

Thermodynamics of Systems with Different Geometric Constraints and Intermolecular Correlations

Y. Chen,[†] R. R. Kilburg,[‡] and M. D. Donohue^{*,†}

Department of Chemical and Biomolecular Engineering and Carey Business School, The Johns Hopkins University, Baltimore, Maryland 21218

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Four types of systems with different degrees of geometric constraint and intermolecular correlations were studied to determine the differences in their thermodynamics. The average configurational internal energies of these systems were calculated using Monte Carlo simulations, and the results are compared at the same temperatures and constant average bulk density. From the energy profiles for the four systems, the effects of geometry and intermolecular correlations on the systems' phase behavior are discussed. It was observed that indirect intermolecular correlations, rather than geometric constraints, are the key to achieving a first-order phase transition.

1. Introduction

The geometry of a system (i.e., the spatial arrangement of the elements of the system) and the correlations (i.e., the probability, strength, and direction of the interaction between two or more elements of a system) among the constituent elements are important in determining the nature of the system's equilibrium state and phase. In general, correlations are categorized as direct correlations and indirect correlations, which are defined through the Ornstein–Zernike equation

$$h(\vec{r}) = c(\vec{r}) + \rho \int h(\vec{r}')c(|\vec{r} - \vec{r}'|)d\vec{r}' \quad (1)$$

where $h(\vec{r})$ is the total correlation function, ρ is the particle density, $c(\vec{r})$ is the direct correlation function, and $\gamma(\vec{r}) = h(\vec{r}) - c(\vec{r})$ represents the indirect correlation.¹ On the basis of its length scale (correlation length ξ), correlations also can be categorized as short-range correlations and long-range correlations, where short range is defined as the first or second nearest neighbors of an element and long range is defined at longer distances. Geometry also has an intrinsic effect on correlations, as the correlation function depends on the coordination number (i.e., the maximum number of bonds or interactions a molecule can have). Systems with different degrees of intermolecular correlations and geometry exhibit different thermodynamic behaviors. For example, a solid is crystalline when it has both short-range order and long-range order. A solid is amorphous when it has short-range order but lacks long-range order. Most fluids also have some degree of short-range order but lack long-range order. Certain liquids may have short-range order in one direction and long-range order in another direction; these special substances are called liquid crystals.

Different degrees of intermolecular correlations and geometric constraints also play a very important role in the thermodynamics of polymer solutions, molecular networks, and phases. For example, the phase-segregated morphologies typically exhibited

in the majority of shape-memory polymers contain physical cross-links formed through crystallization of polymers or block copolymers^{2–5} well-defined polymers with precisely designed molecular architectures, and nanostructured morphologies can be formed using living polymerization;⁶ elastomers with reversibly associating side groups and end groups exhibit certain thermomechanical stability and polymer–polymer miscibility.^{7,8} Different degrees of intermolecular correlations and geometric constraints also play an important role in the three-dimensional configurations that biological polymers adopt as well as the flexibility of the macromolecules and their interactions in living cells.^{9–13}

During a phase change at thermodynamic equilibrium of a liquid–vapor system, sharp discontinuities in macroscopic properties are observed. At the critical point, these discontinuities vanish but there still is a divergence of correlation length.^{14–16} Outside the critical region, the study of phase transitions has been based on the study of the indirect correlation function in fluids through the Ornstein and Zernike^{17,18} equation. With the Ornstein–Zernike equation, it became possible to analyze the influence of higher order correlations on the structure of fluids and vapor–liquid boundaries.^{19,20} Influences of geometry on indirect correlations and phase transitions also have been studied extensively,^{21,22} including systems like ferroelectrics,^{23,24} superfluids,²⁵ and liquid crystals.²⁶ However, to our knowledge, there have been no systematic studies of the differences in the effects of indirect correlations and geometry on phase behavior of complex systems outside the critical region.

In this paper, four types of systems that have different geometric constraints and different degrees of indirect intermolecular correlations are studied and compared. The average configurational internal energies of these systems were calculated using Monte Carlo simulations, and the results are compared to each other at the same temperatures and constant average bulk density. From the energy profiles for the four systems, the effects of geometry and indirect correlation on the systems' phase behavior are discussed, with the hope of providing a better understanding of the fundamental differences among these systems.

* To whom correspondence should be addressed. E-mail: mdd@jhu.edu.

[†] Department of Chemical and Biomolecular Engineering, The Johns Hopkins University.

[‡] Carey Business School, The Johns Hopkins University.

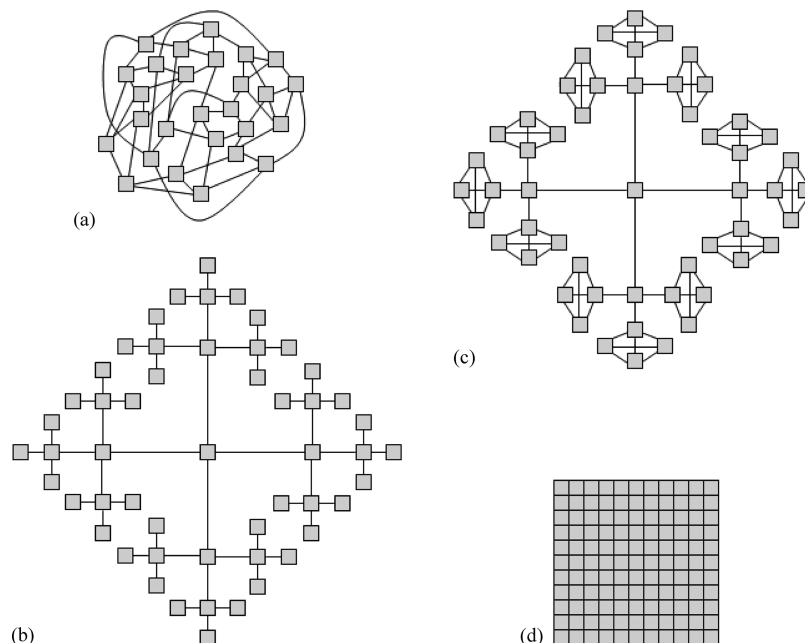


Figure 1. (a) System without geometric constraint where each site has four bonds and there are no correlations between bonded sites; (b) system with quasi-fractal geometry where each site has four bonds that are dictated by the geometry of the system but there are no correlations between neighbors; (c) system with quasi-fractal geometry where each site has four neighbors but there are correlations between neighbors at the system boundary; (d) square lattice, as an example of a system with geometric constraint and correlations between neighbors.

2. Systems Studied

Four types of systems are discussed in this paper, including the following. (a) A system without geometric constraints where each molecule has four bonds (with nearest neighbor interaction ϵ) to other molecules and where there are no indirect correlations among bonded molecules. This system is illustrated schematically in Figure 1a. Though this is a highly idealized, hypothetical system, it is not without molecular analogy. For example, a real molecular system that would behave in a manner similar to this is an elastomeric block copolymer, such as Elasthane 80A.²⁷ As shown in Figure 2a, Elasthane 80A is composed of hard segments and soft segments. The hard segments can segregate to form hard crystalline domains via hydrogen bonding within a continuous soft-segment matrix. For this system, it is a very good approximation to assume that the hard segments group can bond to any other hard segments in the polyurethane matrix and that there are no indirect correlations among them.

(b) A system with a quasi-fractal geometry where each site has four neighbors but there are no indirect correlations between neighbors. This system is illustrated schematically in Figure 1b. A molecular system that would behave in a manner similar to this system would be a “living” star polymer. Star polymers are made from reactive molecules that have multiple functional groups. Living polymers are molecules in which the polymerization reaction is reversible because the strength of the polymerization bonds is similar to that of van der Waals or hydrogen-bonding forces rather than that of covalent bonds. Since in star polymers the bonding groups are relatively distant from each other, it is possible for such systems to have few or no indirect correlations from one bond to another. Figure 2b shows the molecular structure of the fourth-generation dendrimer, [G4]–OH₄₈, formed by the core, branches, and branch joints.²⁸ As the bonding groups, indicated by the branch joints, are separated from each other by branches, there are only very weak indirect correlations between them.

(c) A system with a quasi-fractal geometry where each site has four neighbors like that of system b above but where there

are correlations between neighbors at the system boundary. This system is illustrated in Figure 1c. Again, this system would be representative of a living star polymer but one that has terminus groups that are more strongly interactive with each other than they are with the solvent. This would occur, for example, if the terminus groups have large carbon-ring structure but the solvent was aliphatic. Figure 2c shows the molecular structure of a AuNP-cored silylferrocenyl dendrimer containing tethers terminated by ferrocene redox groups.²⁹ In an aliphatic solvent, these terminus groups would be more interactive with each other, which introduces indirect correlations between them in the outer shell of the dendrimer.

(d) The final system is one where the molecules can arrange themselves on a square lattice. This system has both geometric constraints and correlations among the molecules. This system is illustrated in Figure 1d. A real system that would behave in this way would be argon vapor adsorbed onto the surface of a cubic crystal such as sodium chloride.

Note that in Figure 1 the squares represent sites in the systems that can be either vacant or occupied by molecules and each molecule occupies only one site. In system a, one site can bond with any of the other four sites, and these four neighbors also can interact with any of the other three sites. In this way, all the sites have direct correlations with four other sites, regardless of where the sites are with respect to each other geometrically. In fact, the concept of “physical location” or “distance” does not exist in this particular system. Thus, system a is an example of a system without either geometric or indirect correlations. In system b, except for the central site, all other sites interact with one upper-level site and three lower-level sites. This forms a quasi-fractal geometry where each site has four neighbors, except for the sites at the boundary that have one neighbor. Also, it should be noted that the schematic is meant to illustrate the pattern of site–site interactions, but this is not necessarily related to the physical location of the sites. This gives an example of a system that exhibits some geometric constraint but no indirect correlations among neighboring sites. System c

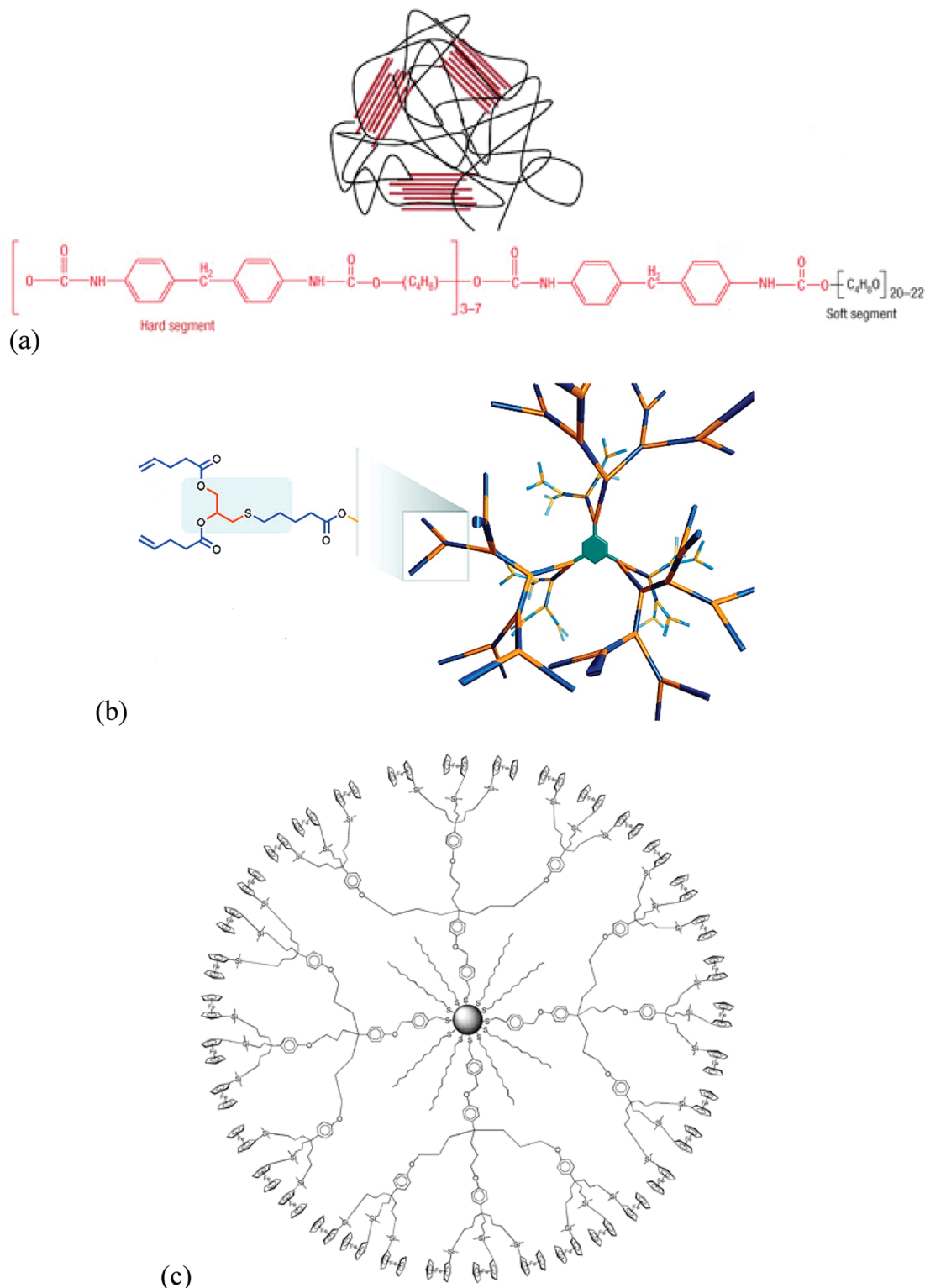


Figure 2. (a) Elastane 80A, an elastomeric block copolymer composed of MDI-BDO hard segment and PTMO soft segment. The hard segments segregate to form hard crystalline domains via hydrogen bonding within a continuous soft matrix (from ref 27; permission for reproduction is granted by Nature Publishing Group). (b) Structure of the fourth-generation dendrimer, [G4]-OH₄₈, formed by the core, branches, and brunch joints (from ref 28; permission for reproduction is granted by the American Chemical Society). (c) Structure of the AuNP-cored silylferrocenyl dendrimer containing tethers terminated by ferrocene redox groups (from ref 29; permission for reproduction is granted by the Royal Society of Chemistry).

has nearly the same fractal geometry as system b, but for the sites at the boundary. Instead of having only one interaction with their upper-level neighbors, each of these sites also interacts with the other two sites in the same branch and level. Therefore, at the system boundary, each site has three neighbors and there

are correlations between the nearest neighbors in the parallel branch. This gives an example of a system with certain geometric constraint and limited degree of indirect correlations. Last but not least, system d is a finite-size square lattice. This is an example of a system with geometric constraint and indirect

correlations. These four systems were chosen to illustrate the differences in their thermodynamics as the degrees of indirect correlation and geometric constraint are varied systematically. When any two bonded sites both are occupied by molecules, we assume there are attractive nearest neighbor interactions between them with intermolecular interaction energy ϵ . We use the Monte Carlo method to study how geometric constraint and indirect correlations affect the thermodynamic properties of these systems.

3. Monte Carlo Algorithms

Canonical Monte Carlo simulations were performed to obtain the average configurational energy of the four proposed systems. Due to the differences between these systems' characteristics, some of the Monte Carlo simulations were different from the standard Monte Carlo method. In system a, we first assume the system has 10 000 sites. Two hundred of these sites are occupied by molecules, and all remaining sites are vacant. This gives an average bulk density, or fractional occupancy, $\rho_\infty = 0.02$. To initialize the system, bonds were created randomly between each site and four other sites, until all the sites were saturated with four bonds. If two bonding sites are both occupied by molecules, there is attractive interaction energy ϵ between them. In all other cases, the interaction energy of the bonds is zero. This gives the initial state of system a. To perform a Monte Carlo move, two pairs of bonded sites were randomly chosen and the bonds between them switched (a–b plus c–d becomes a–c plus b–d). The potential energy of the attempted move was calculated for the original and new bonding patterns, and the moves are accepted according to the Metropolis algorithm with probability

$$P = \min\left[1, \exp\left(\frac{-\Delta U}{kT}\right)\right] \quad (2)$$

where k is Boltzmann's constant, T is the system temperature, and ΔU is the energy difference before and after an attempted move.

In systems b and c, the systems had 8050 sites and 161 molecules were randomly distributed in the system. This gives the same average bulk density of $\rho_\infty = 0.02$. If two molecules are nearest neighbors, there was attractive interaction energy ϵ between them. For vacancy–vacancy and vacancy–molecule neighbors, the interaction energy between sites is zero. This gives the initial state for systems b and c. To perform a Monte Carlo move, molecules were chosen randomly and moved to a new (unoccupied) site that also was chosen randomly. The potential energies were calculated for the original and new molecular positions with the Metropolis algorithm used to determine acceptance.

In system d, a standard lattice Monte Carlo simulation was performed for 100×100 square lattice (without periodic boundary condition) with 200 molecules, which gives the same $\rho_\infty = 0.02$. Note that in all simulations the system was equilibrated for a minimum of 1×10^6 steps and then sampled for every $1000N$ steps, where N is the number of molecules in the system. The configurational internal energy value was obtained by averaging over 100 samples, and the final average configurational energy was obtained by averaging over 100 experiments.

4. Results and Discussion

The resulting average configurational internal energies per molecule for the four systems as a function of density are shown

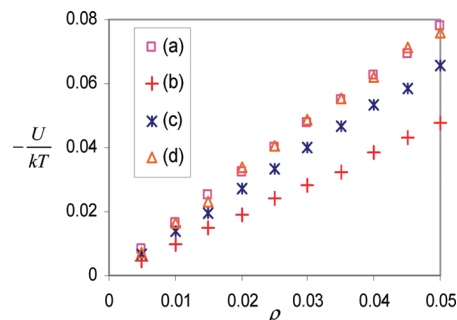


Figure 3. Average configurational internal energies per molecule for systems a–d as a function of density at $\epsilon/kT = -0.5$, where a represents a system without either geometric constraint or correlations between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.5%, b represents a system with quasi-fractal geometry and no correlation between neighbors where all data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 3.0%, c represents a system with quasi-fractal geometry and limited degree of correlations where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 3.0%, and d represents a square lattice where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 2.0%.

in Figure 3 at a constant temperature ($\epsilon/kT = -0.5$). At small densities, when the intermolecular interactions are also quite small, configurational internal energies of the four systems increase linearly as the system density increases. The slopes of the curves indicate the second Virial coefficient of the corresponding systems, which depend on the pair interaction between molecules.³⁰ Although the intermolecular interactions of the four systems are set the same, their second Virial coefficients are not necessarily the same due to the differences between their boundary conditions, which are significant for the fractal geometries. In system a, each and every site has four neighbors; in system d, more than 96% of the sites have four neighbors; thus, the two corresponding curves have nearly the same slope. In system b, sites at the system boundary only have one neighbor; thus, the slope of the corresponding curve is smaller than systems a and d. In system c, sites at the system boundary (more than 45% of all sites) have three neighbors, which give results between the previous two cases.

The resulting average configurational internal energies per molecule for the four systems as a function of dimensionless intermolecular interaction energy are shown in Figure 4. When the intermolecular interactions are quite small (high temperature, $-\epsilon/kT < 2.0$), configurational internal energies of the four systems are nearly the same; all increase gradually as temperature decreases. In the region of $2.0 < -\epsilon/kT < 3.0$, for systems without correlations a and b, configurational internal energy increases smoothly as temperature decreases and no phase transition was observed; for square lattice system d, a steep increase of configurational internal energy occurs which indicates the system approaches a first-order phase transition; for the system with limited correlations c, configurational internal energy increases but not as rapidly as system d, which results in a not as steep of an energy profile. To achieve a better understanding of the configurational internal energy profile when phase transition occurs, Monte Carlo simulations also have been performed for different types of square lattice. The total number of sites (10 000) and number of molecules (200) in the system remains constant but the dimension of lattice changes from $1 \times 10\,000$ (a quasi 1D case) to 2×5000 , 4×2500 , and 100×100 . Figure 5 shows the resulting configurational internal

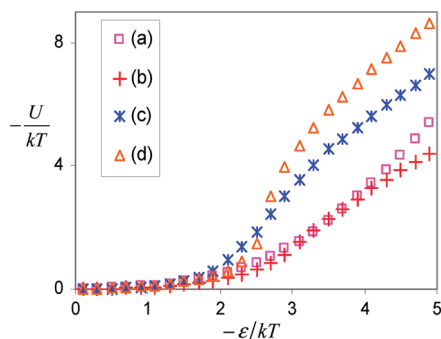


Figure 4. Average configurational internal energies per molecule for systems a–d as a function of dimensionless intermolecular interaction energy, where a represents a system without either geometric constraint or correlations between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.6%, b represents a system with quasi-fractal geometry and no correlation between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.2%, c represents a system with quasi-fractal geometry and limited degree of correlations where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.0%, and d represents a square lattice where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.7%.

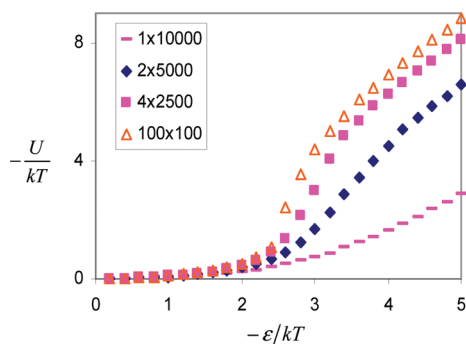


Figure 5. Average configurational internal energies per molecule for lattices with the same size (10 000 sites) and number of molecules (200 molecules). The dimension of lattice changes from $1 \times 10\,000$ (a quasi 1D case) to 2×5000 , 4×2500 , and 100×100 (a quasi 2D case). All data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.0%.

energies as a function of dimensionless intermolecular interaction energy. Similar to the case in Figure 3, when the intermolecular interactions are quite small (high temperature, $-\epsilon/kT < 2.0$), the configurational internal energies of the different lattices are nearly the same: all increase gradually as temperature decreases. In the region of $2.0 < -\epsilon/kT < 3.0$, for $1 \times 10\,000$ lattice, configurational internal energy continues to increase smoothly as temperature decreases. There is no phase transition in this quasi 1D lattice due to the lack of long-range correlation in one direction. When the dimension of lattice changes to 2×5000 and 4×2500 , the correlation length increases, which results in steeper configurational internal energy profile. In addition, for the 100×100 lattice, there is a quasi 2D lattice large enough that the system has long-range correlations in both directions. As the system is still finite, the correlation length does not diverge. Simulations show the steepest increase of configurational internal energy, which indicates the system is approaching a first-order phase transition. Thus, combining the results in Figure 5 with Figure 4, we can see that to achieve first-order phase transition there must be

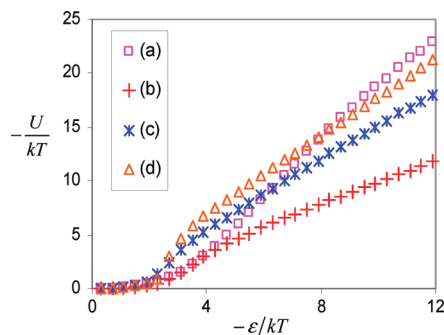


Figure 6. Average configurational internal energies per molecule for systems a–d as a function of dimensionless intermolecular interaction energy, where a represents a system without either geometric constraint or correlations between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.6%, b represents a system with quasi-fractal geometry and no correlation between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.2%, c represents a system with quasi-fractal geometry and limited degree of correlations where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.0%, and d represents a square lattice where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.7%.

long-range correlations in at least two dimensions. The geometry of the system does not play an important role in the phase transitions.

By increasing intermolecular interactions further (low temperature, $-\epsilon/kT > 5.0$), configurational internal energies of the four systems keep increasing, until the simulation results depend linearly on inverse temperature ($-\epsilon/kT > 8.0$), as shown in Figure 6. At these low temperatures, clusters with the most energetically favorable structure have been formed, and the slopes of the lines depend on the structure of the clusters. When the temperature is low enough, in system a, eventually each and every molecule bonds with four other molecules, which gives an average internal energy of $2\epsilon/kT$ per molecule. Thus, the slope of the energy profile of system a approaches 2.0 as temperature decreases. In system b, all the molecules form one large cluster with a quasi-fractal structure; this gives an average internal energy of ϵ/kT per molecule. Thus, the slope of the energy profile of system b approaches 1.0 at very low temperatures. The situation in system c is quite different from system b because of the bonds and correlations at the boundary. When the intermolecular interactions are strong enough, molecules will first saturate the system boundary to achieve the most energetically favorable state, which results in a slope approaching 1.6. In system d, as temperature decreases a liquid state is reached. Every molecule has four neighbors in the square lattice, except for the molecules at the cluster boundary. This makes the slope of energy profile for system d slightly less than 2.0.

It also is possible to look at the data in another way by normalizing the energies by their low-temperature limits and their intermolecular interactions. Figure 7 shows the normalized configurational internal energies of the four systems as a function of $-\epsilon/kT$. The normalized energy, U^* , is calculated as

$$U^* = \frac{U/\epsilon}{-U_{12}/kT} \quad (3)$$

where U_{12} represents the corresponding internal energies at $-\epsilon/kT = 12$ for each system. As shown by the figure, by decreasing

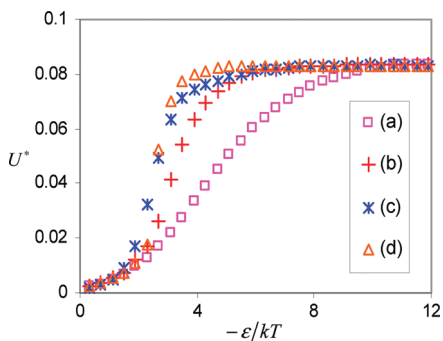


Figure 7. Normalized average configurational internal energies per molecule for systems a–d as a function of dimensionless intermolecular interaction energy, where a represents a system without either geometric constraint or correlations between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.6%, b represents a system with quasi-fractal geometry and no correlation between neighbors where all the data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.2%, c represents a system with quasi-fractal geometry and limited degree of correlations where all data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 1.0%, and d represents a square lattice where all data were obtained by averaging over 100 experiments, which corresponds to an average relative error of 0.7%.

the temperature, the normalized configurational internal energies of the four systems keep increasing until the values level off, which indicate the most energetically favorable structures have been formed in the systems. In system a, the most stable structure is formed at a much lower temperature. This is not only due to the lack of correlations between molecules, as compared to the cases in systems c and d but also due to the higher energy cost to form the most stable structure as compared to the case in system b.

5. Conclusion

Four types of systems with different degrees of geometric constraint and indirect intermolecular correlations were studied to determine the differences in their thermodynamics and phase behavior. Monte Carlo simulations were used to obtain average configurational internal energies per molecule for the four systems as a function of average bulk density and dimensionless intermolecular interaction energy. The resulting energy profiles are compared to each other. As expected, it was observed that indirect intermolecular correlations, rather than a geometric constraint, are the key to achieving a first-order phase transition.

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