

# Lattice versus continuum models of a polymer chain

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A self-avoiding, self-interacting polymer chain is studied both on a lattice and in the continuum using a Born–Green–Yvon integral equation approach. Equivalent theoretical approximations are made in both cases, allowing for an unambiguous comparison between the lattice and continuum models. The theory preserves the universal scaling behavior for polymer chain dimensions in the high-temperature limit and, with a lowering of temperature, predicts a universal collapse transition behavior for both lattice and continuum chains. Implications for the modeling of polymer solutions are discussed. © 1999 American Institute of Physics. [S0021-9606(99)50642-9]

## I. INTRODUCTION

When is it appropriate to use a lattice model in the analysis of what are invariably experimental data on continuum systems? Such a procedure typically leads to questions regarding the extent to which discrepancies may be attributed to use of the lattice model itself as distinct from the approximations made in the theoretical analysis. These questions can be addressed to some degree by comparing theory with simulation results, however, simulations on complex dense systems are not always feasible. Such is the case, for example, in the area of polymer solutions and blends, where large-scale simulations are notoriously demanding.<sup>1</sup>

While the issue of lattice versus continuum models is long-standing, there is recent renewed interest in this question in the field of polymer physics.<sup>2–5</sup> The use of lattice models is well established in the polymer community, however, there is much current effort in adapting the integral equation techniques of liquid state physics to build accurate theories for continuum models of polymers.<sup>6–8</sup> Since different approximations are used in the derivation of lattice and continuum theories, an unambiguous comparison between them has been impossible. Continuum models are, in principle, well suited for capturing the sometimes subtle interplay between local microscopic structure and macroscopic properties. Yet, such an approach typically leads to equations that require numerical solutions, in contrast to the analytic expressions and relatively simple calculations associated with lattice models. To date there have not been any theoretical studies that probe the differences in results obtained using the *same* theoretical approach applied to a lattice and a continuum model. Such an investigation would provide some insight as to when it is necessary to keep the level of microscopic detail associated with the continuum approach, and when the more simplified lattice model will do.

In this work we present results for a first attempt at elucidating the differences between using a lattice theory and a continuum theory to investigate the same system. We are

particularly interested in phase separation in polymer systems, but here we address the related but simpler problem of the collapse transition for a single polymer chain. We employ a Born–Green–Yvon (BGY) integral equation technique,<sup>9–13</sup> using a Markov closure,<sup>11</sup> to study an isolated polymer chain both on a lattice and in the continuum. In general, the local structure and average dimensions of a polymer are entirely model dependent. However, in the limit of long chain length, all polymers are expected to display model-independent scaling behavior.<sup>14,15</sup> For example, the mean-square end-to-end distance  $\langle R^2 \rangle$  and radius of gyration  $\langle S^2 \rangle$  should scale with chain length  $n$  as  $n^{2\nu}$  such that both the exponent  $2\nu$  and the amplitude ratio  $\langle R^2 \rangle / \langle S^2 \rangle$  are universal constants. This universality provides a stringent test to any approximate theory and is central to this study. In particular, we ask the question, “Can a single microscopic theory, applied to both a lattice and continuum model, truly preserve this universal scaling behavior, or do the approximations inherent in any liquid-state theory inevitably result in model-dependent global behavior?” We find that, even when solved at a fairly crude level of approximation, the BGY integral equation *does* preserve this universal scaling. For example, in the high-temperature limit our results for the average chain dimensions for both lattice and continuum polymers follow exactly the same scaling relationship. More importantly, with decreasing temperature, both the lattice and continuum chains collapse and the theory *predicts* a universal collapse transition behavior. The size scaling exponent and amplitude ratio, when plotted against a reduced temperature, fall onto master curves independent of model details. The results obtained here suggest that using an integral equation theory to study a lattice model of a polymer solution should be sufficient to capture many of the most important details of polymer phase separation. A full continuum model is, however, necessary to obtain accurate local structural details. Finally, we also find that the lattice and continuum versions of the BGY theory with the Markov closure not only show the same strengths but exhibit the same weaknesses.

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## II. THEORY

### A. The BGY equation

In this work we study a flexible linear polymer chain composed of  $n + 1$  interaction sites labeled 0 through  $n$  that are located by the set of vectors  $\{\vec{r}_0, \vec{r}_1, \dots, \vec{r}_n\}$ , with  $\vec{r}_0 = \vec{0}$ . In the lattice version of this model bonded interaction sites occupy adjacent lattice sites and the bond length equals the fixed lattice spacing  $a$ . In the continuum version the interaction sites are connected by universal joints of fixed bond length  $a$ . In either case, nonbonded sites interact via a site-site potential  $U(\vec{r}_i - \vec{r}_j)$ , where  $|i - j| > 1$ . The microscopic structure of the polymer can be described in terms of site-site probability functions.<sup>16</sup> For example, the two-site function  $p_{0n}(\vec{r}_n)d\vec{r}_n$  gives the probability that, for site 0 fixed at the origin, site  $n$  will be located within a volume  $d\vec{r}_n$  about  $\vec{r}_n$ . The analogous three-site function  $p_{0,i,n}(\vec{r}_i; \vec{r}_n)d\vec{r}_i d\vec{r}_n$  gives the probability that, for site 0 fixed at the origin, sites  $i$  and  $n$  will be similarly located about  $\vec{r}_i$  and  $\vec{r}_n$ , respectively. The two-site probability function is subject to the normalization condition

$$\int d\vec{r}_n p_{0n}(\vec{r}_n) = 1, \quad (1)$$

and the three-site functions obey the following reduction condition:

$$p_{0n}(\vec{r}_n) = \int d\vec{r}_i p_{0,i,n}(\vec{r}_i; \vec{r}_n). \quad (2)$$

Chain connectivity imposes the following boundary conditions:

$$p_{0n}(\vec{r}_n) = 0, \quad |\vec{r}_n| > na, \quad (3a)$$

$$p_{0,i,n}(\vec{r}_i; \vec{r}_n) = 0, \quad |\vec{r}_i| > ia \quad \text{or} \quad |\vec{r}_n - \vec{r}_i| > (n - i)a. \quad (3b)$$

An exact hierarchy of integrodifferential equations relating such single chain site-site probability functions can be constructed after the fashion of Born, Green, and Yvon.<sup>9,10</sup> Following Whittington and Dunfield, the BGY equation for the end-to-end probability function  $p_{0n}(\vec{r}_n)$  is

$$\vec{\nabla}_n p_{0n}(\vec{r}_n) = \int d\vec{r}_{n-1} p_{0,n-1,n}(\vec{r}_{n-1}; \vec{r}_n) \vec{\nabla}_n \ln p_{01}(\vec{r}_n - \vec{r}_{n-1}) - \sum_{i=0}^{n-2} \int d\vec{r}_i p_{0,i,n}(\vec{r}_i; \vec{r}_n) \vec{\nabla}_n [\beta U(\vec{r}_n - \vec{r}_i)], \quad (4)$$

where  $\beta = 1/k_B T$ ,  $k_B$  being the Boltzmann constant and  $T$  the temperature.<sup>11-13</sup> This BGY equation is exact, however, in order to obtain a workable theory (i.e., close the hierarchy at the two-site level) we must supply a closure approximation that expresses the three-site functions in terms of two-site functions. Here we use the Markov closure<sup>11</sup>

$$p_{0,i,n}(\vec{r}_i; \vec{r}_n) = C_n p_{0,i}(\vec{r}_i) p_{0,n-i}(\vec{r}_n - \vec{r}_i), \quad i < n, \quad (5)$$

where  $C_n$  is a constant and we define  $p_{0,0}(\vec{r}) = \delta(\vec{r})$ . This simple closure obeys the connectivity constraint of Eq. (3b) and allows for a straightforward solution to the above BGY equation for both lattice and continuum chains. The Markov closure is, in general, not exact [for example, it does not

generally satisfy the Eq. (2) reduction condition] and thus the BGY–Markov theory will yield only an approximate solution. However, the emphasis here is not on the “exactness” of the Markov closure, but is rather on how this closure preserves the universal scaling features of the solution and, more importantly, whether it preserves them in the same way for both lattice and continuum.

To make such a lattice–continuum comparison we require a comparable site–site potential  $U(\vec{r})$  for the different models. Here we consider a lattice contact potential and the analogous continuum square-well potential, both of which can be represented by

$$\beta U(\vec{r}) = \begin{cases} \infty, & |\vec{r}| < a, \\ -\beta\epsilon, & a \leq |\vec{r}| \leq \lambda a, \\ 0, & |\vec{r}| > \lambda a. \end{cases} \quad (6)$$

In the lattice case,  $a$  is the lattice spacing,  $\lambda = 1$ , and  $-\epsilon$  is the attractive contact energy. For the continuum version,  $a$  is the hard core diameter,  $\lambda a$  is the square-well diameter ( $1 \leq \lambda \leq 2$ ), and  $-\epsilon$  is the well depth.<sup>17</sup> In both cases the potential strength is used to define a reduced temperature  $T^* = 1/\beta\epsilon$ .

### B. Lattice solution

For the lattice model, an analytic solution of the BGY equation is facilitated by mapping the above contact potential onto the following delta-function pseudopotential,<sup>13</sup>

$$\beta U^{\text{pseudo}}(\vec{r}) = \frac{v}{q} \sum_{\gamma=1}^q \delta(\vec{r} - \vec{u}_\gamma), \quad (7)$$

where  $v$  is the potential strength,  $q$  is the lattice coordination number,  $\{\vec{u}_\gamma\}$  is the set of vectors connecting a lattice site to its  $q$  nearest neighbors, and volume exclusion is enforced by imposing the boundary condition  $p_{0i}(\vec{0}) = 0$  for  $i \neq 0$ . This pseudopotential applies to a Bravais lattice with equal length base vectors,  $|\vec{u}| = a$ , and, as we have shown previously,<sup>13</sup> can be related to the contact potential via the relation  $v = 2b(1 - T_\theta/T^*)$ , where  $b$  is the lattice unit cell volume and  $T_\theta$  is the lattice theta temperature, which, for the three-dimensional lattices considered here, is well approximated by  $T_\theta = 3(q - 1)/4$ .

Combining Eqs. (4), (5), and (7) leads to the following lattice BGY–Markov equation:<sup>13</sup>

$$p_{0n}(\vec{r}_n) = \frac{C_n}{q} \sum_{\gamma=1}^q \left( p_{0,n-1}(\vec{r}_n - \vec{u}_\gamma) - v \sum_{i=0}^{n-2} p_{0i}(\vec{r}_n - \vec{u}_\gamma) p_{0,n-i}(\vec{u}_\gamma) \right), \quad (8)$$

where the constant  $C_n$  is determined via the normalization condition of Eq. (1). The above equation yields the exact one bond probability function,

$$p_{01}(\vec{r}) = \frac{1}{q} \sum_{\gamma=1}^q \delta(\vec{r} - \vec{u}_\gamma), \quad (9)$$

and can be solved recursively for any value of  $n > 1$ .

### C. Continuum solution

In our continuum model of a polymer chain we assume, a spherically symmetric site-site potential,  $U(r_{ij})$ , which leads to spherically symmetric site-site probability functions, i.e.,  $p_{0n}(\vec{r}_n) = p_{0n}(r_{0n})$  and  $p_{0,i,n}(\vec{r}_i; \vec{r}_n) = p_{0,i,n}(r_{0i}, r_{0n}, r_{in})$ , where  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ . This simplification allows one to reduce the exact BGY equation [Eq. (4)] from a vector to a strictly scalar form.<sup>18</sup> Inserting the Markov closure [Eq. (5)] into Eq. (4) leads to the following three-dimensional single chain BGY–Markov equation,

$$\begin{aligned} \frac{d}{dr} p_{0n}(r) = & -p_{0n}(r) \frac{d}{dr} [\beta U(r)] + \frac{2\pi C_n}{r} \int_0^\infty ds s \frac{d}{ds} p_{01}(s) \\ & \times \int_{|r-s|}^{r+s} dt t p_{0,n-1}(t) \cos \theta \\ & - \frac{2\pi C_n}{r} \sum_{i=1}^{n-2} \int_0^\infty ds s p_{0,n-i}(s) \frac{d}{ds} [\beta U(s)] \\ & \times \int_{|r-s|}^{r+s} dt t p_{0,i}(t) \cos \theta, \end{aligned} \quad (10)$$

where  $\cos \theta = (r^2 + s^2 - t^2)/(2rs)$  and the one-bond probability function is

$$p_{01}(r) = \frac{\delta(r-a)}{4\pi a^2}. \quad (11)$$

In arriving at Eq. (10) we have taken  $C_n = 1$  in the Eq. (5)  $i=0$  Markov approximation to be consistent with our previous continuum single chain BGY studies.<sup>12</sup> In this earlier work we used a normalized superpositionlike closure, and the resulting BGY equation [Eq. (13) of Ref. 12] had to be integrated numerically over the distance  $r$ . Use of the Markov closure allows this integration to be done analytically, which leads to

$$\begin{aligned} p_{0n}(r) = & \int_r^\infty dR p_{0n}(R) \beta U'(R) + C_n B_n(r) \\ & + C_n \sum_{i=1}^{n-2} \int_0^\infty ds p_{0,n-i}(s) \beta U'(s) F_{0,i}(r, s), \end{aligned} \quad (12)$$

where the primes denote differentiation and, defining  $p_{0,i}(-t) = p_{0,i}(t)$ ,

$$B_n(r) = \frac{1}{2ar} \int_{r-a}^{r+a} dt t p_{0,n-1}(t) \quad (13)$$

and

$$F_{0,i}(r, s) = \frac{\pi}{r} \int_{r-s}^{r+s} dt t [s^2 - (r-t)^2] p_{0,i}(t). \quad (14)$$

We now specialize to the case of the square-well potential given by Eq. (6) for which the required derivative is

$$-\beta U'(r) = \delta(r-a^+) - (1 - e^{-\beta\epsilon}) \delta(r-\lambda a^-). \quad (15)$$

Inserting this result into Eq. (12) yields our final square-well chain BGY–Markov equation,

$$\begin{aligned} p_{0n}(r) = & (1 - e^{-\beta\epsilon}) p_{0n}(\lambda a^-) \Theta(r - \lambda a) + C_n B_n(r) \\ & - C_n \sum_{i=1}^{n-2} [p_{0,n-i}(a) F_{0,i}(r, a) - (1 - e^{-\beta\epsilon}) \\ & \times p_{0,n-i}(\lambda a^-) F_{0,i}(r, \lambda a)], \quad r > a, \end{aligned} \quad (16)$$

where  $p_{0n}(r) = 0$  for  $r < a$  and  $\Theta(x)$  is the Heaviside step function that is unity for  $x < 0$  and otherwise vanishes. The constant  $C_n$  is determined via the Eq. (1) normalization condition. As expected for a square-well chain, the above site-site probability function is discontinuous at the square-well boundary  $r = \lambda a$  by a factor of  $e^{\beta\epsilon}$  [i.e.,  $p_{0n}(\lambda a^-) = e^{\beta\epsilon} p_{0n}(\lambda a^+)$ ].<sup>19</sup>

### III. RESULTS

Equations (8) and (16) are the lattice and continuum versions, respectively, of our BGY–Markov theory for a self-interacting polymer chain. Here we compare the results obtained from these two equations for  $n$ -bond chains ( $n \leq 600$ ) over a wide range of reduced temperatures  $T^* = 1/\beta\epsilon$ . We also compare the integral equation results with corresponding lattice and continuum Monte Carlo (MC) simulation data. The latter have been obtained using a standard pivot algorithm,<sup>20–22</sup> as described in Refs. 13 and 23.

A solution of the single chain BGY–Markov equation yields an end-to-end probability density  $p_{0n}(\vec{r}_n)$ . For the lattice model this probability density depends on the complete set of lattice vectors  $\{\vec{r}_n\}$  and is thus rather unwieldy. Therefore, it is useful to introduce a reduced probability function  $P_n(r)$  that depends only on the distance  $r = |\vec{r}_n|$ . The lattice version of this dimensionless probability function is defined as

$$P_n(r) = a^3 \sum_{\{\vec{r}_n\}} p_n(\vec{r}_n) \delta_{|\vec{r}_n|^2, r^2}, \quad (17)$$

where the sum extends over the complete set of lattice vectors and  $\delta_{a,b}$  is the Kronecker delta function. The corresponding continuum definition of this reduced probability function is simply

$$P_n(r) = a \int d\vec{r}_n p_{0n}(\vec{r}_n) \delta(|\vec{r}_n| - r) = 4\pi a r^2 p_{0n}(r). \quad (18)$$

In Fig. 1 we show such reduced probability functions for 100 bond lattice and continuum polymer chains both in the athermal limit ( $T^* = \infty$ ) and at the temperatures corresponding to theta conditions ( $T^* \approx T_\theta$ ). The lattice is simple cubic ( $q=6, b_0=a^3, T_\theta \approx 3.7$ ) and the continuum square-well diameter is  $\lambda = 1.5$  ( $T_\theta \approx 3.1$ ). For the lattice results, rather than show the fully discrete probability function, we show a “coarse-grained” histogram version of this function. The overall shape and widths of the BGY probability functions are seen to be quite similar to the MC functions, although, in comparison with the MC results, the BGY distribution functions are shifted to a larger size for  $T^* = \infty$  and to a smaller size at the theta temperature. The theory correctly predicts that the continuum chain is larger than the lattice chain. The quality of these distribution function results is representative

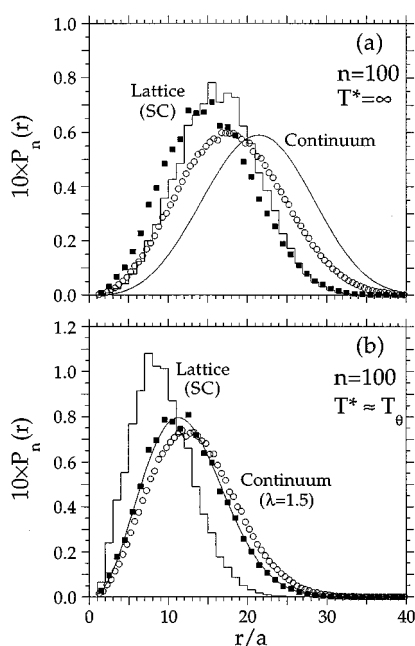


FIG. 1. End-to-end probability function  $P_n(r)$  for 100 bond lattice and continuum polymer chains at reduced temperatures (a)  $T^* = \infty$  and (b)  $T^* \approx T_\theta$ . The solid lines are the results from the BGY–Markov theory (histogram=lattice; smooth curve=continuum) while the symbols are corresponding MC simulation data ( $\blacksquare$ =lattice;  $\circ$ =continuum). The lattice is simple cubic and the continuum square-well diameter is  $\lambda = 1.5$ .

of what we obtain from the BGY–Markov theory for other temperatures, chain lengths, lattice types, and square-well diameters.

For the remainder of this section we will consider averages over such probability distribution functions. In particular, we study the mean-square end-to-end distance of a polymer chain, given by the second moment of the reduced probability function as

$$\langle R_n^2 \rangle = \sum_{r^2=a^2}^{(na)^2} r^2 P_n(r) \quad (\text{lattice}), \quad (19a)$$

$$\langle R_n^2 \rangle = \frac{1}{a} \int dr r^2 P_n(r) \quad (\text{continuum}). \quad (19b)$$

We first discuss the behavior of  $\langle R_n^2 \rangle$  for self-avoiding polymers without a site–site attractive potential ( $\beta\epsilon = 0$ ) and then we consider the general case of self-avoiding, self-interacting polymers ( $\beta\epsilon > 0$ ).

### A. Self-avoiding chains ( $\beta\epsilon = 0$ )

In the athermal limit, i.e.,  $T^* = 1/\beta\epsilon = \infty$ , our model for a polymer on a lattice reduces to a self-avoiding walk and our continuum model reduces to a tangent-hard-sphere chain. In Fig. 2 we show the mean-square end-to-end separation as a function of chain length  $n$  for such self-avoiding polymers. In comparison with the MC data, both the lattice and continuum BGY–Markov theories are seen to overestimate the size of a self-avoiding polymer for large  $n$ . This overestimation is more severe in the continuum model. However, the straight-line behavior of the BGY–Markov results in this log–log plot indicates a power law scaling of the chain size

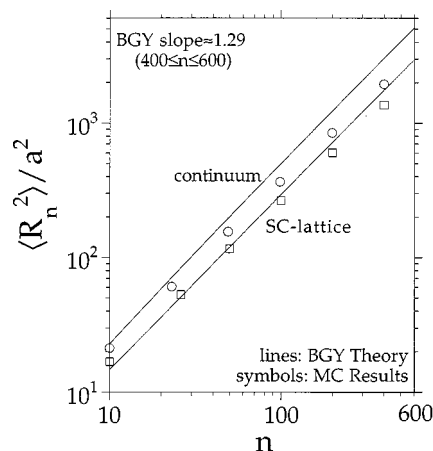


FIG. 2. Mean-square end-to-end separation  $\langle R_n^2 \rangle$  versus the chain length  $n$  for lattice (simple cubic) and continuum chains in the athermal limit (i.e.,  $T^* = \infty$ ). In this limit the lattice polymer is a self-avoiding walk while the continuum polymer is a tangent-hard-sphere chain. The solid lines are the BGY–Markov results while the symbols are corresponding MC simulation data ( $\square$ =lattice;  $\circ$ =continuum). The scaling exponent  $2\nu$  is given approximately by the slopes of these lines.

with length, i.e.,  $\langle R_n^2 \rangle \sim n^{2\nu}$ , as expected for athermal polymers. The scaling exponent, as given by the slopes of the lines in this figure, is found to be approximately  $2\nu \approx 1.29$  for both the lattice and continuum results.

A more careful calculation of this exponent is provided by considering the asymptotic behavior of the following effective exponent:

$$2\nu(n) = \frac{\ln[\langle R_n^2 \rangle / \langle R_{n-1}^2 \rangle]}{\ln[n/(n-1)]}. \quad (20)$$

In Fig. 3 we plot the BGY–Markov results for this effective exponent versus  $1/n$ . Quadratic extrapolation of these data give limiting  $n \rightarrow \infty$  exponents of  $2\nu = 1.280$  and  $1.281$  for the lattice and continuum models, respectively. [If we also include our BGY results for the  $q = 8$  body-centered and  $q = 12$  face-centered cubic lattices, we arrive at an exponent of  $2\nu = 1.279(2)$ , where the number in parentheses indicates the uncertainty in the last digit shown associated with the

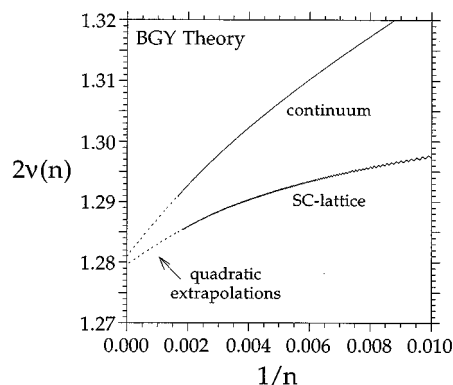


FIG. 3. Effective  $\langle R_n^2 \rangle$  scaling exponent  $2\nu(n)$  vs  $1/n$  for  $n$ -bond lattice (simple cubic) and continuum chains in the athermal limit (i.e.,  $T^* = \infty$ ). The solid lines are the BGY–Markov results while the dashed lines show quadratic extrapolations of these data. The  $n \rightarrow \infty$  scaling exponents are found to be  $2\nu = 1.280$  (lattice) and  $1.281$  (continuum).



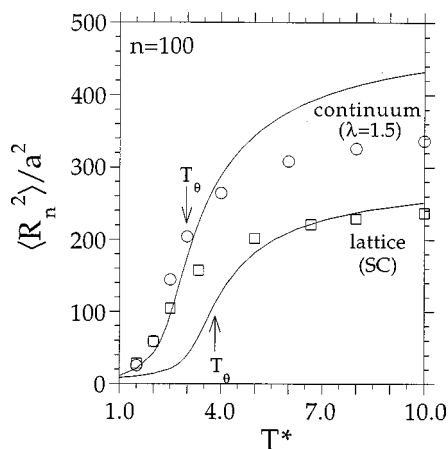


FIG. 4. Mean-square end-to-end distance  $\langle R_n^2 \rangle$  versus reduced temperature  $T^*$  for 100 bond lattice and continuum polymers. The lattice is simple cubic and the continuum square-well diameter is  $\lambda=1.5$ . The solid lines are the BGY–Markov results while the symbols are corresponding MC simulation data ( $\square$ =lattice;  $\circ$ =continuum). The vertical arrows locate the lattice and continuum theta temperatures.

variance between models.] This calculated exponent exceeds the accepted correct value of  $2\nu=1.175(1)^{20}$  due to the approximate closure in the integral equation theory. However, the fact that the computed lattice and continuum exponents are essentially identical indicates that the BGY–Markov theory correctly preserves the universality of this exponent.

Another such universal quantity, at least for self-avoiding walks on a lattice,<sup>20</sup> is the ratio of the mean-square end-to-end distance to radius of gyration. The radius of gyration is defined as

$$\langle S_n^2 \rangle = \frac{1}{(n+1)^2} \sum_{i,j} \langle r_{ij}^2 \rangle \approx \frac{1}{(n+1)^2} \sum_{i=1}^n (n+1-i) \langle R_i^2 \rangle, \quad (21)$$

where  $\langle r_{ij}^2 \rangle$  is the mean-square distance between chain sites  $i$  and  $j$ . Although we cannot directly determine the intrachain distances  $\langle r_{ij}^2 \rangle$  from the end-to-end function  $p_n(\vec{r}_n)$ , we can estimate these distances using the approximation  $\langle r_{ij}^2 \rangle \approx \langle R_{|i-j|}^2 \rangle$ , which leads to the final expression given above. This latter approximation will slightly underestimate  $\langle S_n^2 \rangle$ , however, the error incurred in the lattice and continuum models is comparable. The BGY–Markov results for  $\langle R_n^2 \rangle / \langle S_n^2 \rangle$  do indeed approach very similar limiting values for large  $n$  in both the lattice and continuum models. An  $n \rightarrow \infty$  extrapolation of  $\langle R_n^2 \rangle / \langle S_n^2 \rangle$  vs  $1/n$  yields an asymptotic ratio of 7.49(1) for the lattice and continuum models. Once again, although this computed ratio exceeds the “true” asymptotic value [6.26(2)]<sup>21</sup> due to both the closure and  $\langle S_n^2 \rangle$  approximations, the theory does preserve the universality of this ratio.

### B. Self-interacting chains ( $\beta\epsilon>0$ )

In Fig. 4 we show both BGY–Markov and MC results for the temperature dependence of the mean-square end-to-end distance of self-interacting lattice and continuum polymers. These  $\langle R_n^2 \rangle$  vs  $T^*$  curves are sigmoidal in shape, characteristic of a collapse transition. At high temperatures the

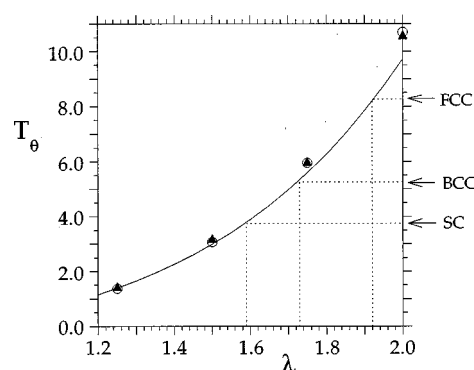


FIG. 5. Theta-temperature  $T_\theta$  versus square-well diameter  $\lambda$  for continuum square-well chains. The solid line is the result of the BGY–Markov theory, the open symbols are MC data (Ref. 24), and the filled symbols are results of a previous version of the single chain continuum BGY theory (Ref. 12). The dotted lines locate the theta temperatures (and associated square-well diameters) for self-interacting chains on the simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) lattices.

chain size approaches the fully expanded athermal self-avoiding-chain limit. With decreasing temperature the chains become increasingly compact and a rapid falloff in chain size is observed in the vicinity of the theta temperature. At low temperatures the chain size approaches a fully collapsed limit. In comparison with the MC data, the BGY–Markov theory yields qualitatively correct  $\langle R_n^2 \rangle$  vs  $T^*$  behavior, although, in general, the lattice theory is quantitatively more accurate at high temperatures while the continuum theory is more accurate in the vicinity of the theta temperature. Both theories slightly underestimate the chain size at low temperatures and suggest that lattice and continuum chains possess similar limiting low-temperature sizes, in agreement with the MC data.

The variation of  $\langle R_n^2 \rangle$  with temperature and chain length can be used to locate the theta temperature  $T_\theta$  for a single polymer chain. By definition, at  $T_\theta$  the chain size exhibits ideal or random-walk scaling ( $\langle R_n^2 \rangle \sim n$  or  $2\nu_\theta=1$ ) and thus by analyzing the temperature dependence of the scaling exponent  $2\nu(T^*)$  one can determine  $T_\theta$ . Results from such an analysis for  $T_\theta$  of square-well chains using our BGY–Markov theory are shown in Fig. 5. Also included in this figure are MC data<sup>24</sup> and results from our previous continuum BGY calculation, which utilized a more complicated closure. The simple continuum BGY–Markov theory is seen to give quite accurate results for the square-well chain  $T_\theta$  values, especially for  $\lambda \leq 1.5$ . We note that in the lattice version of our BGY–Markov theory, values of  $T_\theta$  have been “put into the theory” by our introduction of the Eq. (7) pseudopotential, and thus we do not predict this quantity. However, the self-consistency of the lattice theory is verified by the fact that the above scaling analysis recovers the input values of  $T_\theta$ . In Fig. 5 we have located the  $T_\theta$  values for various three-dimensional lattices and suggestively indicate the square-well diameters corresponding to these lattice  $T_\theta$  values. The theta temperature provides one possible mapping between lattice and continuum models, as one can draw a correspondence between a lattice type and a continuum

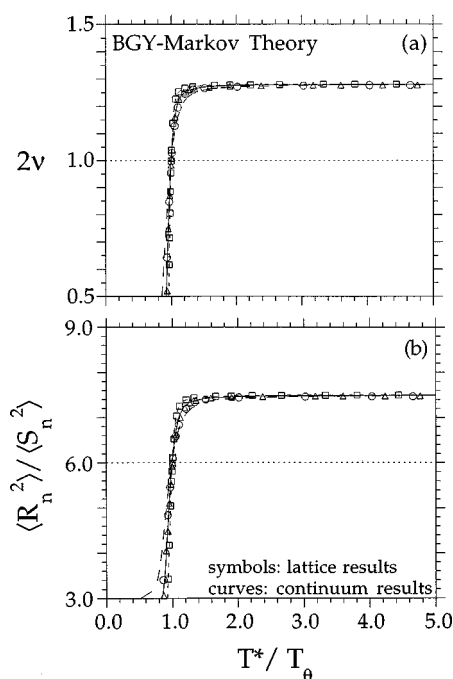


FIG. 6. BGY-Markov results (extrapolated to  $n \rightarrow \infty$ ) for the (a) scaling exponent  $2\nu$  and (b) size ratio  $\langle R_n^2 \rangle / \langle S_n^2 \rangle$  versus reduced temperature  $T^*/T_\theta$  for lattice and continuum polymers. The symbols are results for the simple cubic ( $\square$ ), body-centered cubic ( $\triangle$ ), and face-centered cubic ( $\circ$ ) lattices and the curves are results for square-well chains with well diameters  $\lambda = 1.25$  (---),  $1.5$  (—), and  $2.0$  (---). The dotted lines locate the ideal or random walk values expected at  $T^* = T_\theta$ .

square-well diameter yielding the same value of  $T_\theta$  (e.g., simple cubic  $\leftrightarrow \lambda = 1.59$ ;  $T_\theta = 3.7$ ).

At  $T^* = T_\theta$  the rate of change of  $\langle R_n^2 \rangle$  vs  $T^*$  (i.e.,  $\partial \langle R_n^2 \rangle / \partial T^*$ ) is expected to scale with the chain length as  $n^{2\nu_\theta + \phi_t} [\ln(n)]^{-4/11}$ , where  $\phi_t$  is the tricritical crossover exponent.<sup>20,25</sup> By considering the  $n \rightarrow \infty$  behavior of the ratio approximant  $\phi_t(n)$  [defined similarly to  $2\nu(n)$  in Eq. (20)] we find an asymptotic exponent of  $\phi_t = 0.55(7)$  for the lattice and continuum models. The correct value for this exponent is  $\phi_t = \frac{1}{2}$ .<sup>26</sup>

In addition to exhibiting universal behavior in the athermal limit, the scaling exponent  $2\nu$  and size ratio  $\langle R_n^2 \rangle / \langle S_n^2 \rangle$  also display a universal temperature dependence for both lattice and continuum polymers. We find that our integral equation results for  $2\nu$  or  $\langle R_n^2 \rangle / \langle S_n^2 \rangle$ , when plotted against the reduced temperature  $T^*/T_\theta$ , fall on master scaling curves independent of model details. In Fig. 6 we construct such scaling plots with results (extrapolated to  $n \rightarrow \infty$ ) from our BGY-Markov lattice and continuum theories. In this figure we include data for self-interacting chains on the simple cubic, body-centered cubic ( $q=8, b=4a^3/3^{3/2}$ ), and face-centered cubic lattices ( $q=12, b=a^3/2^{1/2}$ ) and for square-well chains with well diameters  $\lambda = 1.25, 1.5$ , and  $2.0$ . As seen in the figure, both the lattice and continuum BGY data all collapse onto single master curves, which, at  $T^* = T_\theta$ , give the correct random walk values of  $2\nu = 1$  and  $\langle R_n^2 \rangle / \langle S_n^2 \rangle \approx 6$ . Although such master curve behavior has been previously observed in simulation studies of lattice polymers,<sup>27</sup> here we predict that such universal behavior ex-

tends to continuum results as well. Finally, we note that for  $T^* < T_\theta$ , the BGY-Markov theory yields “overcollapsed” chain dimensions in both the lattice and continuum models. That is, the size exponent  $2\nu$  falls below the expected collapsed state value of  $\frac{2}{3}$ . Thus, while the BGY-Markov theory correctly predicts the same universal behavior for the collapse transition of both lattice and continuum polymers, it also gives the same, incorrect, low-temperature overcollapse for both models.

#### IV. DISCUSSION

The results presented here are but a first attempt to unravel some of the ambiguities to be found in comparing lattice and continuum models for complex fluid systems. Currently, differences arising from the choice of model and the theoretical approximations employed are intertwined. Here we use the same theoretical approach with the same set of approximations to study both a lattice and continuum model of a polymer chain. As expected, local structural details and absolute chain dimensions are completely model dependent and thus one can conclude that continuum models are necessary to accurately describe such local details in real systems. However, the model-independent scaling behavior expected for long chain molecules is preserved by the approximate integral equation theory. More to the point, the theory predicts exactly the same scaling relationships for both the lattice and continuum models. The universal quantities predicted here are not quantitatively exact due to the approximations made in the theoretical formalism. However, the degree of inaccuracy introduced by these approximations is found to be identical for all models studied, be they continuum or lattice. This finding has implications for the use of lattice and continuum models in the description of much more complicated systems. In particular, since the single chain collapse transition is closely related to polymer solution phase separation,<sup>15</sup> the results obtained here indicate that an approximate integral equation theory for a lattice polymer solution should be sufficient to capture many of the important details of polymer phase separation. Finally, these results suggest that a more accurate closure relationship developed for a continuum model may be transferable to the comparable lattice model, and *visa versa*. This observation could prove useful in the development of more accurate theories.

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