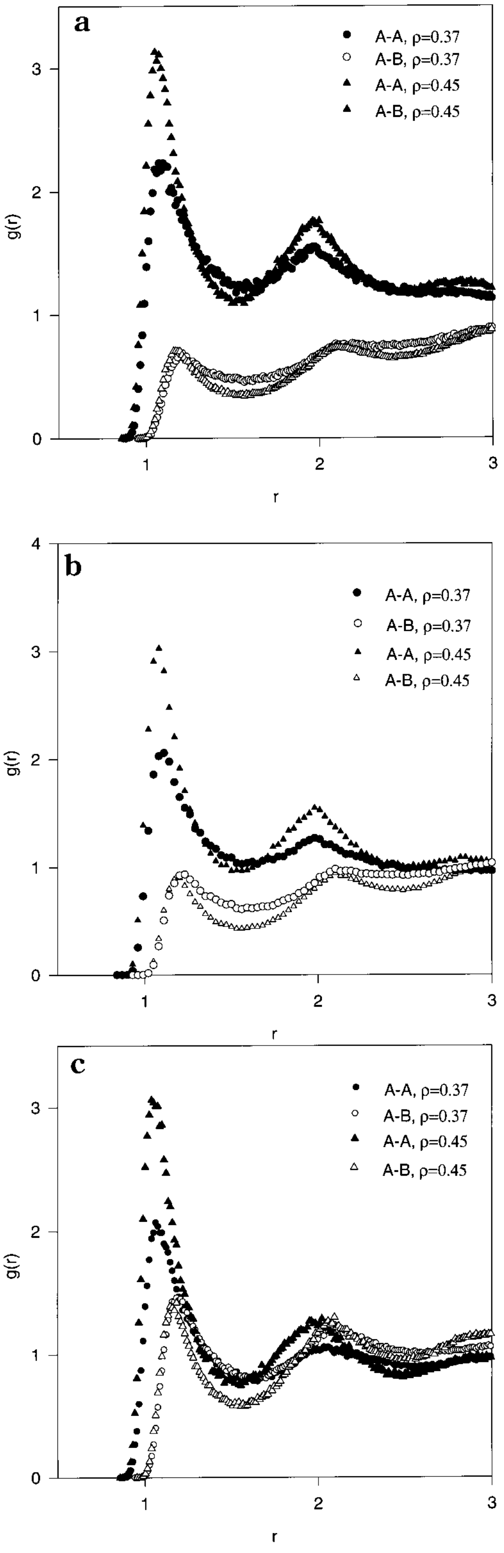


**Figure 3.** Site–site pair correlation functions for the like (A–A) and unalike (A–B) pairs of block copolymers at reduced densities of 0.37 and 0.45. $\Delta_{12} = 0.1$. (a) 16-mer, (b) 8 -mer, and (c) 4-mer.

segments are plotted (Figure 5), no microphase separation can be identified in the simulation cells.

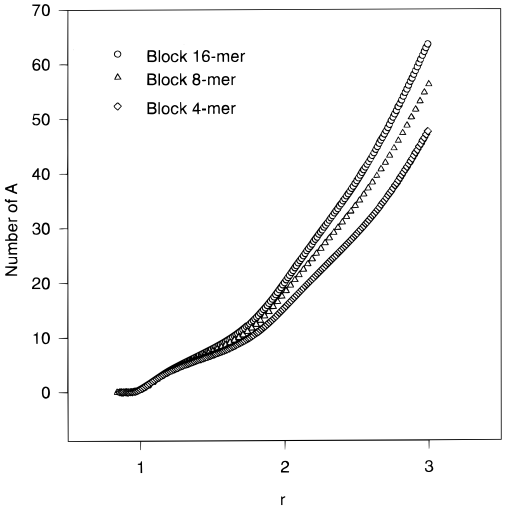
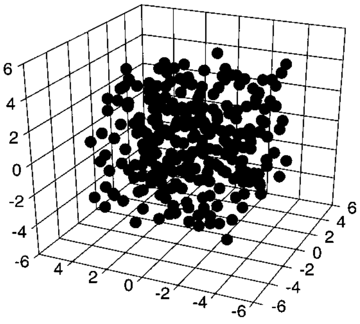


**Figure 4.** Average number of (A) segments within a sphere of radius *r* surrounding another A segment.



Segment B

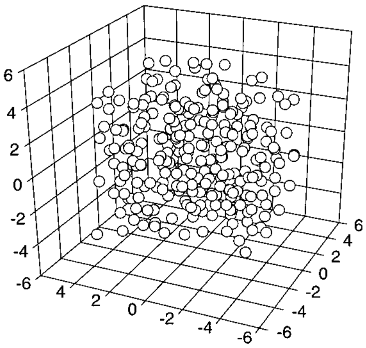


**Figure 5.** Simulation cell after $4.5 \times 10^5$ time steps for the alternating 16-mer at the reduced density of 0.45 and $\Delta_{12} = 0.1$. Black and white circles represent nonadditive segments.

The values of the compressibility factor for chains of different length are shown in Table 1. For the case of additive interactions our results agree well with the values reported in the literature by Smith et al.[26] To test the model presented above for nonadditive chains, we compare its prediction with the simulation data in Figures 6–12. The agreement is generally acceptable except for block copolymers with positive nonadditivity parameter at the highest density. This region is where the phase separation was observed. There are three sources of approximation in the developed model. First, eq 4 itself is a first-order perturbation theory. However, it has already been established in the literature that it is fairly accurate for linear *additive* chains. The second source of approximation is the specific expression used for the NAHS pair correlation functions, eq 10. This is not likely to be the source of the deviations observed for positive nonadditivity parameter at the highest density because these expressions are fairly accurate for all densities at the value of nonadditivity used, 0.1. The third and most likely source of error is the approximation in using eq 4 for nonadditive size interac-

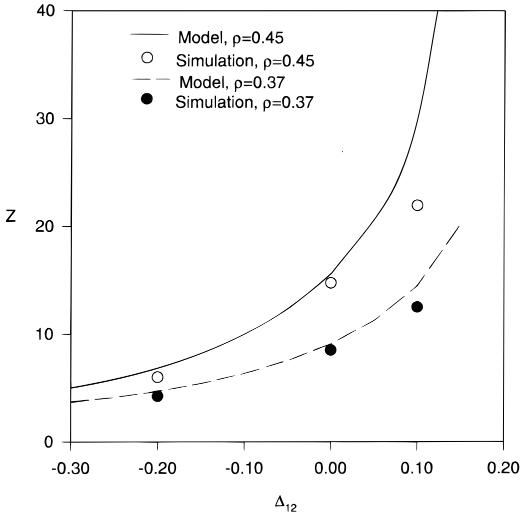


**Figure 6.** Model and simulation compressibility factor data for the dumbbells as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

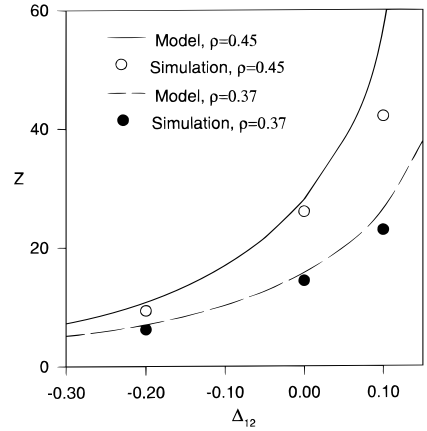


**Figure 7.** Model and simulation compressibility factor data for the block 4-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

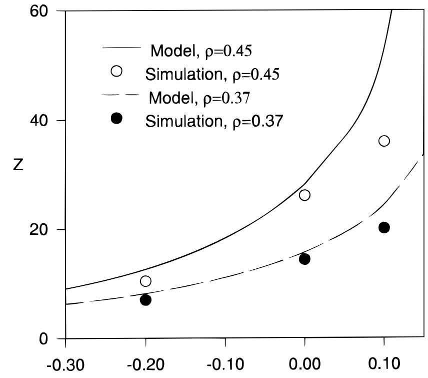


**Figure 8.** Model and simulation compressibility factor data for the alternating 4-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

tions. As mentioned before, it was found that this equation is accurate for additive spheres, but it has not been tested for nonadditive spheres until now.

## Conclusions

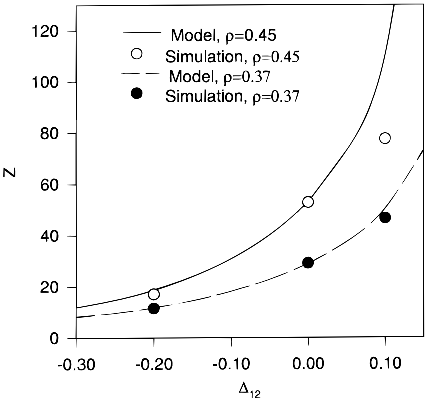


**Figure 9.** Model and simulation compressibility factor data for the block 8-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

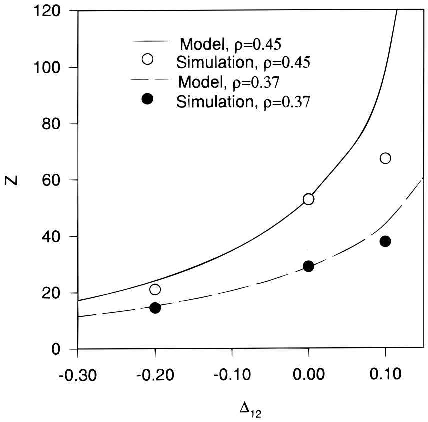


**Figure 10.** Model and simulation compressibility factor data for the alternating 8-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

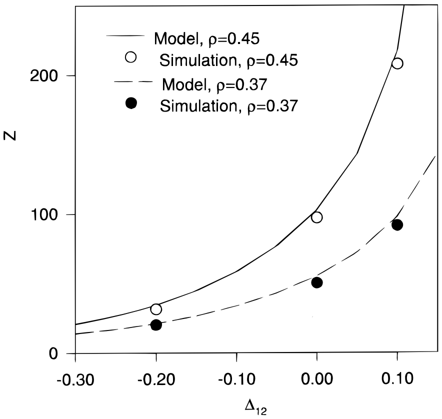


**Figure 11.** Model and simulation compressibility factor data for the block 16-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

Diblock hard chains consisting of 4−16 segments in which the two blocks interact with positive nonadditivity were simulated using MD simulation and found to microphase separate into domains in which segments of the same type self-assemble. The level of segregation was found to increase with increasing density and number of segments per chain. Self-assembly was not observed for additive chains and chains interacting with negative nonadditivity. In addition, alternating copolymers did not self-assemble into separate domains. A model for the equation of state of these chains was developed on the basis of the TPT1 theory. The agreement between the simulation and model compressibility factors was excellent for additive chains and chains with negative nonadditivity. However, the model overesti-

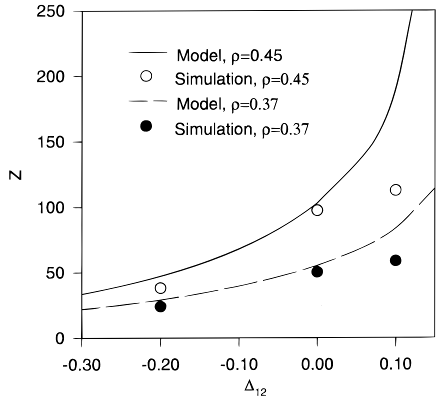


**Figure 12.** Model and simulation compressibility factor data for the alternating 16-mer as a function of nonadditivity parameter at two reduced densities (0.37 and 0.45).

mates the compressibility factors when positive nonadditivity was introduced. This is a result of the phase separation which acts to lower the compressibility factors of the simulated systems.

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