

Collapse of a polymer chain: A Born–Green–Yvon integral equation study

Mark P. Taylor and J. E. G. Lipson

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

(Received 13 November 1995; accepted 21 December 1995)

A Born–Green–Yvon (BGY) type integral equation is developed for the intramolecular distribution functions of an isolated flexible polymer chain. The polymer is modeled as a linear array of n identical spherical interaction sites connected by universal joints of bond length σ . In particular we study chains composed of up to $n=400$ square-well spheres with hard-core diameters σ and well diameters $\lambda\sigma$ ($1 \leq \lambda \leq 2$). Intramolecular distribution functions and the resulting average configurational and energetic properties are computed over a wide range of temperatures. In the high temperature (good solvent) limit this model is identical to the tangent hard-sphere chain. With decreasing temperature (worsening solvent) the square-well chain undergoes a collapse transition identified by a sudden reduction in chain dimensions and a peak in the single chain specific heat. Extensive comparison is made between the BGY results and Monte Carlo results for square-well chains with $\lambda=1.5$. The BGY theory is extremely accurate for square-well 4-mers at all temperatures. For longer chains the theory yields reasonably accurate results for reduced temperatures greater than $T^* \approx 1$ (expanded and theta states) and qualitatively correct behavior for $T^* < 1$ (collapsed state). Very accurate values for the theta temperatures for square-well chains with $1.25 \leq \lambda \leq 2.0$ are also obtained. © 1996 American Institute of Physics. [S0021-9606(96)51212-9]

I. INTRODUCTION

The conformation of a polymer molecule in dilute solution is generally classified as being expanded, compact, or ideal and the corresponding solvent conditions are termed good, poor, or theta.^{1–3} In the ideal, or theta, state long-range excluded volume forces, which tend to expand the polymer, are exactly balanced by short-range attractive forces, which tend to compress the polymer, and thus the metric properties of the polymer are identical to those of a random walk (e.g., the average size of the polymer molecule R scales with the polymer length n as $R^2 \sim n^{2\nu}$ where $2\nu=1$). When the repulsive excluded volume forces dominate the polymer is expanded relative to the ideal state ($2\nu>1$) and when the short-range attractions dominate the polymer is compact with respect to this state ($2\nu<1$). Transitions between these three conformational states are observed when appropriate changes are made to the solution conditions. In particular, a transition from the expanded to the compact state is known as the coil-globule or collapse transition. This transition has been observed in several synthetic polymer/solvent systems^{4–11} and is relevant to biological polymers as, in many cases, the initial stage of protein folding (or refolding) is thought to be a transition of the coil-globule type.^{3,12}

The collapse transition of a polymer is in many ways analogous to the condensation transition observed in a simple fluid. A large macromolecule can be viewed as a small system of simple fluid monomers with bonding constraints and the techniques of liquid state theory can be applied to study the structure and thermodynamics of a single chain molecule.^{13–16} In this approach the site–site potential between monomers in the chain is generally assumed to be an effective potential which implicitly includes the effects of a continuum solvent. For such an interaction-site chain good and poor solvent conditions correspond to high and low tem-

peratures, respectively. The collapse of an isolated interaction-site chain has been the focus of several recent theoretical investigations. In particular, Gan and Eu studied the collapse of Lennard-Jones chains using a Kirkwood integral equation¹⁶ and Taylor has obtained exact results for the collapse of very short square-well chains.¹⁷ Simulation studies of this transition have considered chain molecules interacting via both realistic atomistic potentials^{18,19} and simple-fluid-monomer site–site potentials including the Lennard-Jones,^{20–22} Morse,²³ and square-well potentials.²⁴

Here we construct a Born–Green–Yvon (BGY) type integral equation for the site–site intramolecular distribution functions of a linear homopolymer and use this equation to study the collapse of an isolated square-well-sphere chain. We compute distribution functions and associated configurational and energetic quantities for chains of length up to $n=400$ over a wide range of temperatures. Detailed comparisons are made between our integral equation theory and recent computer simulation results for the mean-square radius of gyration, average energy, and single chain specific heat for square-well chains with a well diameter of $\lambda=1.5$. In the high temperature (good solvent) limit our model is identical to a tangent hard-sphere chain and the BGY theory yields a scaling exponent of $2\nu=1.31$, in reasonable accord with Monte Carlo results and with Flory's value of $6/5$. With decreasing temperature (worsening solvent) the square-well chain undergoes a collapse transition; this is signaled by a sudden reduction in the chain dimensions and the appearance of a peak in the single chain specific heat. In the collapsed state the intramolecular distribution functions display short-range local structure similar to that of a simple liquid. The theta state, which is intermediate between the high temperature expanded and low temperature collapsed states, is located by a scaling exponent of $2\nu=1$. Using this criteria, we

obtain very accurate values of the theta temperatures for square-well chains with $1.25 \leq \lambda \leq 2.0$.

II. THEORY

A. Intramolecular distribution functions

In this work we study an isolated linear polymer molecule which is modeled as a flexible chain of n identical simple fluid monomers. These monomers, or interaction sites, are connected by "universal joints" of bond length σ and interact via a spherically symmetric site-site potential $u_{ij}(r)$ where r is the distance between nonbonded sites i and j (i.e., $|i-j| > 1$). The intramolecular distribution function between such sites i and j is given by

$$w_{ij}(r, T) = \frac{1}{Z_n(T)} \int \cdots \int \prod_{a=1}^{n-2} \prod_{b=a+2}^n \exp(-\beta u_{ab}) \times \prod_{\alpha=1}^{n-1} s_{\alpha, \alpha+1} \prod_{m \neq i, j}^n d\mathbf{r}_m, \quad (1)$$

where $\beta = 1/k_B T$, $s(r) = \delta(r - \sigma)/4\pi\sigma^2$ is the intramolecular distribution function between bonded sites, and $Z_n(T)$ is the single chain partition function, which ensures the normalization condition

$$\int d\mathbf{r} 4\pi r^2 w_{ij}(r, T) = 1. \quad (2)$$

Due to the constraints of chain connectivity the $w_{ij}(r, T)$ functions are identically zero for $r > |i-j|\sigma$. In the case of noninteracting monomers ($u_{ij} = 0$) this model reduces to the freely jointed chain and Eq. (1) can be evaluated analytically for an arbitrary value of n .²⁵ For more realistic site-site potentials exact evaluation of Eq. (1) is difficult and generally only possible for very short chains (i.e., $n=3$ and 4). In the case of 3-mers the exact end-to-end distribution function can be determined for an arbitrary site-site potential and is found to be

$$w_{13}(r, T) = \frac{1}{Z_3(T)} \frac{e^{-\beta u(r)}}{8\pi\sigma^2 r}, \quad 0 \leq r \leq 2\sigma. \quad (3)$$

For chains with a length of four, exact results have only been obtained for the hard-sphere²⁶ and square-well potentials.¹⁷ For chains longer than four, exact evaluation of Eq. (1) is generally not feasible and one must resort either to Monte Carlo methods of solution or other approximate approaches such as the integral equation theory developed here.

From the intramolecular distribution functions one can compute average configurational and energetic properties of the isolated chain molecule. In particular, the mean-square distance between sites i and j is

$$\langle r_{ij}(T)^2 \rangle = 4\pi \int d\mathbf{r} r^4 w_{ij}(r, T) \quad (4)$$

and the mean-square radius of gyration is

$$\langle R_g(T)^2 \rangle = \frac{1}{n^2} \sum_{i < j}^n \langle r_{ij}(T)^2 \rangle. \quad (5)$$

Similarly, the average energy of the isolated chain molecule is

$$\langle E(T) \rangle = 4\pi \int d\mathbf{r} r^2 \sum_{i=1}^{n-2} \sum_{j=i+2}^n u_{ij}(r) w_{ij}(r, T) \quad (6)$$

and the single chain specific heat is

$$C_v(T) = \frac{d\langle E(T) \rangle}{dT}. \quad (7)$$

B. The BGY equation

An integral equation theory for the intramolecular distribution functions of an isolated chain molecule can be constructed following the general approach of Born, Green, and Yvon.^{27,28} Taking the translational gradient of the end-to-end distribution function w_{1n} [Eq. (1), $i=1, j=n$] with respect to site "1" yields the following single chain BGY equation:

$$\nabla_1 w_{1n} = \nabla_1 [-\beta u_{1n}] w_{1n} + \int d\mathbf{r}_2 \nabla_1 [\ln s_{12}] w_{12n} + \sum_{\nu=3}^{n-1} \int d\mathbf{r}_\nu \nabla_1 [-\beta u_{1\nu}] w_{1\nu n}, \quad (8)$$

where $w_{1\nu n}$ is the three-site distribution function which satisfies the reduction condition

$$w_{1n} = \int d\mathbf{r}_\nu w_{1\nu n}. \quad (9)$$

This single chain BGY equation was originally derived by Whittington and Dunfield²⁹ and is equivalent to the terminal site version of Attard's intramolecular BGY equation in the zero density limit.³⁰ Equation (8) differs from our own previously derived *intermolecular* BGY equation in that the latter was developed from a molecular (as opposed to site) point of view and contains additional terms involving four-site correlations.³¹

Although Eq. (8) is exact, it is not immediately useful as it expresses the desired two-site distribution function in terms of a set of three-site functions. In order to achieve a closed theory we must express these three-site distribution functions in terms of the two-site functions. For chains having a length of three this can be done exactly:

$$w_{123} = \frac{1}{Z_3} s_{12} s_{23} e^{-\beta u_{13}} = \frac{w_{12} w_{23} w_{13}}{\int d\mathbf{r}_2 w_{12} w_{23}}, \quad r_{13} \leq 2\sigma. \quad (10)$$

For longer chains Attard has suggested the asymptotic behavior $w_{1\nu n} \propto w_{1\nu} w_{\nu n}$ when r_{1n} is greater than some cross-over distance r^* .³⁰ This form is reminiscent of the exact closure for rigid rods in one dimension³² and is identical to the Markov approximation used by Whittington and Dunfield.²⁹ In this work we assume the following superpositionlike decomposition of the three-site function which provides an interpolation between the above two functional forms:

$$w_{1\nu n} = w_{1\nu} w_{\nu n} \Gamma_{1(\nu)n}(r_{1n}), \quad 1 < \nu < n, \quad (11)$$

where

$$\Gamma_{1(\nu)n}(r_{1n}) = \begin{cases} \frac{A_n w_{1n}(r_{1n})}{\int d\mathbf{r}_\nu w_{1\nu} w_{\nu n}}, & r_{1n} \leq r^*, \\ \Gamma_{1(\nu)n}(r^*), & r_{1n} > r^*, \end{cases} \quad (12)$$

and A_n is a constant of $O(1)$ which ensures that the BGY solution for $w_{1n}(r)$ is continuous at $r=r^*$. We assume that the crossover distance r^* is on the order of the range of direct interaction between three sites and thus, for the numerical results presented here, we have taken $r^*=3\sigma$. Substitution of this superposition approximation [Eqs. (11) and (12)] into the above BGY equation [Eq. (8)] yields, after some manipulation,^{30,33}

$$\begin{aligned} w'_{1n}(r) = & -\beta u'(r) w_{1n}(r) - \frac{1}{2} \Gamma_{1(2)n}(r) \left(\frac{r-\sigma}{r\sigma} w_{2n}(r-\sigma) \right. \\ & - \frac{r+\sigma}{r\sigma} w_{2n}(r+\sigma) + \frac{1}{r^2\sigma} \int_{r-\sigma}^{r+\sigma} dt t w_{2n}(t) \Big) \\ & + \frac{\pi}{r^2} \sum_{\nu=3}^{n-1} \Gamma_{1(\nu)n}(r) \int_0^\infty ds [-\beta u'(s)] w_{1\nu}(s) \\ & \times \int_{|r-s|}^{r+s} dt t (r^2 + s^2 - t^2) w_{\nu n}(t), \end{aligned} \quad (13)$$

where the primes denote differentiation and $w_{1n}(r)=0$ for $r > (n-1)\sigma$. Solution of the above equation requires knowledge of the set of functions $w_{1\nu}$ and $w_{\nu n}$ for $2 \leq \nu \leq n-1$. In order to achieve a tractable integral equation theory we will assume that the functions $w_{1\nu}$ and $w_{\nu n}$ can be approximated by the end-to-end distribution functions of chains of length ν and $n-\nu+1$, respectively. This latter approximation is analogous to the commonly invoked assumption of translational invariance of the intramolecular distribution functions.¹⁶ The above equation is exact for chains having a length of three and can be solved for a chain of arbitrary length using a recursive approach (i.e., one sequentially solves for w_{13} , w_{14} , w_{15} , etc.). For each value of n the corresponding BGY equation is readily solved by direct numerical integration.

III. RESULTS FOR A SQUARE-WELL CHAIN

The above single chain BGY equation is valid for an arbitrary site-site potential. Here we restrict ourselves to the square-well potential

$$\beta u(r) = \begin{cases} \infty, & r < \sigma, \\ -\beta\epsilon, & \sigma < r < \lambda\sigma, \\ 0, & r > \lambda\sigma, \end{cases} \quad (14)$$

where σ is the hard core diameter (identical to the bond length), $\lambda\sigma$ is the square-well diameter ($1 \leq \lambda \leq 2$), and $-\epsilon$ is the well depth (which is used to define a reduced temperature $T^*=1/\beta\epsilon$). The derivative of the square-well potential, required in Eq. (13), is given by

$$-\beta u'(r) = \delta(r-\sigma^+) - (1 - e^{-\beta\epsilon}) \delta(r-\lambda\sigma^-), \quad (15)$$

where $\delta(r)$ is the Dirac delta function. In the limit of $\lambda \rightarrow 1$ or $\epsilon \rightarrow 0$ ($T^* \rightarrow \infty$) this model reduces to a tangent hard-sphere chain.

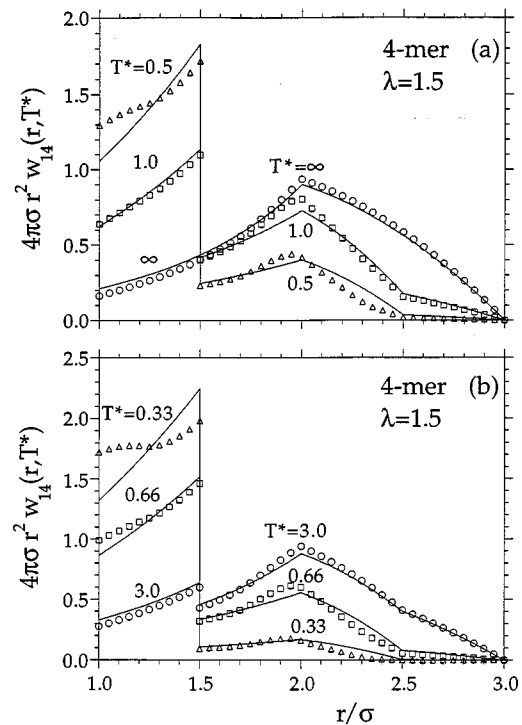


FIG. 1. End-to-end probability distribution function, $4\pi\sigma r^2 w_{14}(r, T^*)$, for a square-well 4-mer with well diameter $\lambda=1.5$ for a range of reduced temperatures T^* as indicated. The solid lines are results from the present BGY theory while the symbols are the corresponding exact results (Ref. 17). These functions are discontinuous at the square-well boundary ($r=\lambda\sigma$) by a factor of e^{1/T^*} .

A. Intramolecular distribution functions

The intramolecular distribution functions of the square-well chain possess a number of distinctive features which reflect the discontinuous nature of the square-well potential.¹⁷ In particular, these functions are identically zero for $r < \sigma$ and are discontinuous at the hard-sphere and square-well boundaries (i.e., $r=\sigma$ and $r=\lambda\sigma$, respectively). The magnitude of the discontinuity at $r=\lambda\sigma$ is e^{1/T^*} [i.e., $w(\lambda\sigma^-) = e^{1/T^*} w(\lambda\sigma^+)$]. These functions also display slope discontinuities at a distance equal to the bond length plus the hard-sphere diameter (i.e., $r=2\sigma$) and at a distance equal to the bond length plus the square-well diameter (i.e., $r=\sigma + \lambda\sigma$).

As noted above, the single chain BGY equation given here [Eq. (13)] is exact for chains having a length of three. In the case of square-well 3-mers the exact end-to-end distribution function is given by Eq. (3) with $Z_3(T^*) = 3/4 + (\lambda^2 - 1)(e^{1/T^*} - 1)/4$. In the case of square-well 4-mers a closed form analytic expression for the end-to-end distribution function is also readily obtained from Eq. (13). In Fig. 1 we show the BGY results for the end-to-end probability distribution function for a square-well 4-mer with $\lambda=1.5$, along with the corresponding exact results, over a wide range of reduced temperatures. The BGY theory is seen to be very accurate for this short chain length with the only significant deviations from the exact results appearing at low

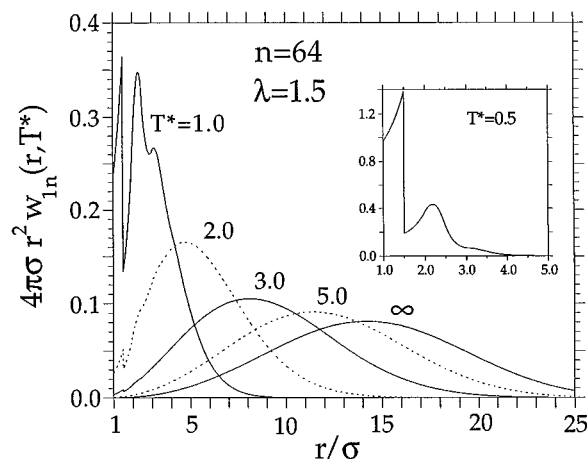


FIG. 2. BGY results for the end-to-end probability distribution function, $4\pi\sigma r^2 w_{1n}(r, T^*)$, for a square-well chain of length $n=64$ with well diameter $\lambda=1.5$ for a range of reduced temperatures T^* as indicated.

temperatures and within the square well (i.e., $T^* \leq 0.5$ and $r \leq \lambda\sigma$). With decreasing temperature the 4-mer end-to-end distribution function increases for $r < \lambda\sigma$ while decreasing for $r > \lambda\sigma$. This shift in the distribution function demonstrates the collapse of the polymer chain as the probability for compact chain conformations (with square-well overlaps) increases and the corresponding probability for extended chain conformations (without square-well overlaps) decreases. We note that the BGY theory yields similarly accurate 4-mer results for other values of the square-well diameter λ .

For chains longer than four sites obtaining analytic solutions for $w_{1n}(r, T^*)$ becomes cumbersome and thus we carry out a straightforward numerical solution of Eq. (13). In Fig. 2 we show the end-to-end probability distribution function for a square-well 64-mer with $\lambda=1.5$ for a range of reduced temperatures. A rather dramatic chain collapse with decreasing temperature is evident from these intramolecular distribution functions. At high temperatures ($T^* \geq 10$) the distribution is a smooth function with a maximum at $r \approx \langle r_{1n}^2 \rangle^{1/2} \approx 15\sigma$. With decreasing temperature the peak position of the distribution function moves to smaller r values and the distribution narrows as the overall size of the chain is compressed. At $T^* \approx 3.0$ an initial buildup of configurations possessing square-well overlaps becomes apparent indicating the onset of the chain collapse while for $T^* < 2.0$ the distribution function begins to display well-defined short-range features indicating a local fluidlike structure in the collapsing chain.

B. Average configurational and energetic properties

From the intramolecular distribution functions computed above we can determine average configurational and energetic properties of the square-well chain molecule. These average quantities provide a concise picture of the collapse transition. In Fig. 3 we show the mean-square radius of gyration $\langle R_g^2 \rangle$ [Eq. (5)] divided by chain length n as a function

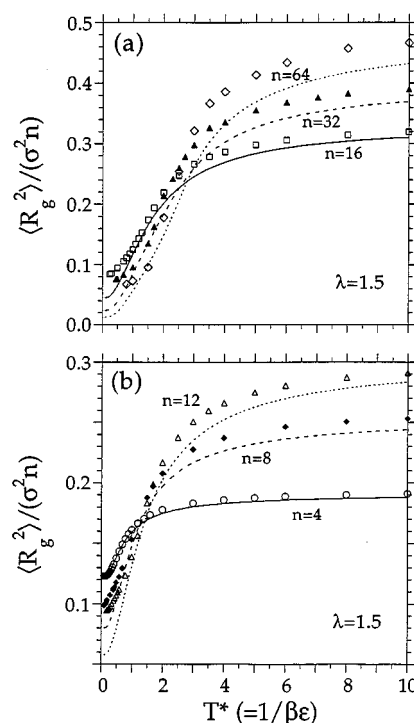


FIG. 3. Scaled mean-square radius of gyration $\langle R_g^2 \rangle / n\sigma^2$ as a function of reduced temperature T^* for square-well n -mers ($4 \leq n \leq 64$ as indicated) with well diameter $\lambda=1.5$. The solid and dashed lines are the results from the present BGY theory while the symbols are the corresponding exact results for $n=4$ (\circ) (Ref. 17) and Monte Carlo results of Zhou *et al.* (Ref. 24) for $n=8$ (\diamond), 12 (\triangle), 16 (\square), 32 (\blacktriangle), and 64 (\diamond). The crossing of the $n=32$ and 64 curves at $T^* \approx 3$ approximately locates the theta temperature.

of reduced temperature T^* for square-well n -mers with $4 \leq n \leq 64$ and well diameter $\lambda=1.5$. For high temperatures (i.e., $T^* \geq 10$) the square-well chain is in the expanded state and its configurational properties are essentially those of the corresponding hard-sphere chain. As the temperature is reduced below $T^*=10$ there is an initial slow decrease in the average size of the chain followed by a more rapid reduction in $\langle R_g^2 \rangle$, indicating the onset of the collapse transition, around $T^* \approx 1 \rightarrow 3$. With increasing chain length the fall off in $\langle R_g^2 \rangle$ becomes steeper and the transition region appears to sharpen. As the temperature is further reduced below $T^*=1$ the chains rapidly achieve a completely collapsed state. The BGY results for chains of length four are seen to be very accurate in comparison with the exact results. For longer chains, comparison with the simulation data included in Fig. 3 shows that, although the BGY theory underestimates $\langle R_g^2 \rangle$, it gives a qualitatively correct description of the configurational properties of square-well n -mers across the full range of temperatures. We note that at very low temperatures, where the chains are in the fully collapsed state, the BGY theory yields unphysically small chain dimensions for $n \geq 16$.

Corresponding plots of the average energy per monomer $\langle E \rangle / n$ [Eq. (6)] for square-well n -mers are shown in Fig. 4. As with the radius of gyration, the average energy exhibits an initial gradual decline with decreasing temperature fol-

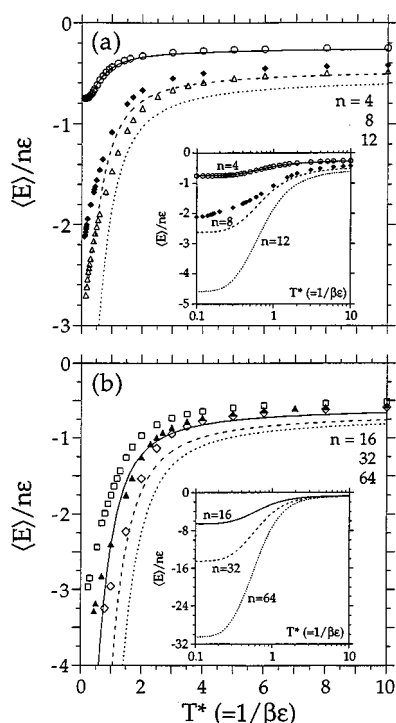


FIG. 4. Average energy per site $\langle E \rangle / n\epsilon$ as a function of reduced temperature T^* for square-well n -mers ($4 \leq n \leq 64$ as indicated) with well diameter $\lambda = 1.5$. The solid and dashed lines are the results from the present BGY theory while the symbols are the corresponding exact results for $n=4$ (\circ) (Ref. 17) and Monte Carlo results of Zhou *et al.* (Ref. 24) for $n=8$ (\blacklozenge), 12 (\triangle), 16 (\square), 32 (\blacktriangle), and 64 (\diamond). The inset semilog plots show the asymptotic low temperature behavior of the BGY theory.

lowed by a more rapid drop around $T^* \approx 1 \rightarrow 3$. Again, the BGY results for chains of length four are seen to be very accurate. For longer chains the BGY results are qualitatively correct although comparison with simulation data shows that the theory underestimates the average energy and becomes increasingly inaccurate in the low temperature limit ($T^* < 1$). The inaccuracy in this limit is due to the unphysically small size of the fully collapsed chain predicted by the theory, as noted above. For square-well chains, the quantity $|\langle E \rangle / n\epsilon|$ is simply one-half the average number of square-well overlaps per site and thus, due to geometric constraints, should not exceed ~ 5 . The BGY theory gives a limiting result of $|\langle E \rangle / n\epsilon| \rightarrow (n-2)(n-1)/2n \approx n/2$ as $T^* \rightarrow 0$ which, for long chains, violates this geometric constraint.

The above results for chain dimensions and average energy clearly demonstrate the collapse of a square-well chain with decreasing temperature, however, the exact location of this transition is not apparent from Figs. 3 or 4. The collapse transition temperature can be defined as the temperature at which the single chain specific heat C_v [Eq. (7)] displays a maximum. A semilog plot of C_v / nk_B vs T^* is shown in Fig. 5 for square-well chains of lengths four and eight with $\lambda = 1.5$. The BGY theory gives a smooth peak in C_v through the collapse transition with a maximum at $T^* \approx 0.4$ for both $n=4$ and 8 . For longer chains ($8 < n \leq 64$) the BGY theory gives essentially the same transition temperature. In general,

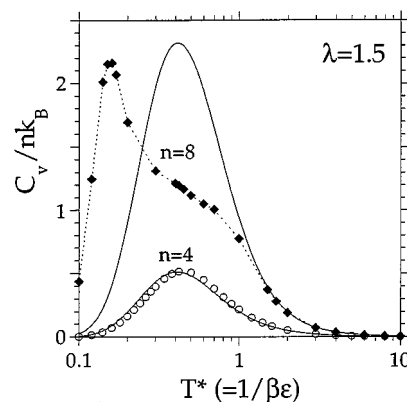


FIG. 5. Specific heat per site C_v / nk_B as a function of reduced temperature T^* for square-well 4-mers and 8-mers with well diameter $\lambda = 1.5$. The solid lines are the results from the present BGY theory while the symbols are the corresponding exact results for $n=4$ (\circ) (Ref. 17) and Monte Carlo results of Zhou *et al.* (Ref. 24) for $n=8$ (\blacklozenge). (The dashed line is meant only as a guide for the eye).

the predicted collapse transition temperatures for square-well chains are nearly independent of chain length n and increase monotonically with well diameter λ . As expected, the BGY results for C_v are in very good agreement with the exact results for the case of $n=4$. For $n=8$, the BGY and simulation results are in quantitative agreement for $T^* \geq 1$, however, for $T^* < 1$ they are seen to be markedly different. The Monte Carlo results display a much broader peak in C_v with a shoulder nearly coincident with the BGY peak at $T^* \approx 0.4$ and a sharp low temperature maximum at $T^* \approx 0.16$. A similar complex structure in C_v is observed in the simulation results for square-well chains with $\lambda = 1.5$ for $6 \leq n \leq 64$ and has been interpreted as evidence for a multistage collapse transition.²⁴

C. Flory exponent and theta temperatures

As noted in Sec. I, the conformation of an isolated polymer molecule in solution can be considered to be expanded, ideal, or collapsed. These three states are distinguished by how the average size of the polymer R (e.g., mean end-to-end distance or radius of gyration), scales with the polymer length n . For long flexible chains the scaling relationship $R^2 \sim n^{2\nu}$ generally holds true and the expanded and compact states are characterized by scaling exponents $2\nu > 1$ and $2\nu < 1$, respectively. The special case of $2\nu = 1$ defines the ideal, or theta state, in which the metric properties of the polymer are essentially those of a random walk. In the good solvent limit (expanded state) the exponent 2ν is believed to be very nearly equal to the Flory value $6/5$ while in the poor solvent limit (fully collapsed state) it should approach $2/3$.¹⁻³ For the square-well chains considered here good and poor solvent conditions correspond to high and low temperatures, respectively.

The limiting high temperature scaling behavior of chain dimensions with length is shown in Fig. 6. Here we plot both the mean-square radius of gyration $\langle R_g^2 \rangle$ and end-to-end dis-

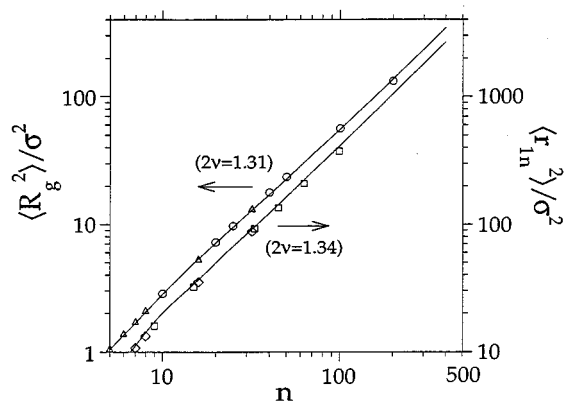


FIG. 6. Mean-square radius of gyration $\langle R_g^2 \rangle / \sigma^2$ and end-to-end distance $\langle r_{1n}^2 \rangle / \sigma^2$ vs chain length n for tangent hard-sphere chains (i.e., $T^* \rightarrow \infty$). The solid lines are the results from the present BGY theory while the symbols are the simulation results of Dautenhahn and Hall (○) (Ref. 34), Denlinger and Hall (△, ◇) (Ref. 35), and Kranbuehl *et al.* (□) (Ref. 36). The scaling exponent 2ν is given by the slope of these lines.

tance $\langle r_{1n}^2 \rangle$ versus chain length n for a hard-sphere chain. The slopes of the straight lines in this log-log plot give the scaling exponent 2ν . The BGY results for the radius of gyration and the end-to-end distance yield the very similar exponents of $2\nu=1.31$ and 1.34 , respectively. As is clear from Fig. 6, the BGY results are in near quantitative agreement with the simulation data. The corresponding scaling exponents determined from this simulation data are $2\nu=1.24$ and 1.28 , respectively. Although these values of 2ν for the hard-sphere chain are somewhat greater than the Flory value of $6/5$ we note that only data from relatively short chains ($40 \leq n \leq 400$) has been used in computing these exponents.

BGY and Monte Carlo results for the scaling behavior of the mean-square radius of gyration with chain length for

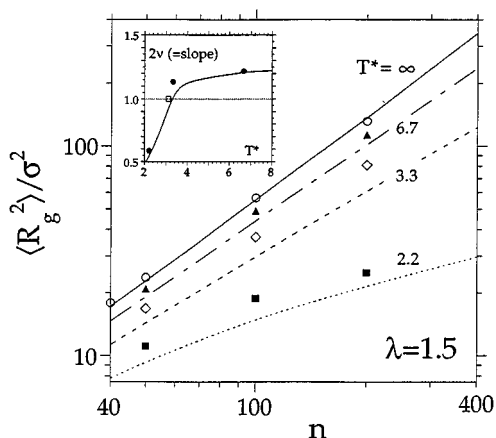


FIG. 7. Mean-square radius of gyration $\langle R_g^2 \rangle / \sigma^2$ vs chain length n for square-well chains with well diameter $\lambda=1.5$ for a range of reduced temperatures T^* as indicated. The solid and dashed lines are the results from the present BGY theory while the symbols are the simulation results of Dautenhahn and Hall (Ref. 34) for $T^*=\infty$ (○), 6.7 (▲), 3.3 (◇), and 2.2 (■). Inset: Scaling exponent 2ν (i.e., slope of above lines), determined from the Born, Green, Yvon theory (—) and the above simulation data (●), vs T^* . The open square locates the Monte Carlo result for the theta temperature (Ref. 37).

TABLE I. Theta temperatures for square-well chains with well diameter $\lambda\sigma$ as determined from the present BGY theory and the Monte Carlo simulations of Wichert and Hall (Ref. 37). The numbers in parentheses indicate the approximate error in the last digit shown.

λ	BGY	Monte Carlo
1.25	1.45(5)	1.37(2)
1.50	3.2(1)	3.07(3)
1.75	6.0(1)	5.95(6)
2.00	10.6(2)	10.70(8)

square-well chains with $\lambda=1.5$ are shown in Fig. 7 for a series of temperatures. Although the BGY theory underestimates $\langle R_g^2 \rangle$ for all finite temperatures, the scaling properties of the BGY results (i.e., the slopes of the straight lines in Fig. 7) are very similar to those of the Monte Carlo data. These slopes give the scaling exponent 2ν and a value of $2\nu=1$ locates the theta temperature T_θ^* . As seen in the inset, the exponent 2ν (determined here using $40 \leq n \leq 400$) decreases with decreasing temperature and passes through unity at $T^* = T_\theta^* \approx 3.2$. This BGY result for the theta temperature is in very good agreement with the corresponding Monte Carlo value (determined from the vanishing of the second virial coefficient) of $T_\theta^* \approx 3.1$.³⁷ In addition, the results summarized in Table I show that equally good agreement is found between the BGY and Monte Carlo results for T_θ^* for square-well chains with other square-well diameters $\lambda\sigma$.

IV. DISCUSSION

In this work we have derived an integral equation for the intramolecular distribution functions of an isolated interaction-site chain molecule using the approach of Born, Green, and Yvon. We use this equation to study the configurational and energetic properties of flexible square-well chains of lengths up to $n=400$ over a wide range of temperatures and have made extensive comparison between our integral equation results and available exact and simulation results. The BGY theory is exact for chains of length 3 and is extremely accurate for chains of length 4. For longer chains the theory yields semiquantitative results for $T^* > 1$ and gives qualitatively correct behavior for lower temperatures.

The square-well chain undergoes a collapse or coil-globule transition in the vicinity of $T^* \approx 1$. This collapse is evident from both the narrowing and shifting of the site-site distribution functions with decreasing temperature and the corresponding sudden reduction in average chain dimensions and average chain energy. The single chain specific heat exhibits a peak through the transition and the maximum of this function can be used to define a transition temperature. Using this definition, the BGY theory yields a transition temperature of $T^* \approx 0.4$ for square-well chains with $\lambda=1.5$ which is nearly independent of chain length. Although this result is correct for short chains, for longer chains one expects the collapse transition temperature to approach the theta temperature ($T_\theta^* \approx 3$ for $\lambda=1.5$).²³ Such behavior is in fact indicated in our plot of $\langle R_g^2 \rangle / n$ vs T^* (Fig. 3). The curves in Fig.

3(a) intersect in the vicinity of the theta temperature and, with increasing chain length, become steeper through this intersection point. This is similar to what is seen experimentally⁵ and suggests that in the long chain limit there will be a very sharp transition occurring at the theta temperature.³

The recent simulation results of Zhou *et al.* suggest that the square-well chain collapse transition is a multistage process;²⁴ a result not found in the present integral equation study. The multistage transition appears to involve an initial global collapse of the chain followed by one or more low temperature conformational rearrangements. Our theory correctly describes the initial collapse, but does not account for the latter stages of the transition. The secondary internal reorganization of the collapsed polymer, indicated in the simulation results, involves multisite correlations which are not considered in the present BGY study.

The BGY theory yields accurate results for the scaling exponent 2ν as a function of temperature although it underestimates the average chain dimensions. In particular, the theory gives very accurate results for the theta temperature (i.e., the temperature at which $2\nu=1$) for square-well chains with well diameters $1.25 \leq \lambda \leq 2.0$. In the high temperature limit the theory yields an exponent of $2\nu \approx 1.3$ which is slightly larger than the expected Flory value of $6/5$. This overestimation of the Flory exponent is probably due to our use of relatively short chains in this study. A similar overestimation of this exponent is observed in Monte Carlo results for chains with a site-site Morse potential,²³ and for hard-sphere chains.^{34–36} In the low temperature limit the BGY theory produces unphysically small chain dimensions for $n \geq 16$ and thus a scaling exponent which is less than the expected limiting value of $2/3$.

We have made two primary approximations in developing the present BGY integral equation theory for isolated polymer chains. These are the superposition approximation given by Eqs. (11) and (12) and our assumption that the intramolecular site-site distribution function w_{ij} can be approximated by the end-to-end distribution function of a chain of length $|i-j|+1$. This latter assumption is found to be reasonable for square-well 4-mers¹⁷ and hard-sphere 8-mers³⁸ and is also supported by Baumgartner's analysis of the intramolecular site-site separations for Lennard-Jones chains with lengths $n \leq 64$.²⁰ Baumgartner's results suggest that this approximation becomes less accurate with decreasing temperature and this may, in part, account for the poor quantitative performance of our theory for $T^* < 1$. Of course, the central approximation in the present theory is our superpositionlike decomposition of the three-site distribution function. Our proposed functional form provides an interpolation between the exact result for a short chain and the expected asymptotic behavior for long chains. A crossover distance between these two forms is required. We have assumed that this crossover distance r^* is on the order of the range of direct interaction between three sites and thus, for the square-well chains studied here, we considered $2\sigma \leq r^* \leq 4\sigma$. All values of r^* in this range give qualitatively similar behavior. We have used $r^*=3\sigma$ in the present study since this value gives

the best overall results for the dimensions of long hard-sphere chains. While further simulation studies would serve to test the quantitative accuracy of these approximations, it appears that the BGY theory developed in this work does yield a sensible picture of the physical properties of an isolated polymer chain.

ACKNOWLEDGMENTS

The authors would like to thank Yaoqi Zhou, John Wichert, and Carol Hall for making their Monte Carlo data available before its publication. Financial support from the National Science Foundation (Grant No. DMR-9122337) and the Dreyfus Foundation is also gratefully acknowledged.

- ¹ P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953).
- ² P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).
- ³ A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP, New York, 1994).
- ⁴ I. Nishio, S.-T. Sun, G. Swislow, and T. Tanaka, *Nature* **281**, 208 (1979).
- ⁵ S.-T. Sun, I. Nishio, G. Swislow, and T. Tanaka, *J. Chem. Phys.* **73**, 5971 (1980).
- ⁶ P. Stepánek, C. Konak, and B. Sedláček, *Macromolecules* **15**, 1214 (1982).
- ⁷ P. Vidaković and F. Rondelez, *Macromolecules* **17**, 418 (1984).
- ⁸ I. H. Park, Q.-W. Wang, and B. Chu, *Macromolecules* **20**, 1965 (1987).
- ⁹ B. Chu, I. H. Park, Q.-W. Wang, and C. Wu, *Macromolecules* **20**, 2833 (1987).
- ¹⁰ K. Kubota, S. Fujishige, and I. Ando, *J. Phys. Chem.* **94**, 5154 (1990).
- ¹¹ M. Nakata, *Phys. Rev. E* **51**, 5770 (1995).
- ¹² O. B. Ptitsyn, R. H. Pain, G. V. Semisotnov, E. Zеровnik, and O. I. Razgulyaev, *FEBS Lett.* **262**, 20 (1990); V. R. Agashe, M. C. R. Shastri, and J. B. Udgankar, *Nature* **377**, 754 (1995).
- ¹³ J. Naghizadeh, *J. Chem. Phys.* **48**, 1961 (1968); J. Naghizadeh and N. K. Ailawadi, *ibid.* **63**, 650, 657 (1975).
- ¹⁴ J. G. Curro, P. J. Blatz, and C. J. Pings, *J. Chem. Phys.* **50**, 2199 (1969).
- ¹⁵ B. C. Eu and H. H. Gan, *J. Chem. Phys.* **99**, 4084 (1993); H. H. Gan and B. C. Eu, *ibid.* **99**, 4103 (1993).
- ¹⁶ H. H. Gan and B. C. Yu, *J. Chem. Phys.* **100**, 5922 (1994).
- ¹⁷ M. P. Taylor, *Mol. Phys.* **86**, 73 (1995).
- ¹⁸ N. Karasawa and W. A. Goddard III, *J. Phys. Chem.* **92**, 5828 (1988).
- ¹⁹ G. Tanaka and W. L. Mattice, *Macromolecules* **28**, 1049 (1995).
- ²⁰ A. Baumgartner, *J. Chem. Phys.* **72**, 871 (1980).
- ²¹ I. Webman, J. L. Lebowitz, and M. H. Kalos, *Macromolecules* **14**, 1495 (1981).
- ²² J. Ma, J. E. Straub, and E. I. Shakhnovich, *J. Chem. Phys.* **103**, 2615 (1995).
- ²³ A. Milchev, W. Paul, and K. Binder, *J. Chem. Phys.* **99**, 4786 (1993).
- ²⁴ Y. Zhou, J. M. Wichert, and C. K. Hall (preprint).
- ²⁵ P. J. Flory, *Statistical Mechanics of Chain Molecules* (Hanser, Munich, 1969), pp. 313–316.
- ²⁶ J. G. Curro, Ph.D. thesis, California Institute of Technology, 1969; J. Blatz and J. G. Curro, *Polym. Prepr.* **9**, 272 (1968).
- ²⁷ M. Born and H. S. Green, *Proc. R. Soc. London, Ser. A* **188**, 10 (1946).
- ²⁸ J. Yvon, *Actual. Sci. Ind.* **203** (1935).
- ²⁹ S. G. Whittington and L. G. Dunfield, *J. Phys. A* **6**, 484 (1973).
- ³⁰ P. Attard, *J. Chem. Phys.* **102**, 5411 (1995).
- ³¹ M. P. Taylor and J. E. G. Lipson, *J. Chem. Phys.* **102**, 2118, 6272 (1995).
- ³² Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, *J. Chem. Phys.* **21**, 1098 (1953).
- ³³ T. L. Hill, *Statistical Mechanics* (Dover, New York, 1956), Chap. 6.
- ³⁴ J. Dautenhahn and C. K. Hall, *Macromolecules* **27**, 5399 (1994).
- ³⁵ M. A. Denlinger and C. K. Hall, *Mol. Phys.* **71**, 541 (1990).
- ³⁶ D. E. Kranbuehl, D. Eichinger, and P. H. Verdier, *Macromolecules* **24**, 2419 (1991).
- ³⁷ J. M. Wichert and C. K. Hall, *Macromolecules* **27**, 2744 (1994).
- ³⁸ A. Yethiraj, C. K. Hall, and K. G. Honnell, *J. Chem. Phys.* **93**, 4453 (1990).