MOLECULAR DYNAMICS SIMULATION OF THE LENNARD–JONES POLYMERS IN A GOOD SOLVENT*

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We carried out united-atom Langevin dynamics simulations of polymer's equilibrium state in a good solvent. Our primary goal was a pedagogical exposition of fundamental equilibrium properties of isolated polymers in dilutions with a model that contains many features of real materials. The polymer was chosen to be a three-dimensional chain of N identical beads (monomers) without internal structure. Each monomer interacted with its two neighbors by a harmonic potential, which modeled a chemical bond. Additionally all monomers within a chain were assumed to interact through the Lennard–Jones (LJ) potential. Interaction with solvent and with other polymers was introduced using Langevin forces. Analyzing internal energy per polymer and radius of gyration as function of temperature we observed a rapid globule to coil phase transition. Also we studied elastic properties of single polymer chain for temperatures below the transition and identified three regions with different elastic behavior. Typical chain lengths in our simulations ranged from 100 to 1000 monomers. The elaborated software package can easily be modified to study *e.g.* the effect of polymer stiffness on thermodynamic behavior.

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1. Introduction

Polymer properties are extremely sensitive to internal chemical structure of their building blocks and to applied solvent [1,2]. One of common example here are proteins, which change their functionality during denaturation. For instance, a 70% alcohol solution is able to denature proteins and enzymes inside of the bacterial cell. During the process both the secondary and tertiary

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protein's structures are disrupted and possibly destructed, which causes the protein to uncoil into a random shape. A similar in spirit is a general globule to coil transition in polymers between the high temperature coil and the lower temperature dense globule. It was predicted by Stockmayer [3] and observed experimentally by Tanaka group [4], where shape and size of the polymer was changed by modification of solvent conditions.

Most of theoretical work on the thermodynamics of globule-coil transition has been limited to isolated homopolymers. Two different approaches can be identified. The first one tries to construct free energy expression for polymer-solvent system with a single parameter denoting polymer size [5], while the second approach focuses on complex order parameter description of the spatial density distribution [6]. An alternative way to look into this transition comes from Monte Carlo and molecular dynamics simulations. Typically, the solvent is incorporated into effective interaction between monomers [7], while more advanced studies include solvent dynamics into the system [8]. The relative ease of simulations at low polymer densities provided detailed tests of theoretical predictions up to very large sizes [9]. A comprehensive overview of these studies has recently been given by Baysal and Karasz [10].

In this paper we look into details of this transition using a very simple, but still realistic solvent model, namely Langevin's thermal bath. The only control parameters are temperature, viscosity and number of monomers that built up a polymer. Our polymer chain consists of monomers interacting through Lennard–Jones potential between each other and by harmonic forces between nearest-neighbors along the chain. The model is described in details in Sec. 2. To solve polymer equations of motion we use molecular dynamic methods summarized in Sec. 3. The results are presented in Sec. 4. Paper ends with a short summary. Our primary motivation behind these studies is a pedagogical one, namely a comprehensive exposition of fundamental equilibrium properties of isolated polymers in a dilution with the model that contains many features of real materials.

2. Model

Present model is an extension of the one studied earlier by Oliveira *et al.* [11] and Calvo *et al.* [12]. It incorporates just enough details to observe the folding-unfolding transformations without impeding the efficiency of the simulations. More specifically, the united-atom model is chosen for a polymer chain, in which each monomer unit is treated as a bead in a bead-spring model. The polymer consists of N particles of mass m with their positions given by the three-dimensional vectors $\vec{x}_1, \ldots \vec{x}_N$. The motion of the l-th particle is governed by the Langevin equation:

$$m\ddot{\vec{x}}_l = \vec{F}_l(\vec{x}_1, \ldots, \vec{x}_N) - m\gamma\dot{\vec{x}}_l + \vec{\xi}_l(t) , \tag{1}$$

where the first term is a deterministic force; the second and the third ones stand for interaction with thermal bath obeying solvent and other polymers. The deterministic part $\vec{F}_l(\vec{x}_1, \ldots, \vec{x}_N)$ consists of two components: the harmonic interaction between nearest-neighbor particles and the Lennard–Jones interaction between all particles within the chain. It reads

$$\begin{aligned} \vec{F}_l(\vec{x}_1, \ldots, \vec{x}_N) &= -\boldsymbol{\nabla} U_{\mathrm{H}}(\vec{x}_{l+1} - \vec{x}_l) - \boldsymbol{\nabla} U_{\mathrm{H}}(\vec{x}_{l-1} - \vec{x}_l) \\ &\quad - \sum_{i=1, i\neq l}^{N} \boldsymbol{\nabla} U_{\mathrm{LJ}}(\vec{x}_i - \vec{x}_l) , \end{aligned} \tag{2}$$

where

$$U_{\mathrm{H}}(\vec{r}) = K(|\vec{r}| - a)^2 , \tag{3}$$

and where

$$U_{\mathrm{LJ}}(\vec{r}) = \varepsilon \left[\left(\frac{a}{|\vec{r}|} \right)^{12} - 2 \left(\frac{a}{|\vec{r}|} \right)^{6} \right] . \tag{4}$$

Here ε is the potential depth and a describes optimal distance between interacting molecules. The Lennard–Jones interaction contains a coefficient of 2 for the attractive part so that the minimum of this potential occurs at $|\vec{r}| = a$; $K = 16.67\,\varepsilon/a^2$ is chosen to make both potentials comparable on the right hand side of this minimum, see Fig. 1. A single chain is
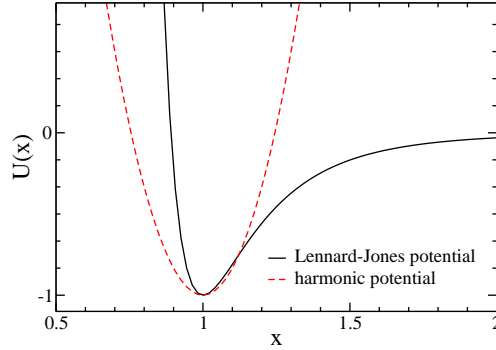

Fig. 1. Lennard–Jones potential and harmonic potential used in simulations. The first one acts between all pairs of monomers, while the harmonic interactions obey only nearest-neighbor united atoms. The zero of the harmonic potential is shifted on the vertical scale by -1 for clarity. The potentials cross at x close to the inflection point of the LJ part.

brought to thermal equilibrium by the random Gaussian force $\vec{\xi_l}(t)$ satisfying fluctuation–dissipation theorem:

$$\left\langle \xi_l^a(t)\xi_k^b(t') \right\rangle = 6m\gamma k_{\mathrm{B}}T\delta_{kl}\delta^{ab}\delta(t - t'), \tag{5}$$

where a and b represent vector coordinates; l and k enumerate chain components; T stands for temperature and k_{B} for Boltzmann constant.

3. Simulation

Simulation of the model is performed using ordinary molecular dynamics [13]. The equations of motion (1) are integrated with the help of the velocity Verlet algorithm [14]. Unit of time is chosen to be approximately equal to the chain's shortest period of the harmonic normal mode: $\frac{\pi}{6}\sqrt{\frac{2\varepsilon}{ma^2}}$. This, in turn, allows to set the optimal time step Δt of 0.01 for the numerical integration. Energy is measured in units of ε and temperature in $k_{\mathrm{B}}T/\varepsilon$. Natural unit of distance is given by the constant a. The random force is fixed constant over one time step and, in agreement with (5), taken equal to

$$\vec{\xi_l}(t) = \sqrt{\frac{6m\gamma\, k_b T}{\Delta t}} \cdot \vec{\eta}_l(t), \tag{6}$$

where components of the random vector $\vec{\eta}_l(t)$ are independent Gaussian variables of vanishing mean and of unit variance. The random numbers from the Gaussian distribution are generated with the help of Marsaglia and Zaman generator [15]. Typical simulation run takes about 10^6 time steps.

4. Results

Our first objective is to explore properties of the chain as function of T and N. At low temperatures the polymer forms a globule due to Lennard–Jones interaction between every pair of molecules. Three examples of polymer configurations at $T = 0$ are shown in Fig. 2. Taking approximation of uniform mass distribution within the globule leads to proportionality between its volume and the number of monomers N. In this case the gyration radius r is proportional to $N^{1/3}$. It is worth to point out, that the above assumption is not a priori obvious. For example, in the case of purely harmonic interaction between all molecular pairs one would get at $T = 0$ a uniform distribution of monomers on a sphere, without molecules in its interior [16]. Interestingly, the folding process is found to be very fast away from the transition. For $T = 1$ it takes only a few thousands time steps to convert an extended polymer configuration into a globule, as illustrated in Fig. 3.
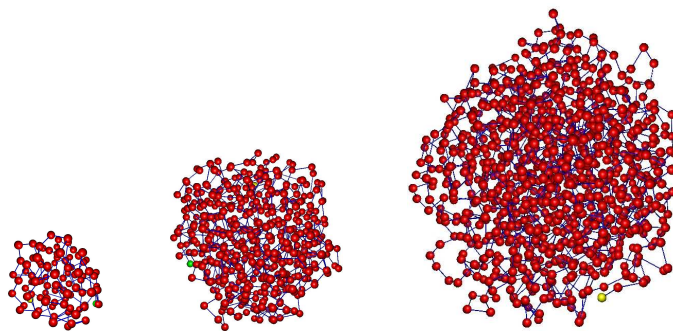
Fig. 2. Snapshots of chain configuration taken from equilibrium states at $T \to 0$. Pictures differ in chain's length: the left one is for $N = 100$ and it's gyration radius is equal to $r = 2.85$; the middle one is for $N = 500$ with $r = 4.80$, while the right one is for $N = 1000$ with $r = 8.15$.
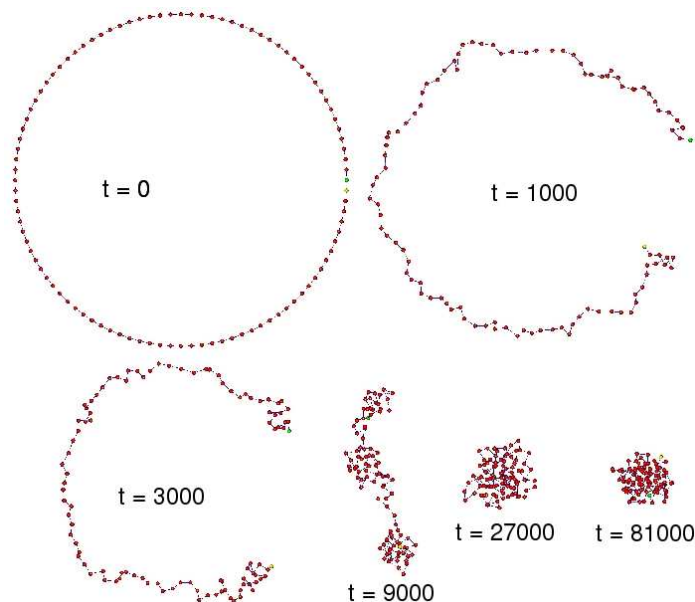

Fig. 3. Snapshots displaying folding process at $T = 1$ for polymers of $N = 100$. Successive snapshots are parameterized by simulation time t.

At high enough temperatures the interaction with thermal bath overcomes the Lennard–Jones forces and polymer unwinds. Fig. 4 shows typical equilibrium snapshots for different temperatures.

The unwinding scenario goes in the following way: with increasing temperature the $T = 0$ state starts to fluctuate, where fluctuations are strongest close to the surface. The Lennard–Jones forces alone cannot hold parti-
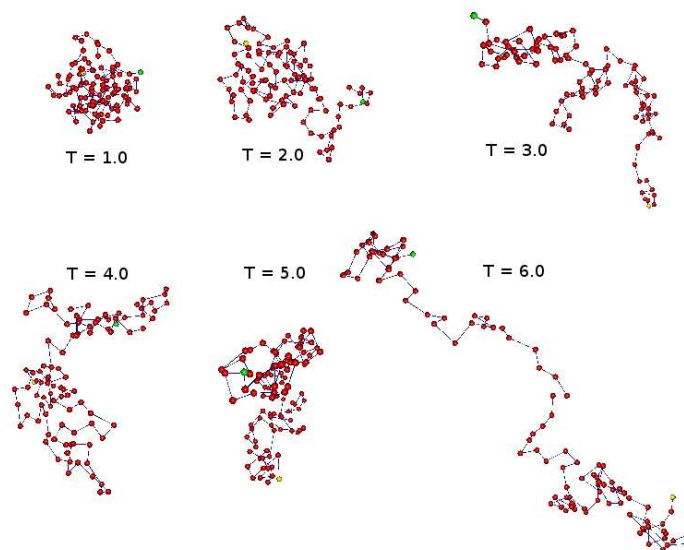
Fig. 4. Temperature evolution of polymer containing $N = 100$ monomers. Example snapshots for $1 < T < 6$.

cles together, so for $T = 3.0$ the shape of the polymer looks random, but neighboring monomers keep, on average, fixed distance. This is enforced by harmonic potential, which protects chain from breaking at nonzero temperatures. The transition between the two regimes takes place at $2 \lesssim T \lesssim 2.5$ Thus, for $T \gtrsim 2.5$ we expect the shape of the polymer to match a self avoiding random walk path with gyration radius following a simple power low $r \sim N^\nu$. Exact value of ν for the three dimensional self avoiding random walk is unknown, but the Flory brilliant calculation [1, 2] gives $\nu = 3/5$, which so far agreed to within a percent with numerical estimates. To verify as whether these estimates also hold in our case we examined dependence of the gyration radius on temperature for chains with number of monomers varying from $N = 10$ to $N = 1000$. Results, shown in Fig. 5, fully support the predicted behavior for ν. The transition between the globule and the coil is clearly seen for $T \approx 2 - 2.5$ and is associated with a peak in the heat capacity. The peak becomes sharper as the size of the polymer increases. Additionally, the temperature where the shape transformation takes place is practically independent of polymer's size. To explain this universality one observes that the transition appears when the thermal energy becomes comparable with the Lennard–Jones interaction between nearest-neighbor monomers. The lowest number of neighbors is on the surface of the globule, where the unwinding process is initialized. As the Lennard–Jones potential does not allow particles to penetrate the core $|\vec{r}| < a$ and it vanishes at
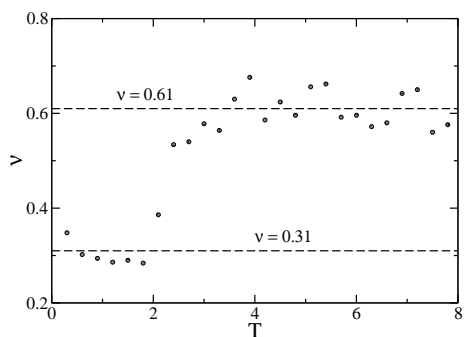
Fig. 5. Scaling exponent ν obtained from relation between polymer's radius and polymer's size *versus* temperature. For low temperatures $\nu \approx 0.31$ and for high temperatures $\nu \approx 0.61$. Each point on the plot results from the least square linear fit between $\ln r$ and $\ln N$ for fixed temperature, where N varies between 10 and 1000. Error bar along ν axis is of the order of 0.1.

large distances this number is almost independent of the globule size. Consequently, the temperature behavior of unwinding process for small and large globules appears similar. Exact transition temperature is connected with the average number of nearest-neighbors close to the surface of the globule. This number can be extracted from the radial distribution of monomers measured relative to the polymer's center of mass, which is shown in Fig. 6. At low temperatures ($T \approx 0.1$) this distribution shows clear substructure with maxima around $r \approx 1.3$ and $r \approx 2.1$. It suggests that monomers inside the globule tend to form spherical shells. For higher temperatures ($T \geq 3.0$) the distribution does not show any temperature dependence.
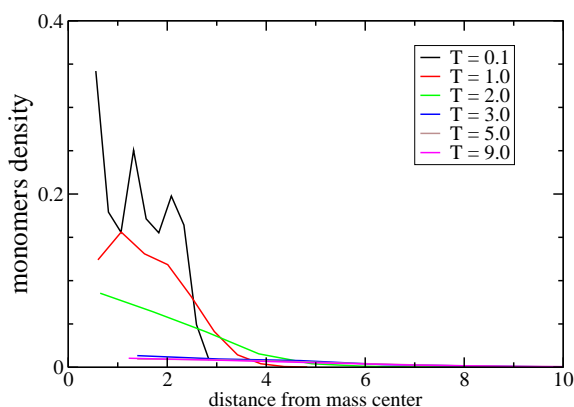

Fig. 6. Radial distribution $\rho(|\vec{r}|)$ calculated from polymer's center of mass for $N = 100$.

The above observations give us already a rough estimate for the transition temperature. A more precise number can be obtained from the analysis of the average energy of the chain. This is presented in Fig. 7 along with temperature variation of the gyration radius. Clearly, from energy plot two regions of different heat capacity can be distinguished. The transition temperature separating these regions is $T_0 \approx 2.18$.
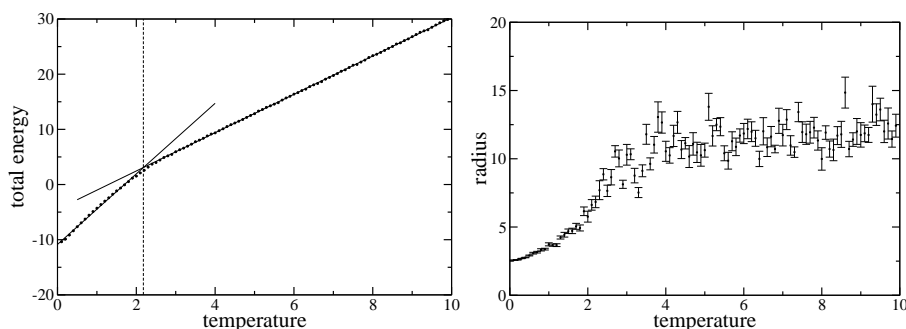

Fig. 7. Average energy per monomer and gyration radius *versus* temperature for polymer containing $N = 100$ monomers. Transition occurs at $T \approx 2.18$.

Finally, we examine the elastic properties of the chain. More specifically the polymer is stretched out by an external stretching force F acting on the chain's ends. F is measured with respect to $F_0 = 2.70 \, \varepsilon/a$, the maximal attractive force between nearest neighbors interacting through the Lennard–Jones potential. The effect of stretching on radius of gyration at $T = 1.0$ and $N = 100$ is shown in Fig. 8. Note that a little stretching ($F < 1.5$)
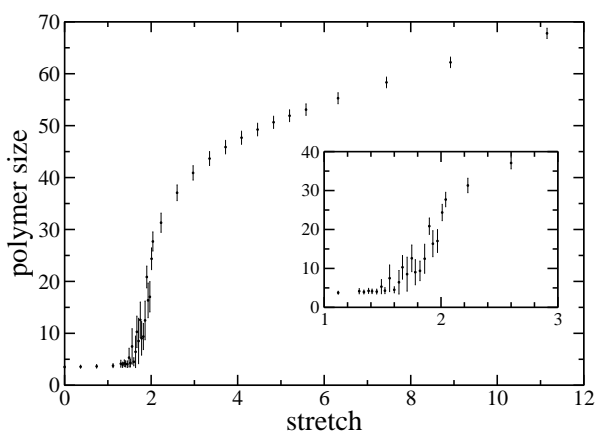

Fig. 8. Radius of gyration under stretch at $T = 1.0$. The chain consists of $N = 100$ monomers.

has almost no influence on the globule. For larger external forces ($1.5 < F < 2.5$) the Lennard–Jones interactions start to "crack", which rapidly unwinds the polymer. Further stretching causes linear elongation due to linear characteristic of harmonic force.

5. Summary

The Lennard–Jones polymer studied in this paper is characterized by strong chemical bond between nearest neighbors and weaker, short-ranged van der Waals interaction between all monomers. It displays two distinct equilibrium states: the high temperature coil state and the lower temperature dense globule state. Simulations show that the transition occurs between these two states at the temperature, which is practically independent of the number of monomers. In addition, the scaling exponent ν for N dependence of radius of gyration follows the estimates given by Flory. Therefore, the model can serve as a prototype for studying globule to coil phase transition. The globule-coil transition can also be induced by an external stretching force, even at very low temperatures, in which case three regions of different elastic behavior can be identified.

Considerable theoretical effort has recently been put into studying the evolution of the coil-globule transition as function of polymer stiffness, which is yet another important parameter characterizing real polymers and not included in our modeling. In particular, for flexible polymers this transition is predicted to be continuous, but becomes first order as the stiffness increases. In our simulation the results shown in Fig. 7 support the view of continuous transition for the flexible case. The same transition character is observed under applying the external stretching force.

Associated with polymer stiffness is another interesting phenomenon, namely a possibility for the coil-globule transition to become preempted by a coil-solid transition. Such highly ordered phases are indeed known for stiff polymers, where hexagonal order of dense DNA state can serve here as an example. All these effects can be modeled with extended version of the simulated system.

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