THE JOURNAL OF CHEMICAL PHYSICS **129**, 174901 (2008)

# Computer simulation study of a single polymer chain in an attractive solvent

Dmytro Antypov[a] and James A. Elliott[b]
*Department of Materials Science and Metallurgy, Pembroke St., Cambridge CB2 3QZ, United Kingdom*

(Received 19 June 2008; accepted 5 September 2008; published online 5 November 2008)

The behavior of a linear polymer chain is studied in a solvent with high affinity for the polymer. The coil dimensions and specific heat are calculated as a function of chain length, solvent concentration, and polymer-solvent attraction strength $\varepsilon_{ps}$. All other interactions are limited to excluded volume repulsion, which implies that the Flory–Huggins $\chi$ parameter is negative. Using both on-lattice and off-lattice models of a polymer chain in explicit solvent, we study a transition from weak to strong association regimes. In all cases studied, the system's heat capacity is a nonmonotonic function of $\varepsilon_{ps}$ with a maximum at attraction strengths of the order of several $k_BT$. This peak originates from restriction of local conformational degrees of freedom due to the associated solvent rather than from a partial chain collapse which onsets as attractive solvent content is decreased. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2991178]

## I. INTRODUCTION

The solvent quality has long been known to affect the conformational behavior of a long linear polymer chain in a solution. In very simplistic terms, the polymer chain adopts an extended coil-like conformation in a good solvent, whereas in a poor solvent it collapses into a compact globule. This conformational behavior is a result of a rather complex competition between a number of entropic and enthalpic effects. For a single chain in equilibrium, the conformational entropy and the entropy of the solvent, as determined by the density, size, and shape of the solvent molecules, are balanced against all enthalpic interactions in the solution.

When a dilute polymer solution is studied theoretically or by means of computer simulations, it is common to coarse grain the effect of the solvent and consider an *effective* monomer-monomer interaction. Under conditions where, on average, all repulsive and attractive interactions balance each other out (known as the theta or Flory conditions), a polymer behaves as a phantom chain and can be modelled as a random walk (RW). For a RW consisting of $N$ uncorrelated segments of length $l$, the gyration radius defined as

$$R_g^2 = \left\langle \frac{1}{N}\sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{cm})^2 \right\rangle, \tag{1}$$

and its scaling behavior are known exactly: $R_g^2 = Nl^2/6$. In Eq. (1), each vector $\mathbf{r}_i$ defines the position of the $i$th segment, vector $\mathbf{r}_{cm} = 1/N\Sigma_{i=1}^{N}\mathbf{r}_i$ defines the center of mass of the chain, and the brackets indicate the ensemble average. The gyration radius is a commonly used measure of the polymer dimensions since it can be readily calculated in computer simulations via Eq. (1) and can also be determined from small-angle scattering experiments.[1] Note that a particular experimental solution can be mapped on the RW model only at its theta temperature $T_\theta$ by choosing an appropriate length $l$.

Under good solvent conditions at temperatures higher than $T_\theta$, the polymer behaves as a self-avoiding walk (SAW). In the SAW model, the monomer-monomer interactions include steric repulsions which increase the dimensions of the SAW when compared to the RW of the same length. The gyration radius of the SAW scales as $R_g^2 \propto N^{2\nu}$, where the exponent $\nu \approx 0.588$.[2] Additional monomer-monomer interactions between the monomers can be incorporated into the model to mimic the effect of the solvent. For a relatively weak monomer-monomer attraction, the radius of gyration is smaller than that of a noninteracting SAW while preserving the same scaling properties. Around $T_\theta$ the RW scaling $\nu = 1/2$ is recovered, which, however, does not imply that the radius of gyration itself matches that of the RW model; in fact, it is still larger for the same chain lengths.[3] At lower temperature the chain collapses into a compact globule, whose size scales with $\nu = 1/3$.

For a finite chain, the coil-to-globule transition described above is continuous, which means that it occurs gradually over a range of temperatures. The Boyle temperature $T_B$, at which the second virial coefficient turns to zero, is often used to pinpoint the location of the transition.[4] Although this criterion of "repulsive and attractive interactions balancing each other out" does not mean that RW scaling has to be recovered at $T_B$,[5] $\nu = 1/2$ with an error of less than 1.6% is already achieved for SAWs of length $N = 500$ on a simple cubic lattice.[6] Extrapolating $T_B$ down for long chains gives $T_\theta$ in the thermodynamic limit. Interestingly, the specific heat reaches its maximum well below $T_B$ and $T_\theta$ even for SAWs of length $N = 5000$.[3] Hence, this signature of a phase transition is greatly affected by the finite size effect. Same is also true for the scaling exponent at very low temperatures: even SAWs of length $N = 10\,000$ do not reach the scaling of $\nu = 1/3$ at temperatures of the order of $0.5T_\theta$.[7]

Once the chain has collapsed into a compact globule,

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[a] Electronic mail: da275@cam.ac.uk.
[b] Electronic mail: jae1001@cam.ac.uk.

there is a possibility of a crystallization transition at temperatures below $T_\theta$. This transition has indeed been seen in both off-lattice[8] and on-lattice models.[9,10] Interestingly, the bond fluctuation model (BFM) predicts that the coil-to-globule and crystallization transitions converge in the thermodynamic limit,[9] whereas SAWs on simple cubic or face-centered-cubic (fcc) lattices are characterized by two separate transitions for very long chains.[10]

The behavior of SAWs described above assumes that additional monomer-monomer interactions are always attractive, i.e., $E_{pp}<0$, and solvent properties worsen as the temperature is decreased. This corresponds to a positive Flory–Huggins $\chi$ parameter, defined for a lattice polymer model as

$$\chi = \frac{z}{k_B T}\left(E_{ps} - \frac{(E_{pp}+E_{ss})}{2}\right), \tag{2}$$

where $z$ is the number of nearest neighbors, $T$ is the temperature, and $E_{\alpha\beta}$ are all possible pair interaction energies between polymer ($p$) and solvent ($s$) sites. Note that the thermodynamic properties of a binary lattice mixture are *exactly* defined by $\chi$ alone. Then, without loss of generality, it is often assumed that $E_{ps}=E_{ss}=0$ and negative $E_{pp}$ results in positive values for $\chi$. One can equally assume that $E_{pp}=E_{ss}=0$ and rationalize the system's behavior in terms of $E_{ps}$, which is positive (i.e., polymer-solvent repulsion) for positive $\chi$. Either way, the limiting value of $\chi=0$ corresponds to an athermal system, which is characterized by the most extended conformation that the chain can adopt.

For off-lattice models and experimental systems, the Flory–Huggins expression for the free energy is often assumed to be exact, while $\chi$ is treated as an adjustable parameter. At theta temperature, where the enthalpic term proportional to $\chi$ wins over always negative entropy of mixing, $\chi$ is set exactly to 0.5. Higher values of $\chi$ correspond to a poor solvent regime, whereas $\chi<0.5$ in a good solvent. The relationship between $\chi$ and temperature in experimental systems is not as straightforward as given by Eq. (2). In polymer solutions, the $\chi$ parameter is known to either increase or decrease with temperature, resulting in correspondingly lower (missed completely by the Flory–Huggins lattice model) or upper critical point.[11] Changes in chain conformations with temperature and finite system compressibility are also neglected in the Flory–Huggins theory, which means that the effective value of $\chi$ has to account for these effects too. Most experimental systems have positive enthalpy of mixing and tend to demix at low temperatures. However, $\chi$ can be negative, as, for example, in aqueous solutions of polar polymers,[12] DNA in cationic surfactants,[13] and other associating fluids.[14] Under these conditions, the mixed phase is favored over the phase separation and the polymer coil is expected to swell as the temperature is decreased. In this paper, we concentrate on polymer solutions for which the Flory–Huggins parameter $\chi$ is negative. In terms of the SAWs on a lattice, this simply means changing $E_{pp}$ to positive values to introduce soft polymer-polymer repulsion additional to the already present excluded volume interactions.

Structural changes are usually accompanied by irregular behavior in the system's calorimetric properties such as specific heat. Even in a finite system, for which a phase transition is not strictly defined, a sharp increase in specific heat is indicative of some structural changes taking place. For example, the temperature at which the protein denaturation occurs can be readily obtained from the calorimetric data. A detailed analysis of protein unfolding reveals that the main contribution to the specific heat capacity change comes from the hydration mechanism (about 95%) while the noncovalent interactions within the protein itself are less important (about 5%).[15] A similar increase in specific heat can also be seen in protein aggregation or protein-ligand binding, indeed, any system with some associating interactions present.[16] Combined microcalorimetry and viscosity studies of polysaccharides in solutions of ionic surfactants can relate this peak in specific heat due to the aggregation to the corresponding increase in the chain dimesions at low temperatures.[17]

In general, the specific interactions between the polymer and the solvent (or some additives such as a second solvent, ligands, and nanoparticles) can affect the polymer conformation and promote formation of novel phases. There are a number of examples of the solvent molecules remaining inside the collapsed polymer globule in a so-called "molten globule" configuration (see Ref. 18 and references therein). Growing evidence from both theory and simulation indicates that the packing of the solvent molecules tends to induce an additional structure in the polymer-polymer pair distribution functions that is not present when the polymers are treated in a continuum solvent.[19,20]

In this paper, we study the equilibrium behavior of a single polymer chain in an attractive solvent. The effect of association between the polymer and the solvent on the chain conformation and its thermodynamic properties is of particular interest. Hence the monomer-monomer and solvent-solvent interactions are modeled as purely repulsive and the only attractive interaction is the interaction between the polymer and the solvent. In the remainder of this paper we present our simulation results first for an on-lattice chain in Sec. II and then for an off-lattice chain in Sec. III. In both cases, changes in coil dimensions and specific heat capacity are studied as a function polymer-solvent attraction strength and the concentration of attractive solvent. The results are discussed and compared to the existing literature data in Sec. IV, followed by conclusions.

## II. RESULTS: ON-LATTICE MODEL

We use a fcc lattice—a high coordination regular three dimensional lattice—where each site has $z=12$ closest equidistant neighboring sites. Each site can be of one of three types: polymer ($p$), solvent ($s$), or a vacancy ($v$). Here we consider both the pure solvent (i.e., a binary mixture) and solvent+vacancy (i.e., a ternary mixture) cases. The latter model allows for the solvent density fluctuations, whereas local solvent concentration is always 1 in a pure solvent. The vacancies can also be viewed as a second solvent with good properties. A linear polymer chain is modeled as a SAW of length $N$ and the rest of the system is occupied by single sites bearing either solvent or vacancy identity. Simple square well site-site potentials describe the pairwise interactions $E_{\alpha\beta}$

between species $\alpha$ and $\beta$. All interactions are set to zero apart from $E_{ps}$, which is negative in the case of attraction.

The partition function of our mixture is given by

$$Z=\sum_i D_s(i)\exp\left(-\frac{N_{ps}(i)E_{ps}}{k_BT}\right), \tag{3}$$

where the sum runs over all possible system macrostates $i$. Each macrostate is defined by a single conformation of the polymer and $D_s(i)$ possible arrangements of the solvent sites which form exactly $N_{ps}(i)$ polymer-solvent closest neighbor pairs. This definition means that each term in Eq. (3) gives the contribution of a given polymer conformation to a given energy level defined by $N_{ps}(i)$. In an athermal system with $E_{ps}=0$, the sum $D_p=\Sigma D_s(i)$ over all $N_{ps}(i)$ for a fixed polymer conformation gives the total contribution of this conformation to $Z$ and is equal to the total number of arrangements of the solvent sites in this system. If each solvent "particle" occupies a single lattice site, this sum is simply $D_p={}_{(V-N)}C_{N_s}$, where $N_s$ is the total number of solvent sites and $V$ is the total size of the system. This means that in an athermal system, each polymer conformation has the same degeneracy factor $D_p$ and Eq. (3) can be factorized into a polymer and a solvent part. Therefore, the addition of a hard one-site solvent would not change the radius of gyration or any other thermodynamic property of the polymer. If a solvent "particle" were to occupy more than one site, then the number of possible arrangements $D_p$ around a given polymer conformation would depend on the conformation itself and will affect its contribution to the partition function. The same is true for any interacting system with $E_{ps}\neq 0$, where the contribution of each macrostate is proportional to its Boltzmann factor in Eq. (3). In the remainder of this paper we consider a polymer lattice model with an interacting single-site solvent. At any solvent concentration, this model recovers the properties of a free self-avoiding chain in the limit of $E_{ps}=0$.

First, it is illustrative to consider a very short chain consisting only of three beads connected by two bonds (i.e., $N=3$) in pure solvent whose properties can be studied by simple enumeration. Such a trimer has 11 possible conformations on a fcc lattice, which differ by the angle between the two bonds. There are four 60°, two 90°, four 120°, and one 180° conformations. The energy of each conformation, $U=N_{ps}E_{ps}$, is defined by the number of polymer-solvent contacts, $N_{ps}$. There are only two energy levels for the trimer: The four 60° conformations have $N_{ps}=30$, while the remaining seven conformations have $N_{ps}=32$. Therefore, the partition function of the trimer reads $Z=4\exp(30\varepsilon_{ps})+7\exp(32\varepsilon_{ps})$, where $\varepsilon_{ps}=-E_{ps}/(k_BT)$ is a positively defined dimensionless parameter giving the strength of the polymer-solvent attraction in units of $k_BT$. The analytical expression for the system's heat capacity $C_V$ can be readily obtained from its definition: $C_V=\delta\langle U\rangle/\delta T$, where $\langle U\rangle=\langle N_{ps}\rangle E_{ps}$ is the system's energy at given temperature. For longer chains, however, the analytical expression for $\langle N_{ps}\rangle$ is impractical to calculate since it requires enumeration of all possible chain conformations. Hence, in computer simulations, the specific heat is calculated as the variation: $C_V=k_B(\langle N_{ps}^2\rangle-\langle N_{ps}\rangle^2)$. Here we normalize $C_V$ by the chain length $N$ and discuss our data in terms of specific heat $c_V=C_V/N$ to compare the calorimetric effects for different chain lengths.

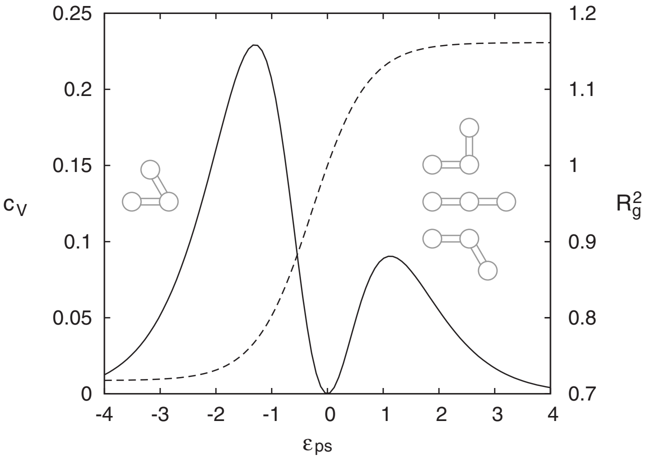

FIG. 1. The specific heat $c_V=C_V/N$ (solid line) and normalized radius of gyration (dashed line) for a short chain of $N=3$ on fcc lattice as a function of attraction strength $\varepsilon_{ps}=-E_{ps}/(k_BT)$.

Figure 1 shows both the specific heat $c_V$ in units of $k_B$ and the gyration radius defined according to Eq. (1) and normalized by its value at $\varepsilon_{ps}=0$. Two maxima of specific heat, indicative of structural changes, clearly separate three regimes, from left to right: strongly attractive chain (collapsed state in a poor solvent), non-interacting chain (SAW in a good solvent) and strongly repulsive chain ("swollen SAW"). Typical conformations of a trimer are depicted in Fig. 1 for strongly attractive and repulsive regimes, whereas all conformations are equally probable at $\varepsilon_{ps}=0$.

Note that the peak at negative $\varepsilon_{ps}$ corresponds to the coil-globule transition, whereas the peak at positive $\varepsilon_{ps}$ is a transition between weak and strong solvent association regimes. As we increase the strength of attraction $\varepsilon_{ps}$, the 60° conformations become less and less probable as the chain wants to maximize the solvent-accessible area. This effect is the opposite to the chain collapse in a poor solvent, where the trimer wants to minimize the solvent-accessible area. Both effects result in the elimination of some of the chain conformations, which is accompanied by a heat capacity peak.

To study behavior of longer chains we used several stochastic computational techniques based on the adaptive Wang–Landau sampling method.[21] This method allowed us to efficiently explore the configuration space of the model polymer chain at a range of temperatures within a single computer simulation. For SAWs in pure solvent we used a straightforward Rosenbluth–Rosenbluth growth method[22] combined with the Wang–Landau technique. This way the complete partition function and the properties of SAWs of lengths up to $N=200$ were calculated. For systems containing both attractive and neutral sites, we performed simulations for a fixed chain length of $N=100$ and fixed solvent contents of 70%, 80%, and 90%. To generate a new chain conformation, a monomer was displaced at random using a cooperative move preserving chain connectivity.[23] This was alternated with a displacement of a solvent site. Then the

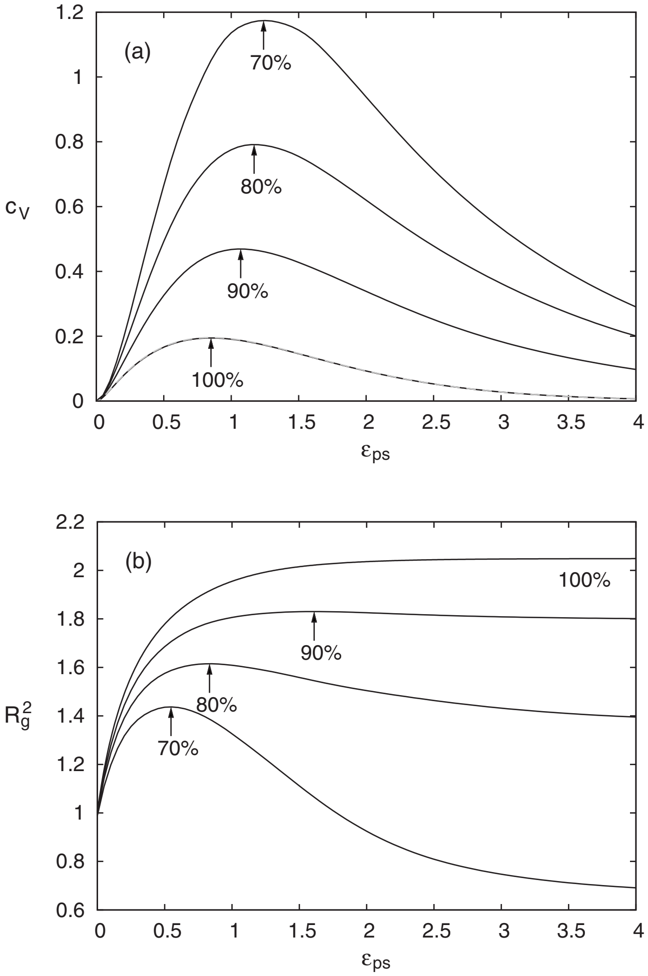

FIG. 2. (a) Specific heat per chain length and (b) radius of gyration normalized by that of an athermal SAW for $N=100$ as a function of interaction strength $\varepsilon_{ps}=-E_{ps}/(k_BT)$ at four solvent concentrations: 70%, 80%, 90%, and 100%. The gray dashed line in part (a) shows the specific heat for $N=200$ in pure solvent for comparison.

new state was accepted or rejected according to a density biased Wang–Landau scheme, with complete details of the algorithm published elsewhere.[24] This method also allowed us to obtain such thermodynamic quantities as free energy, entropy, and specific heat in a wide range of interaction parameters.

Figure 2 summarizes the main results of our on-lattice simulations of a chain in an attractive solvent. Both the specific heat and gyration radius were measured for a chain of length $N=100$ at solvent concentrations of 70%, 80%, 90%, and 100%. The specific heat profile for each solvent concentration appears to be a nonmonotonic function of $\varepsilon_{ps}$ with the position of the maximum marked by an arrow in Fig. 2(a). As the solvent content is decreased, the position of the peak in $c_V$ shifts to higher attraction strengths and its height significantly increases. The gyration radius also changes nonmonotonically with $\varepsilon_{ps}$ in all systems where vacancies are present. The peaks in gyration radius, marked by arrows in Fig. 2(b), shift to lower polymer-solvent attraction strengths at lower solvent concentrations, i.e., the trend is opposite to that for the peaks in the specific heat. This suggests that the increase in $c_V$ is not associated with the collapse of the chain. In fact, a chain in pure solvent swells monotonically as $\varepsilon_{ps}$ is increased, while its specific heat changes nonmonotonically.

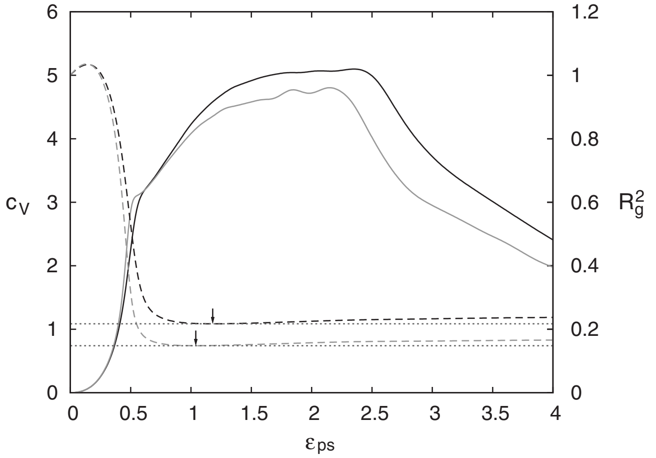

FIG. 3. The specific heat (solid lines) and normalized radius of gyration (dashed lines) for SAWs of length $N=100$ (black lines) and $N=200$ (gray lines) as a function of interaction strength $\varepsilon_{ps}$ at solvent concentration of 10%.

The gray dashed line in Fig. 2(a), which shows the specific heat for $N=200$ in pure solvent, can hardly be distinguished from the black solid line for $N=100$. For both chain lengths, the peak in specific heat at $\varepsilon_{ps}\approx 0.85$ separates the random SAW conformation at low values of $\varepsilon_{ps}$ from something at high values of $\varepsilon_{ps}$ that we will call a swollen SAW conformation. Unlike the peaks in specific heat for the coil-globule and crystallization transitions,[9,10] this peak does not become sharper as the chain length increases. The fact that both chain lengths are characterized by nearly identical specific heat profiles at any strength of the polymer-solvent attraction $\varepsilon_{ps}$ suggests that this transition has a local character. In pure solvent, positive $\varepsilon_{ps}$ means that the effective next-neighbor polymer-polymer interaction is *always* repulsive. In the case of the fcc lattice, this results in an energy penalty for the 60° conformations between the consecutive bonds, whereas 90°, 120°, and 180° conformations are not directly affected. Therefore, the SAWs at high values of $\varepsilon_{ps}$ will be restricted to the latter conformations similar to the trimer considered at the beginning of this section (cf. Fig. 1). This effect is equivalent to chain stiffening and naturally results in a monotonic increase in gyration radius as $\varepsilon_{ps}$ is increased. According to Fig. 2(b), a typical chain conformation at high $\varepsilon_{ps}$ has a gyration radius more than twice than that of the athermal SAW.

The partial chain collapse observed in Fig. 2(b) becomes more profound as the concentration of the attractive solvent is decreased. Figure 3 shows the specific heat and gyration radius for two chains of length $N=100$ and $N=200$ at a relatively low concentration of 10%. The gyration radius curves (dashed lines) indicate a sharp collapse at $\varepsilon_{ps}\approx 0.5$ for both chain lengths. At the attraction strengths marked by the arrows, each chain reaches its most compact conformation and then starts swelling at higher attraction strengths. Due to a higher volume to surface ratio, the longer chain collapses more as demonstrated by the two dotted horizontal lines corresponding to about 22% for $N=100$ and only 15% for $N$

=200. At higher attraction strengths, both chains swell slightly by adsorbing more attractive solvent. The specific heat profiles (solid lines) suggest the presence of two distinct structural changes taking place. First, the chain collapse results in a noticeable increase in $c_V$ at $\varepsilon_{ps} \approx 0.5$. Second, a further increase in $c_V$ originates from the restriction of local degrees of freedom within an already collapsed conformation and does not correspond to any rapid changes in chain dimensions. Despite a relatively sharp chain collapse at concentration of an attractive solvent at as low as 10%, the second mechanism is still characterized by a much larger calorimetric effect. The fine structure of the second peak is similar for both chain lengths, which again indicates their local origin.

To investigate the scaling properties of the swollen SAW in a pure solvent we employed a Rosenbluth–Rosenbluth growth method[22] to compare two ensembles of SAWs: Unrestricted SAWs and SAWs for which the number of nonbonded polymer-polymer pairs was restricted to zero. The latter corresponds to the case of very strong polymer-solvent attractions, which is characterized by the highest possible solvent-accessible polymer surface. All intermediate values of the attraction strength $\varepsilon_{ps}$ result in the chain dimensions between these two extreme cases. Due to the local 60° conformations being prohibited in the restricted SAW ensemble, the lattice connectivity constant, $\mu(\varepsilon_{ps})$, decreases from $\mu(0)=10.0366(5)$ to $\mu(\infty)=6.4635(6)$. These values of $\mu$ were used to fit the total number of conformations $\Omega = C\mu^{(N-1)}(N-1)^{\gamma-1}$ and gave critical exponent $\gamma$ of correspondingly $\gamma(0)=1.164(4)$ and $\gamma(\infty)=1.165(5)$ in the thermodynamic limit. The extrapolated values for scaling exponent $\nu$ for the SAWs' dimensions were found to be $\nu(0)=0.589(4)$ and $\nu(\infty)=0.590(6)$. In the case of the restricted walks the convergence was much slower than for the unrestricted walks, which is indicative of larger logarithmic corrections and also resulted in larger error bars. All the above values calculated for the unrestricted walk compare well with the existing literature data.[25] As expected for the pure solvent case, the presence of soft short-ranged polymer-polymer repulsion does not affect the critical properties of the swollen SAWs.

In the case of vacancies being present in the system, its behavior cannot be described in terms of the effective next-neighbor polymer-polymer interactions. Unlike for the binary lattice model, whose behavior is uniquely defined by a single parameter of form Eq. (2), in a ternary system, three independent parameters, $\chi_{ps}$, $\chi_{pv}$, and $\chi_{sv}$, are required to fully describe its thermodynamic properties. Since we assume that $E_{ps}$ (which enters only $\chi_{ps}$) is the only nonzero interaction energy, the system behavior cannot be rationalized in terms of $E_{pp}$ alone (which enters both $\chi_{ps}$ and $\chi_{pv}$). This results in the nontrivial dependence of the effective polymer-polymer interactions in ternary mixtures. According to Fig. 2(b), the SAW's dimensions in the presence of vacancies are always smaller when compared to the pure solvent case. The higher the concentration of the vacancies, the sharper the collapse. This indicates that the vacancies allow for the solvent-mediated attraction between the polymer sites. Therefore, the effective polymer-polymer interaction depends on both the solvent concentration and its affinity for the polymer. Its range is now extended beyond the nearest neighbor interactions: The effective polymer-polymer potential is repulsive for the first neighboring shell and attractive for the second. It is beyond the scope of this paper to find the exact expression for this potential.

## III. RESULTS: OFF-LATTICE MODEL

To exclude possible lattice artifacts and investigate the effects of solvent concentration effects in more depth, we conducted off-lattice molecular dynamics simulations of a single chain in attractive solvent. Initially both the polymer monomers and the attractive solvent were taken to be of the same diameter $\sigma$. We used a cubic simulation box of size $20\sigma \times 20\sigma \times 20\sigma$ with periodic boundary conditions. The box contained one polymer chain consisting of $N=21$ monomers and $N_s$ solvent particles. Three different values were used for $N_s$ to simulate number densities, $n=N_s/(20\sigma)^3$, of 40%, 50%, and 60% which are equivalent to volume packing fractions of about 0.21, 0.26, and 0.31, respectively. The connectivity of the polymer chain was maintained by stiff harmonic bonds between the consecutive monomers. To describe the polymer-solvent interaction (again the only attractive interaction in the system) we employed a short-ranged attractive potential originally proposed by Soddemann *et al.*[26] to study amphiphilic systems

$$U(r) = \begin{cases} 4\varepsilon\left(\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right), & r \leqslant \sqrt[6]{2}\sigma \\ \dfrac{\varepsilon}{2}\left(\cos\left(a\left(\dfrac{r}{\sigma}\right)^{2} + b\right) - 1\right), & \sqrt[6]{2}\sigma < r \leqslant 1.5\sigma \\ 0, & r > 1.5\sigma, \end{cases} \tag{4}$$

where constants $a \approx 3.173$ and $b \approx -0.856$ ensure that both the potential and the corresponding force are continuous and smoothly approach zero at the cut-off distance. The main advantage of using potential (4) over the Lennard-Jones (LJ) potential is that, due to the short cutoff of $r_{\text{cut}}=1.5\sigma$, the solvent particles can only associate with parts of the chain in their immediate proximity. Polymer-polymer nonbonded interactions and solvent-solvent interactions are described by a shifted purely repulsive LJ potential with the cut-off radius of $\sqrt[6]{2}\sigma$ [also known as the Weeks–Chandler–Andersen (WCA) potential]. For the following set of results, we fixed the interaction parameter $\varepsilon=1$ and varied the temperature in the system at each concentration of the solvent particles.

The specific heat and the normalized gyration radius at different solvent densities are shown in Fig. 4 as functions of the attraction strength $\varepsilon_{ps}=\varepsilon/(k_B T)$. A clear peak in specific heat can be seen at every concentration of the solvent. The peak's position shifts towards weaker interaction strengths $\varepsilon_{ps}$ as the solvent concentration is increased. The corresponding conformational behavior of the polymer chain is depicted in Fig. 4(b). The radius of gyration of the off-lattice chain changes nonmonotonically with $\varepsilon_{ps}$—increases at low $\varepsilon_{ps}$, reaches a maximum, decreases, and then increases again at high $\varepsilon_{ps}$. The position of the maximum and the minimum in

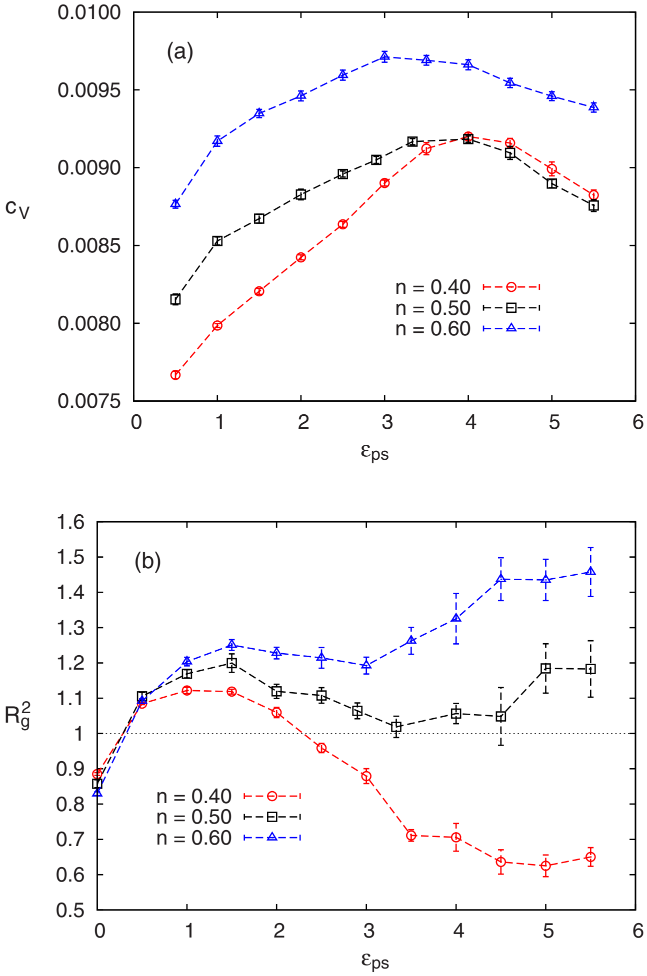

FIG. 4. (Color online) (a) specific heat $c_V = C_V/(N+N_s)$ for a LJ chain of $N=21$ immersed in explicit attractive solvent. (b) The radius of gyration normalized by that of a free chain. Different symbols correspond to different solvent number densities $n$.

the $R_g^2$ profile change monotonically with the solvent concentrations. As the solvent concentration increases, the maximum shifts toward higher values of $\varepsilon_{ps}$ analogous to the on-lattice chain [cf. Fig. 2(b)]. The local minimum, not observed in the on-lattice model, follows the opposite trend—it shifts toward lower values of $\varepsilon_{ps}$ at higher solvent content. In fact, its position correlates well with the position of the specific heat maximum in Fig. 4(a). The local minimum in the $R_g^2(\varepsilon_{ps})$ curve becomes less pronounced as the solvent concentration is increased. It is possible that at high solvent concentration, the transition between weak and strong adsorption regimes can be associated with a monotonic increase in the gyration radius similar to our on-lattice simulations.

If a self-avoiding polymer chain is immersed into a bath of hard particles, its dimensions reduce, as can be seen in Fig. 4(b) at $\varepsilon_{ps}=0$. The higher the content of the solvent particles, the greater this effect: it amounts to approximately a 12% decrease in gyration radius for $n=0.40$, 14.5% for $n=0.50$, and 17% for $n=0.60$. As $\varepsilon_{ps}$ is increased, the presence of weak attractive interactions between the polymer and the solvent effectively improves the solvent quality and results in the initial increase in $R_g^2$. As a result, at $\varepsilon_{ps}\approx 1$, higher values of $R_g^2$ correspond to higher concentration of the solvent; opposite to the trend observed for $\varepsilon_{ps}\approx 0$. The collapse of the chain at stronger polymer-solvent association means that it is more favorable to reduce the conformational entropy of the chain by wrapping it around fewer solvent particles rather than to bind a larger number of solvent particles to an extended coil. Having collapsed in the droplet of attractive solvent, the chain can "adsorb" a greater number of solvent molecules from the bulk if $\varepsilon_{ps}$ is increased further. This explains the final swelling of the chain at very high interaction strengths.

To verify our hypothesis that the specific heat peak seen in Fig. 4(a) is attributed to the conformational degrees of freedom, we performed auxiliary simulations of mixtures with the same interactions and particle composition but different connectivity of the monomers. Three systems in which the chain was split into single freely moving monomers, dimers, or trimers were simulated. As expected, the first two systems did not show nonmonotonic behavior of the specific heat with $\varepsilon_{ps}$—it increased monotonically up to $\varepsilon_{ps}=6.0$. The trimers, however, had a peak in the specific heat similar to those shown in Fig. 4(a). Therefore, this signature of a transition originates from the restriction in rotations of the consecutive bonds between statistical segments in a polymer chain.

It is evident that the packing effects of the solvent around the polymer chain greatly depend on the size (and shape) of the solvent molecules. To explore how this affects the polymer chain in attractive solvent, we simulated mixtures in which the size of the solvent particles was different from that of the monomer. At the same solvent volume fraction of $f\approx 0.26$, mixtures with solvent particles twice the volume of the monomer ($v=2.0$) and half the volume of the monomer ($v=0.5$) were simulated at a range of temperatures. To describe polymer-solvent attractive interaction, we used a modification of potential (4). The interparticle distance was shifted to ensure that the potential and force between two particles are defined by the distance between their surfaces and are the same for all particle sizes.

Figure 5 shows both specific heat and the normalized gyration radius for the three systems we studied. The data indicate that the peak in the specific heat occurs at approximately the same attraction strengths for $v=0.5$ and $v=1.0$, while it shifts to higher $\varepsilon_{ps}$ for $v=2.0$. The position of this maximum correlates well with the local minimum in gyration radius: The specific heat peaks at similar attraction strengths as the gyration radius reaches its minimum. Interestingly, for the cases of $v=0.5$ and $v=2.0$ the chain collapses more than when the monomers and solvent particles are of the same size. This contrasts with the chain swelling at small $\varepsilon_{ps}$ for which the chain dimensions change similarly regardless of the size of the solvent particles. This means that at small $\varepsilon_{ps}$ all three systems are characterized by similar (but not identical) values of the $\chi$ parameter. For purely repulsive particles at $\varepsilon_{ps}=0$, the chain is expected to collapse more in the presence of larger particles.[27] Although the average values of the gyration radius follow the correct trend, this effect is too small to be confirmed when the error bars are about 3%.

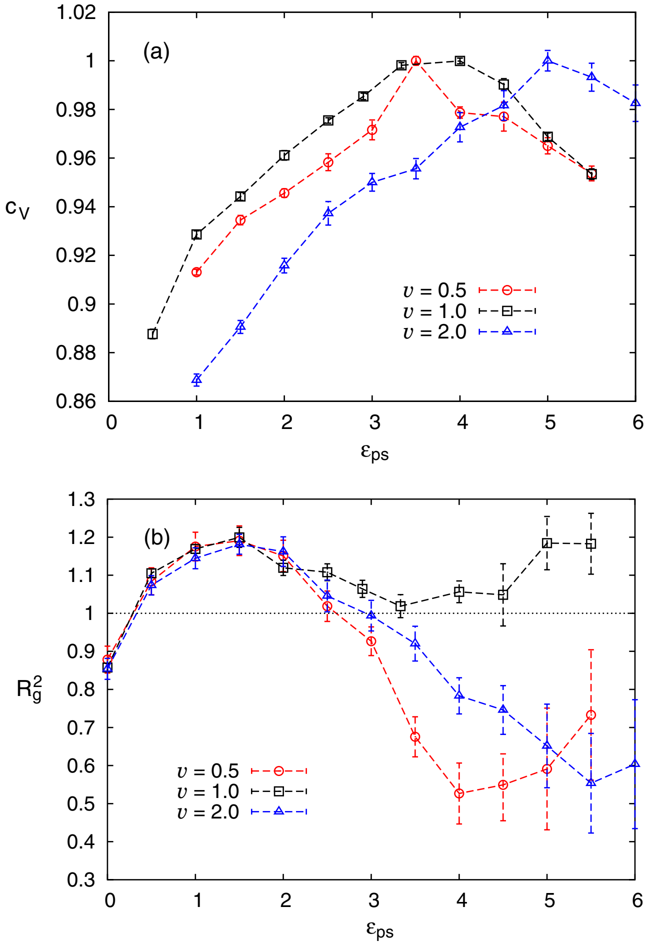

FIG. 5. (Color online) (a) specific heat $c_V$ normalized by its peak value for a LJ Jones chain of $N=21$ immersed in explicit attractive solvent with different volume of the solvent particle $v$. (b) The radius of gyration of this chain normalized by that of a free chain.

## IV. DISCUSSIONS AND CONCLUSIONS

All the simulations reported in Secs. II and III show that the heat capacity of a self-avoiding chain in an attractive solvent is a nonmonotonic function of polymer-solvent interaction strength $\varepsilon_{ps}$. It has a peak at the interaction strength of several $k_BT$, whose exact position depends on the range of the attractive potential, solvent size, and solvent concentration. This peak separates the regime of weak association, where solvent only weakly affects polymer conformations, and the strong association regime, where some conformations become eliminated due to the associated solvent. This mainly affects the degrees of freedom of consecutive monomers which means that this effect is local in nature and only weakly depends on the chain length for long chains. Qualitatively this phenomenon can already be demonstrated for such short chain as a trimer. The enumeration of all possible states for a trimer in a fcc lattice showed that it had only two distinct energy levels. As $\varepsilon_{ps}$ was increased, the more compact 60° conformations gradually became more energetically unfavorable and the trimer was limited to the lower energy level.

The dimensions of a SAW on a fcc lattice in pure solvent were found to increase monotonically with polymer-solvent attraction strength $\varepsilon_{ps}$. For a binary mixture, this is *exactly* equivalent to the presence of effective polymer-polymer repulsion, which explains the stiffening of the chain and its swelling. The scaling properties of such SAWs are the same as those of noninteracting SAWs, i.e., the good solvent scaling. If vacancies are present in the lattice model or an off-lattice system is considered, a possibility of having a solvent density gradient arises. If a self-avoiding polymer chain with no attractions is immersed in the bath of purely repulsive (i.e., hard) solvent particles, the steric repulsions expel the particles from inside the coil which leads to an external osmotic pressure on the coil. As a result the coil dimensions monotonically decrease as the particle concentration is increased [see data in Fig. 4(b) at $\varepsilon_{ps}=0$]. There are numerous theoretical,[28–30] experimental,[31,32] and computational[33–36] studies of this effect in literature. Within a mean-field approach, the addition of hard particles is equivalent to worsening the solvent properties and can be described in terms of the classic Flory–Huggins theory with $\chi$ parameter adjusted appropriately according to the particle size and concentration.[37]

If attractive solvent-solvent interactions are incorporated into the model, they also result in a worsening of the solvent properties (i.e., the $\chi$ parameter increases) and further reduce the coil dimensions.[35] However, some recent studies suggest that cooperative effects in attractive solvent alone can result in an increase in chain dimensions near the critical point.[36] Other theoretical[38] and simulation[39,40] studies predict chain collapse and then re-expansion as the critical temperature is approached in a system with polymer-solvent attractions present. This behavior is similar to that predicted for a binary mixture of good solvents by Brochard and de Gennes[41] and later observed in computer simulations[42] and experiment.[43] As can be seen, the incorporation of the solvent-solvent attractive interactions introduces additional complexity reaching beyond that considered in this paper. Similar comment can be made with respect to the attractive monomer-monomer interactions. Their presence, as considered in Ref. 5 for model A and in Ref. 35 for an attractive chain, make the chain collapse at low solvent content, i.e., vacuum is a poor solvent for a self-attracting chain. As the solvent concentration is increased, the attractive intrachain interactions become screened by the solvent particles and the chain dimensions increase. In our model we choose to limit the monomer-monomer interactions to purely repulsive to concentrate on the effect of the solvent mediated attractions alone.

If weak attractive polymer-solvent interactions are incorporated into the model, the effective solvent properties change toward a better solvent (i.e., the $\chi$ parameter decreases), therefore, the coil dimensions increase. The balance between this swelling due to the improved solvent quality and the contraction due to the steric repulsions defines the coil behavior in our off-lattice model. Our results agree well with the findings reported in Ref. 36 that a self-avoiding WCA chain swells monotonically as the concentration of attractive solvent is increased at $1/\varepsilon_{ps}=1.42$. This interaction strength is too weak to cause chain collapse at any concentration of the solvent.

If attractive interactions between the polymer and the solvent are strong, they can induce polymer-polymer attraction, whose effect greatly depends on the concentration of attractive solvent: The lower the concentration, the higher the contraction of the coil. This is because at high solvent concentrations the strong attractions between the polymer and the solvent do not affect the solvent concentration near the polymer coil—it is already high. If, however, the concentration of the solvent with high affinity for the polymer in the solution is low, the attractive forces result in a large difference between solvent concentration near and far away from the polymer coil. This means a large change in translational entropy of a solvent particle upon its binding to the polymer. Therefore, it is advantageous to increase the polymer-solvent contact area and use as few solvent particles as possible at the same time. As a result, the polymer's conformational entropy is reduced and the chain collapses into a small droplet of attractive solvent.

The increase in the number of the solvent particles around the polymer chain can be observed as the solvent affinity for the polymer is increased after the chain has already collapsed. This results in the increase of the chain dimensions at high $\varepsilon_{ps}$ in our off-lattice simulations [see Fig. 4(b)]. The interaction strength corresponding to the most compact polymer conformation was found to correlate well with the position of the maximum in heat capacity. However, when we varied solvent particle size, there was no apparent correlation between the conformational behavior of the chain and the particle size. We believe that strong steric repulsions for larger particles ($v=2.0$) and strong solvent induced polymer-polymer attraction for smaller particles ($v=0.5$) can be responsible for the reduction in the chain dimensions shown in Fig. 5(b). For the case of ($v=1.0$), these two effects oppose each other and result in a relatively flat $R_g^2$ profile.

To summarize, in this paper we demonstrate how the conformation of a self-avoiding polymer chain is affected by association of attractive solvent. First, we consider a binary on-lattice model in which the presence of attractive solvent results in purely repulsive short-ranged polymer-polymer interactions. The chain dimensions increase monotonically with the interaction strength and have good solvent scaling properties. In the ternary on-lattice model, a possibility of a solvent mediated polymer-polymer attraction arises which results in a nonmonotonic behavior of the gyration radius with the interaction strength. The same is also true for an off-lattice chain in explicit attractive solvent.

In all cases studied, the transition between weak and strong association regimes, as defined by a peak in a system's specific heat, was not manifested by a rapid change in the chain dimensions. Some of the chain conformations become impossible due to the associated solvent, which results in chain stiffening and a continuous transition from a SAW to a swollen SAW state. This effect was found to be sensitive to both the size and concentration of the associating particles but, being local in nature, not the chain length. At lower solvent concentrations, this transition requires stronger association energies and is pre-empted by a partial chain collapse. This collapse only weakly affects the specific heat of the system, whereas the main contribution to the specific heat still comes from the restriction of local polymeric degrees of freedom. We also report on the swelling of the already collapsed polymer at relatively high association energies. It is the first time, to the best of our knowledge, that the conformational behavior of a polymer was rationalized in terms of the polymer-solvent attraction alone.

## ACKNOWLEDGMENTS

We thank A. Windle for useful discussions and acknowledge financial support from EPSRC Materials Modelling Initiative within the research consortium "Modelling of the Biological Interface with Materials."

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