# Phase Behavior of Rigid Objects on a Cubic Lattice<sup>†</sup>

Jonathan R. Davis, Michael V. Piccarreta, Rory B. Rauch, T. Kyle Vanderlick, and Athanassios Z. Panagiotopoulos\*

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540

Grand canonical Monte Carlo simulations were carried out to examine phase transitions of rigid lattice objects. The objects studied are coarse representations of planar, spherical, cubic, and cylindrical shapes on a simple cubic lattice. Multihistogram reweighting methods were used to generate the phase diagrams; critical points were determined using finite-size scaling methods. Spheres and capped cylinders exhibit a first-order transition from fluid to crystalline phases in the athermal limit. Small cubes and planar structures show continuous order–disorder transitions. For a six-armed cross object, there is evidence of a metastable vapor–liquid-phase transition lying within the fluid–solid-phase envelope.

## 1. Introduction

Currently, there is a great deal of interest in the synthesis of small particles of a predetermined size and shape for use as building blocks in the fabrication of electronic and biomedical devices. Simple shapes such as cubes,<sup>1</sup> rods,<sup>2</sup> and tetrahedra<sup>3</sup> can be made at nanometer length scales with high precision. Given the difficulty inherent in manipulating objects of this size, much effort has gone into adding functional groups so that, under a specified set of conditions, these nanoparticles arrange themselves into useful mesoscale structures such as wires or sheaths.<sup>4</sup> Amphiphilic particles similar to naturally occurring lipids and surfactants self-assemble into aggregates much like those of their biological counterparts.<sup>5</sup>

Simulations and theory regarding ordering and phase transitions in systems of regularly shaped two- and three-dimensional particles began with the work of Onsager.<sup>6</sup> Hard spheres have received most attention,7-9 but shapes including cubes,10 spherocylinders,<sup>11,12</sup> and more irregular objects<sup>13</sup> have been studied using a number of intermolecular potentials and at the athermal limit. Tethered nanocube particles were recently studied by simulation.<sup>14</sup> The vast majority of these simulations were done in continuous space. Lattice simulations, though computationally less demanding than their continuum counterparts, often suffer from artifacts that are a consequence of the artificial ordering imposed by the lattice. However, recent work with fine lattice models has shown that the continuum behavior of ionic particles can be reproduced with only a small degree of discretization.<sup>15</sup> Rigid lattice structures have also been used successfully to model the thermodynamic properties of polymer melts.16

In this work, we examine the phase behavior of eight rigid objects constructed from a collection of adjacent sites and confined to a cubic lattice. Phase transitions between fluid and solid phases are obtained for the case of objects with nearest neighbor attractions and for noninteracting hard particles. It is particularly fitting that this paper is part of the special issue in honor of Eduardo Glandt, one of the pioneers of the use of innovative Monte Carlo methods for direct calculations of phase equilibria.<sup>17</sup>

The remainder of this manuscript is arranged as follows. In Section 2, we describe our model objects and the simulation

| Table 1. Models Stu | died |
|---------------------|------|
|---------------------|------|

|                 |                               |       | - |                 |   |                                  |
|-----------------|-------------------------------|-------|---|-----------------|---|----------------------------------|
| Model           | Description                   | Image |   | Model           | Description                                 | Image                            |
| P <sub>4</sub>  | 2x2 square                    |       |   | T4              | flexible chain<br>of 4 beads                | <b>B1</b> <sup>10</sup> <b>1</b> |
| R <sub>7</sub>  | six-arm<br>cross              | •     |   | P <sub>8</sub>  | planar hexagon                              |                                  |
| R <sub>8</sub>  | 2x2x2 cube                    |       |   | $T_8$           | flexible chain<br>of 8 beads                | 5                                |
| R <sub>19</sub> | 3x3x3 cube<br>without corners |       |   | C <sub>22</sub> | capped cylinder                             |                                  |
| R <sub>27</sub> | 3x3x3 cube                    |       |   | R <sub>33</sub> | 3x3x3 cube with added beads at face centers |                                  |

techniques used to obtain the phase behavior and the equation of state at both the athermal limit and at finite temperatures. In Section 3, we present the results of our investigation and compare them to continuum models, theory, and prior results for flexible lattice chains. Finally, we draw some conclusions and discuss possible future applications of the rigid lattice objects to the study of more complex molecular systems.

## 2. Models and Simulation Method

2.1. Models. The objects studied are composed of multiple sites, as listed in Table 1. We identify objects by a letter indicating the geometry and a subscript indicating the number of sites. We have studied multisite objects that belong to four general categories, namely: (a) planar rigid objects ( $P_4$  and  $P_8$ ), (b) compact rigid objects with sites within a certain radius from a central point (R7, R8, R19, R27, and R33), (c) a cylindrical object (C<sub>22</sub>), and (d) flexible chains of length 4 and 8 ( $T_4$  and  $T_8$ ). The flexible chains have links between successive segments that can be along vectors (0,0,1), (0,1,1), (1,1,1), and their reflections on the cubic lattice, resulting in 26 possible directions (coordination number z = 26). Attractions of unit strength exist between sites along these 26 possible directions. This is equivalent to a square-well attraction between sites that are at distances less than or equal to  $\sqrt{3}$  times the lattice spacing. The total interaction between two rigid objects is calculated from pairwise summation of site-site interactions. We have also studied a single case of nearest-neighbor interactions only (z =6, maximum distance for attraction equal to the lattice spacing).

<sup>\*</sup> To whom correspondence should be addressed. E-mail: azp@ princeton.edu.

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2.2. Simulation Method. We use grand canonical Monte Carlo simulations combined with multihistogram reweighting, as described previously.18 In brief, the simulations to compute vapor-liquid equilibrium are performed in cubic boxes of size  $L \times L \times L$  under periodic boundary conditions. For structures which exhibit a crystalline phase (C22, R7, R19, and R33), simulations were first carried out in a large cubic box (typically L = 25) to determine the underlying structure of the dense phase and then repeated in a box of size  $K \times L \times M$  to ensure that the density of the crystalline phase was not affected by defects resulting from the periodic boundaries. The lattice spacing is taken as the unit of length. The inverse temperature  $\beta = 1/kT$ , chemical potential  $\mu$  and volume  $V = L^3$  (or V = KLM) are input parameters to a single simulation run. Temperatures, energies, and chemical potentials are nondimensionalized by the nearest neighbor interaction strength and length with the lattice spacing. The chemical potential reference state is that of an ideal gas with no interactions, so that at low densities the relationship

$$\beta \mu \to \ln \rho \text{ for } \rho \to 0$$
 (1)

holds, with  $\rho = \langle N \rangle / V$ , where *N* is the number of molecules. For the case of flexible chains (T<sub>4</sub> and T<sub>8</sub>), the reference state is the non-self-avoiding random walk, so that even in the case of athermal systems the self-avoidance of the chain is manifested by deviations from eq 1.

Results from multiple runs with overlapping distributions of the particle number histograms (and energy histograms in the case of systems with interactions) are combined using the approach of Ferrenberg and Swedsen.<sup>19,20</sup> Determination of critical points for vapor—liquid-phase transitions is performed with the mixed-field finite-size scaling approach of Wilding and Bruce<sup>21–23</sup> assuming no pressure mixing in the critical fields.<sup>24</sup> The pressure was determined from the relationship  $\ln \Xi = \beta PV$ , where  $\Xi$  is the grand partition function. While the absolute value of  $\Xi$  cannot be obtained, the ratio of the partition function for two overlapping runs, and thus the difference in pressure can be determined. The absolute value of the pressure can be obtained by including simulations at low values of the chemical potential so that the particles are ideal gases.

#### 3. Results and Discussion

Figure 1 shows phase envelopes and critical points for the cubic-shaped objects R8 and R27-statistical uncertainties in this figure and all others herein are smaller than the symbol sizes shown. The liquid is stabilized at higher temperatures, as expected, with an increasing range of attraction. Although the critical density  $\phi_c$  of the R<sub>8</sub> system is essentially unchanged between the z = 6 (nearest neighbor interactions only) and z =26 lattice, the critical temperature  $T_{\rm c}$  increases by a factor of 6, as seen previously for flexible chains.<sup>31</sup> Likewise, the critical temperature of the  $R_{27}$  system is more than twice that of the  $R_8$ system for the same coordination number. Differences between planar objects and fully flexible chains of equal size are more modest. Figure 2 shows a difference of  $\sim 10\%$  in  $T_c$  and 20% in  $\phi_c$  when comparing structures comprised of both four and eight monomers. Critical points for these transitions are tabulated in Table 2. A similar modest increase in  $T_c$  has been observed<sup>32</sup> as the degree of chain stiffness was increased for linear chains.

Simulations were also performed with the same systems at the athermal limit ( $\beta \rightarrow 0$ ). The pressure vs density data for this case are illustrated in Figure 3. Continuous ordering transitions occur at volume fractions of  $\phi = 0.92, 0.87$ , and



**Figure 1.** Phase diagrams for  $R_8$  with z = 6 (circles, L = 16) and z = 26 (triangles, L = 16) and  $R_{27}$  (diamonds, L = 24) with z = 26. Lines are drawn through points for visual clarity.



**Figure 2.** Phase diagrams for  $P_4$  (triangles),  $P_8$  (squares),  $T_4$  (diamonds), and  $T_8$  (circles) with z = 26 and L = 16. Lines are drawn through points for visual clarity.

 Table 2. Critical Points for Gas-Liquid Transitions of Rigid

 Objects<sup>a</sup>

| model           | Ζ  | L  | $T_{\rm c}$ | $\beta_{\rm c}\mu_{\rm c}$ | $\phi_{ m c}$ |
|-----------------|----|----|-------------|----------------------------|---------------|
| $P_4$           | 26 | 10 | 11.14(2)    | -4.002(5)                  | 0.430(1)      |
|                 |    | 16 | 11.15(2)    | -4.000(6)                  | 0.428(9)      |
|                 |    | 20 | 11.14(2)    | -4.003(7)                  | 0.427(2)      |
| $T_4$           | 26 | 10 | 9.84(2)     | -4.127(2)                  | 0.374(8)      |
|                 |    | 16 | 9.85(1)     | -4.123(2)                  | 0.370(1)      |
|                 |    | 20 | 9.85(1)     | -4.123(1)                  | 0.368(1)      |
| $R_7$           | 26 | 20 | 12.93(4)    | -4.82(1)                   | 0.36(1)       |
| $P_8$           | 26 | 16 | 13.44(2)    | -5.14(1)                   | 0.362(1)      |
|                 |    | 20 | 13.44(2)    | -5.145(6)                  | 0.360(2)      |
| $R_8$           | 6  | 16 | 3.29(1)     | -3.50(2)                   | 0.666(2)      |
|                 | 26 | 16 | 19.86(8)    | -3.75(2)                   | 0.660(8)      |
|                 |    | 20 | 19.75(3)    | -3.75(1)                   | 0.654(4)      |
| $T_8$           | 26 | 16 | 11.87(1)    | -5.093(2)                  | 0.309(1)      |
|                 |    | 20 | 11.87(1)    | -5.092(1)                  | 0.307(1)      |
| R <sub>27</sub> | 26 | 24 | 49.9(1)     | -3.47(1)                   | 0.657(4)      |

<sup>*a*</sup> Numbers in parentheses are statistical uncertainties in units of the last significant figure shown.

 $0.70 \ (\pm 0.01)$  for the P<sub>4</sub>, P<sub>8</sub>, and R<sub>27</sub> systems, respectively, as indicated by the inflection points on the isotherms. These continuous transitions are possible because of the presence of the underlying lattice, as even for an overall positionally



**Figure 3.** Pressure vs density diagram for noninteracting hard objects:  $P_4$  (circles, L = 10),  $P_8$  (crosses, L = 16),  $T_4$  (triangles, L = 10),  $R_8$  (diamonds, L = 16),  $R_{27}$  (squares, L = 24), monomers (solid line).  $V_0$  is the number of lattice sites occupied by each object. The values of  $\beta PV_0$  for  $T_4$ ,  $R_8$ , and monomers are reduced by a factor of 2 for visual clarity.



**Figure 4.** Pressure vs density in the athermal limit for R<sub>7</sub> (circles, system size  $7 \times 14 \times 14$ ), R<sub>19</sub> (diamonds,  $10 \times 10 \times 16$ ), R<sub>33</sub> (squares,  $13 \times 13 \times 18$ ), and C<sub>22</sub> (triangles,  $15 \times 15 \times 15$ ). Solid line is the data of Hoover and Ree for a continuum hard sphere fluid.<sup>25</sup>

disordered liquid the particles occupy regular lattice positions. Smaller cubes and fully flexible chains exhibit no ordering transitions. The presence of a transition in  $R_{27}$  not seen in  $R_8$  is caused by the increasing discretization of the rigid cube, in qualitative agreement with the behavior of coarse hard spheres on a cubic lattice.<sup>25</sup> In light of the results of ref 25, the ordering transitions are precursors of first order transitions that are likely to appear when the size of the rigid cubes increases beyond three lattice sites in length.

Figure 4 shows the athermal equation of state for the other objects ( $R_7$ ,  $R_{19}$ ,  $R_{33}$ , and  $C_{22}$ ); these systems undergo a strong first-order transition. These transitions are distinguishable from ordering (continuous) or higher order transitions in two ways. Although phase transitions are always rounded due to finite size effects in simulations, the pressure vs density curve will flatten around a first-order transition point as system size increases. Furthermore, hysteresis and multiple histogram peaks can be observed in runs near a phase transition, an effect which does not occur at an ordering transition.



Figure 5. Solid structure for R<sub>7</sub>.



Figure 6. Solid structure for R<sub>19</sub>.

 Table 3. Maximum Density of the Crystalline Phases and Minimal

 Simulation Box Dimensions Needed To Achieve that Density

| model                 | $\phi_{ m max}$ | K  | L  | М |
|-----------------------|-----------------|----|----|---|
| <b>R</b> <sub>7</sub> | 1               | 7  | 7  | 7 |
| R <sub>19</sub>       | 0.95            | 10 | 10 | 4 |
| R <sub>33</sub>       | 0.846           | 13 | 13 | 3 |
| C <sub>22</sub>       | 0.88            | 5  | 5  | 5 |

| model                 | $K \times L \times M$    | βμ      | $\beta PV_{\rm o}$ | $\phi_{ m F}$ | $\phi_{ m C}$ |
|-----------------------|--------------------------|---------|--------------------|---------------|---------------|
| <b>R</b> <sub>7</sub> | $14 \times 14 \times 7$  | 2.74(2) | 2.81(1)            | 0.711(2)      | 0.868(2)      |
| R <sub>19</sub>       | $10 \times 10 \times 16$ | 2.93(1) | 2.89(2)            | 0.579(1)      | 0.910(1)      |
|                       | $10 \times 10 \times 20$ | 2.92(2) | 2.88(1)            | 0.579(1)      | 0.908(1)      |
| C <sub>22</sub>       | $15 \times 15 \times 15$ | 5.32(3) | 4.05(2)            | 0.614(2)      | 0.794(2)      |
|                       | $15 \times 15 \times 20$ | 5.30(2) | 4.02(1)            | 0.613(1)      | 0.792(1)      |
| R <sub>33</sub>       | $13 \times 13 \times 18$ | 3.96(3) | 3.50(3)            | 0.580(1)      | 0.832(1)      |
|                       | $13 \times 13 \times 24$ | 4.02(3) | 3.55(4)            | 0.581(1)      | 0.832(1)      |

<sup>*a*</sup> Numbers in parentheses are statistical uncertainties in units of the last significant figure shown.  $\phi_{\rm F}$  and  $\phi_{\rm C}$  are the volume fractions of the fluid and crystalline phases, respectively, at the phase transition.

For the systems with first-order transitions, the high-density phases are either crystalline solids (with full positional order) or smectic liquid crystals. In particular, Figure 5 shows the structure of the R7 solid, which is a base-centered monoclinic Bravais lattice. Figure 6 shows the structure of the R<sub>19</sub> solid, in which the unit cell aligns with the lattice so that layers stack into an arrangement that is precisely body-centered tetragonal. R<sub>33</sub> forms planes with the center bead of each rigid object arranged in a square lattice of unit length  $\sqrt{13}$  and a spacing of three sites between planes. The centers of the C22 objects also form square lattice planes with length  $\sqrt{5}$  and a spacing of 5. The axial directions along each spherocylinder in the crystalline structure are aligned and perpendicular to these planes. In both cases, there are four equivalent configurations in which one plane of the dense phase can stack upon another, resulting in loss of registry between successive planes. Table 3 summarizes the minimal simulation box dimensions needed to ensure a defect-free solid or liquid crystalline structure with periodic boundary conditions for the systems studied. The actual simulations listed in Table 4 were performed in boxes with sides that were integer multiples of the minimal box dimensions.

Comparing the  $R_7$ ,  $R_{19}$ , and  $R_{33}$  structures with the results of Hoover and Ree<sup>26</sup> demonstrates significant deviations between the continuum model for hard spheres and the lattice models presented here. This result is not entirely unexpected since the



**Figure 7.** Fluid-crystalline phase transitions. Symbols and system sizes are the same as in Figure 4. Also shown is the metastable vapor—liquid transition for  $R_7$ . Lines are drawn through points for visual clarity.

maximum packing fraction and crystal structure of these rigid objects are quite different than the face-centered cubic lattice formed by perfect spheres. The phase transitions for these lattice objects occur at a lower pressure than the continuum hard spheres, indicating that the underlying lattice imposes order that is not present in continuous space. However, as the objects increase in size, the pressure of the transition increases toward the continuum limit. The athermal  $C_{22}$  structure also exhibits a phase transition from a disordered state to a smectic state. The transition to a nematic state seen in continuum hard spherocylinders is not present,<sup>11</sup> and the body-centered solid cannot form due to the constraints of the lattice. The locations of the athermal transitions and the densities of the coexisting fluid and crystalline phases are listed in Table 4.

Finally, phase transitions for these objects were determined; the results are shown in Figure 7. Since these transitions do not have a critical point, simulations were carried out at high temperature (T = 100) to ensure that both sides of the phase envelope could be sampled during a single simulation. The absence of a stable vapor-liquid phase envelope for these objects can be understood in terms of the range of attraction for hard particles, which effectively decreases as the size of the lattice objects increase. As seen previously for polymer/ colloid mixtures<sup>27,28</sup> and hard-core Yukawa systems,<sup>29</sup> the vapor-liquid transition eventually disappears below the fluidsolid envelope on reducing the range of attraction. The large lattice objects in the  $R_x$  group are found to exhibit only fluidsolid equilibrium behavior. The rigid cubes (R8, R27) are exceptions, but this observation is most likely an artifact of arranging these cubic objects on a cubic lattice. The presence of the metastable vapor-liquid transition near the edge of the fluid-solid-phase envelope of  $R_7$  is an indication that the ratio of the interaction distance to particle diameter for that system is near the critical value at which a stable liquid phase will form.

### 4. Conclusions

We have quantified vapor—liquid and fluid-solid equilibria for several systems of rigid lattice objects. Hard planar structures four and eight lattice sites in size demonstrate ordering transitions. Hard cubes comprised of 27 lattice sites show a continuous ordering transition that is not observed for the eight monomer cube. Objects similar in structure to hard spheres have firstorder phase transitions at pressures that are lower than those seen in the continuum system, although increasing the discretization of these particles shifts the transition closer to the continuum limit. A metastable liquid phase is present in the  $R_7$  system, indicating that the range of attraction between particles is near the point where a stable liquid phase can form.

In the future, we plan to use these lattice simulations to study amphiphilic particles. Combining athermal rigid objects with flexible tail groups having nearest neighbor attractions will provide a reasonable representation of both the structure and interactions present in real surfactant or lipid particles. Using techniques presented here and elsewhere,<sup>30</sup> it should be possible to study phase separation and micellization of these lattice systems.

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#### Literature Cited

 Gracias, D. H.; Kavthekar, V.; Love, J. C.; Paul, K. E.; Whitesides,
 G. M. Fabrication of micrometer-scale, patterned polyhedra by selfassembly. *Adv. Mater.* 2002, *14*, 235.

(2) Liu, H. T.; Alivisatos, A. P. Preparation of asymmetric nanostructures through site selective modification of tetrapods. *Nano Lett.* **2004**, *4*, 2397.

(3) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. Photoinduced conversion of silver nanospheres to nanoprisms. *Science* 2001, 294, 1901.

(4) Melosh, N. A.; Boukai, A.; Diana, F.; Geradot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112.

(5) Park, S.; Lim, J. H.; Chung, S. W.; Mirkin, C. A. Self-assembly of mesoscopic metal-polymer amphiphiles. *Science* **2004**, *303*, 348.

(6) Onsager, L. Anisotropic solutions of colloids. *Phys. Rev.* 1942, 62, 558.

(7) Wood, W. W.; Jacobson, J. D. Preliminary results of a recalculation of the Monte Carlo equation of state for hard spheres. *J. Chem. Phys.* **1957**, *27*, 1207.

(8) Alder, B. J.; Wainwright, T. E. Phase transition for a hard sphere system. J. Chem. Phys. **1957**, 27, 1208.

(9) Carnahan, N. F.; Starling, K. E. Equation of state for nonattracting rigid spheres. J. Chem. Phys. 1969, 51, 635.

(10) Lafuente, L.; Cuesta, J. A. Phase behavior of hard-core lattice gases: A fundamental measure approach. J. Chem. Phys. 2003, 119, 10832.

(11) McGrother, S. C.; Williamson, D. C.; Jackson, G. A reexamination of the phase diagram of hard spherocylinders. *J. Chem. Phys.* **1996**, *104*, 6755.

(12) Martinez-Haya, B.; Rull, L. F.; Cuetos, A.; Lago, S. Gibbs ensemble simulation of the vapour-liquid equilibrium of square well spherocylinders. *Mol. Phys.* **2001**, *99*, 509.

(13) Zhang, Z. L.; Horsch, M. A.; Lamm, M. H.; Glotzer, S. C. Tethered nano building blocks: Toward a conceptual framework for nanoparticle self-assembly. *Nano Lett.* **2003**, *3*, 1341.

(14) Chan, E. R.; Zhang, X.; Lee, C.-Y.; Neurock, M.; Glotzer, S. C.; Simulations of Tetra-Tethered Organic/Inorganic Nanocube-Polymer Assemblies. *Macromolecules* **2005**, *38*, 6168.

(15) Panagiotopoulos, A. Z.; Kumar, S. K. Large lattice discretization effects on the phase coexistence of ionic fluids. *Phys. Rev. Lett.* **1999**, *82*, 5060.

(16) Buta, D.; Freed, K. F. Lattice polymers with structured monomers: A Monte Carlo study of thermodynamic properties of melts and solutions. J. Chem. Phys. 2002, 116, 10959.

(17) Kofke, D. A.; Glandt, E. D. Monte Carlo simulation of multicomponent equilibria in a semigrand canonical ensemble. *Mol. Phys.* **1988**, *64*, 1105.

(18) Panagiotopoulos, A. Z. Monte Carlo methods for phase equilibria of fluids. J. Phys: Condens. Matter 2000, 12, R25.

(19) Ferrenberg, A. M.; Swendsen, R. H. New Monte Carlo technique for studying phase transitions. *Phys. Rev. Lett.* **1988**, *61*, 2635.

(20) Ferrenberg, A. M.; Swendsen, R. H. Optimized Monte Carlo Data Analysis. *Phys. Rev. Lett.* **1989**, *63*, 1195.

(21) Wilding, N. B.; Bruce, A. D. Density fluctuations and field mixing in the critical fluid. *J. Phys.: Condens. Matter* **1992**, *4*, 3087.

(22) Bruce, A. D.; Wilding, N. B. Scaling fields and universality of the liquid-gas critical point. *Phys. Rev. Lett.* **1992**, *68*, 193.

(23) Wilding, N. B. Critical point and coexistence-curve properties of the Lennard-Jones fluid: A finite-size scaling study. *Phys. Rev. E* **1995**, 52, 602.

(24) Kim, Y. C.; Fisher, M. E. Fluid Critical Points from Simulations: The Bruce-Wilding Method and Yang-Yang Anomalies. *J. Phys. Chem. B* **2004**, *108*, 6750.

(25) Panagiotopoulos, A. Z. Thermodynamic properties of lattice hard sphere models. J. Chem. Phys. 2005, 123, 104504.

(26) Hoover, W. G.; Ree, F. H. Melting transition and communal entropy for hard spheres. J. Chem. Phys. **1968**, 49, 3609.

(27) Gast, A. P.; Russel, W. B.; Hall, C. K. An experimental and theoretical study of phase transitions in the polystyrene latex and hydroxy-ethylcellulose system. *J. Colloid Interface Sci.* **1986**, *109*, 161.

(28) Meijer, E. J.; Frenkel, D. Colloids dispersed in polymer solutions. A computer simulation study. J. Chem. Phys. **1994**, 100, 6873.

(29) Hagen, M. H. J.; Frenkel D. Determination of phase diagrams for

the hard-core attractive Yukawa system. J. Chem. Phys. **1994**, 101, 2093. (30) Panagiotopoulos, A. Z.; Floriano, M. A.; Kumar, S. K. Micellization and phase separation of diblock and triblock model surfactants. Langmuir **2002**, *18*, 2940.

(31) Panagiotopoulos, A. Z.; Wong, V.; Floriano, M. A. Phase equilibria of lattice polymers from histogram reweighting Monte Carlo simulations. *Macromolecules* **1998**, *31*, 912.

(32) Floriano, M. A.; Firetto, V.; Panagiotopoulos, A. Z. Effect of stiffness on the phase behavior of cubic lattice chains. *Macromolecules* **2005**, *38*, 2475.

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