Statistical analysis of two-dimensional cluster structures composed of ferromagnetic particles based on a flexible chain model

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We investigate two-dimensional cluster structures composed of ferromagnetic colloidal particles, based on a flexible chain model, by the configurational-bias Monte Carlo method. We clarify the dependence of the probabilities of the creation of different types of clusters on the dipole-dipole interactive energy and the cluster size.

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It is well known that ferromagnetic colloidal particles coagulate to form clusters under certain conditions, and that a variety of structures are created depending on the control parameters such as the temperature, the number density of particles, the intensity of external magnetic fields, and so on. It is important to study the cluster structures formed by ferromagnetic particles in a liquid solvent from a scientific point of view, since this problem is related to the statistical physics of dipolar hard sphere fluids and the physics of complex fluids such as magnetic fluids. It is also important from a practical point of view since the macroscopic physical properties may be directly related to the cluster structures and therefore may be altered dramatically by changing the control parameters. de Gennes and Pincus [1] predicted that two different cluster structures, that is, randomly oriented chains and closed rings, may appear in ferromagnetic particle disperse systems in the absence of a magnetic field. Since then, a number of experiments have been carried out to observe the actual structures created in ferromagnetic colloidal systems [2–9] and, in fact, chain and ring structures have been observed in monolayer systems [2–4,6]. Such pattern formations created by ferromagnetic particles in two-dimensional systems in the absence of a magnetic field have also been investigated numerically [4,10–14]. One of the important nondimensional control parameters that determine the cluster structures in ferromagnetic colloidal systems is the ratio of the interparticle dipole-dipole interactive energy to the thermal energy: $\lambda \equiv |\boldsymbol{m}|^2/4\pi\mu_0 d^3 kT$, where $\boldsymbol{m}$, μ_0, d, k, and T are, respectively, the dipole moment vector of a particle, the magnetic permeability, the diameter of a particle, the Boltzmann constant, and the temperature. Although the cluster structures formed by ferromagnetic particles have been studied theoretically, numerically, and experimentally, there is still a lack of information about the relation between the probability of the production of different types of clusters such as rings and open chains and the control parameter λ. What is more, the value of λ lay in a relatively narrow range in previous analyses of the relation between the probability and λ, and therefore it is necessary to analyze cluster structures under a wider range of λ.

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In this paper, we investigate the dependence of the cluster structures formed in a two-dimensional dilute ferromagnetic particle disperse system under a zero magnetic field on the control parameter λ. Such a low number density colloidal system can be considered as a mixture of independent clusters of different sizes, in which case the interactions between clusters are negligible [12,15,16], and therefore each cluster is supposed to be in equilibrium. Under the above circumstances, we focus on the structures of such isolated clusters created in a two-dimensional system. It has also been shown both theoretically [17,18] and numerically [12] that there are few branches in each cluster in the case of sufficiently low number density systems. Furthermore, according to the experiment carried out by Helgesen *et al.* [2], networklike branched clusters are not formed even at a very high λ ($\lambda = 1360$). Therefore, we create each cluster using a flexible chain composed of ferromagnetic particles, as illustrated in Fig. 1. We analyze the statistical characteristics of the ferromagnetic cluster structures on the basis of the equilibrium structures of the flexible chains. In this model, all the ferromagnetic particles are spheres of equal diameter d, and they interact with each other via the hard-sphere and dipole-dipole potentials [13,14]. The particle-particle contact angle θ_i and the angle φ_i of dipole moment vector $\boldsymbol{m}_i$ are changed continuously (see Fig. 1). Therefore, this model can create the different types of clusters such as open chains, rings, and clusters composed of a chain with ring(s), which have been observed in experiments [2–4,6]. In this study, we analyze the structures of flexible chains in canonical ensembles by the configurational-bias Monte Carlo method [19,20], which

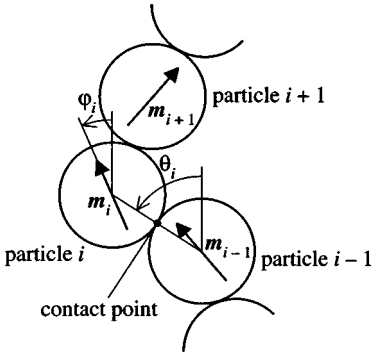

FIG. 1. A flexible chain composed of ferromagnetic particles.

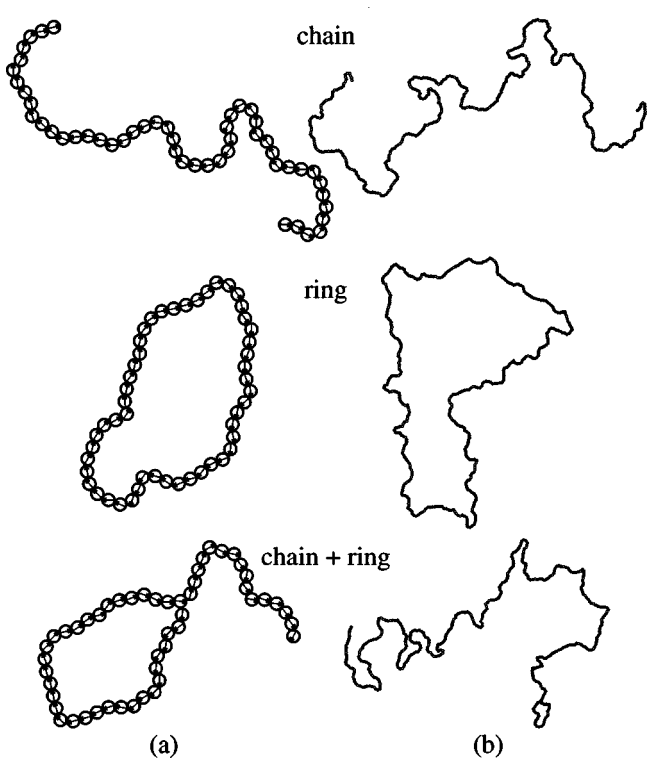

FIG. 2. Typical cluster structures created when $\lambda<10$. (a) $\lambda=5$, $N=50$; (b) $\lambda=5$, $N=400$.

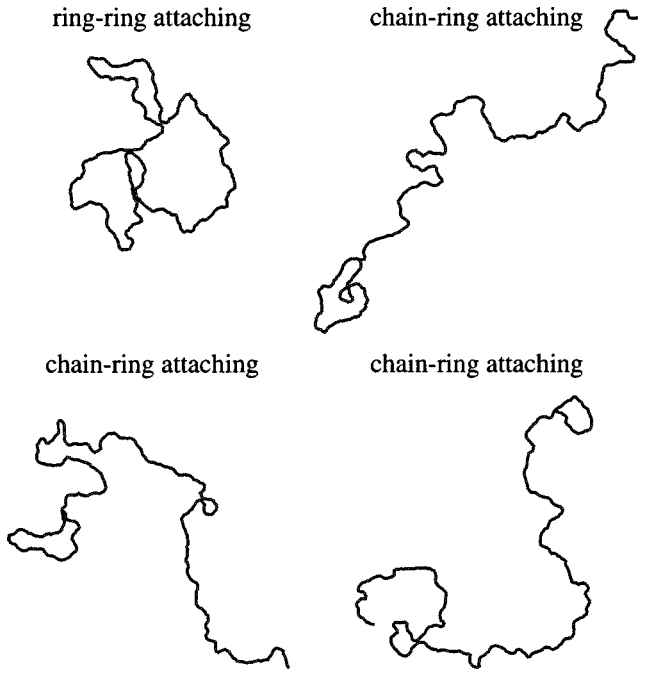

FIG. 3. Typical defect clusters created by the present flexible chain model. $\lambda=7$, $N=400$.

has been used for investigation of the structures of chain molecules, to clarify the dependence of the cluster structures on the control parameter λ and the cluster size N. If we consider a flexible chain cluster composed of N ferromagnetic particles as a chain molecule composed of N segments, in which case the bond length is fixed at the diameter of a ferromagnetic particle and the segment-segment interactions are hard-sphere and dipole-dipole interactions, the configurational-bias Monte Carlo technique can be applied to the structural analysis of ferromagnetic flexible chains as chain molecules [19,20].

We investigate the cluster structures for $5\leqslant\lambda\leqslant100$ and $6\leqslant N\leqslant800$ using 20–1000 ensemble averages depending on λ and N. We generated 100 ensembles of chain clusters for $N\leqslant200$, where N is the number of ferromagnetic particles in a chain cluster, and 50 and 20 ensembles for $200<N\leqslant566$ and $N=800$, respectively, except for the following cases: 1000 ensembles for $(\lambda,N)=(5,6)$, (5,9), (5,13), (5.5,6), (5.5,13) and (5.5,25); 50 ensembles for $(\lambda,N)=(50,200)$ and (100,50); and 20 ensembles for $(\lambda,N)=(50,400)$. First of all, let us focus on the cluster structures when the dipole-dipole interactions are not very strong, $\lambda<10$. Figure 2 shows snapshots of clusters for $\lambda=5$, $N=50$ [Fig. 2(a)] and $\lambda=5$, $N=400$ [Fig. 2(b)]. When $\lambda<10$, mostly chains and rings are created. Although clusters composed of a chain with a ring appear, the mean probability is only 2.1% when $\lambda<10$. We show typical defect clusters obtained by the flexible chain model in Fig. 3 for $\lambda=7$, $N=400$. Defect clusters were defined in Ref. [12] as the ones that contain particles having more than two neighboring particles. The defect clusters obtained by the present flexible chain model are *self-attaching* chains such as chain-ring(s) and multiring composite clusters. These types of cluster were also observed in two-dimensional Monte Carlo simulations carried out by Tavares, Weis, and Telo da Gama [12]. Note that we consider a cluster as a ring when the distance between the two particles at each end of a chain is shorter than the cutoff radius r_c. The dependence of the probability of ring clusters being produced, P_{ring}, on the control parameter λ and the number of particles in a cluster, N, is shown in Fig. 4. We checked the effect of the cutoff radius on P_{ring} by changing r_c to $1.1d$, $1.15d$, and $1.2d$, as was done by Tavares, Weis, and Telo da Gama [12], and confirmed that there is no qualitative change in the ring clusters' production features caused by the difference in the value of r_c. In this study, we set $r_c=1.1d$. When $\lambda<10$, P_{ring} becomes maximum at a certain cluster size and as λ increases P_{ring} increases [Fig. 4(a)]. Once λ reaches 10, P_{ring} becomes almost 1 irrespective of the number of particles as long as $6\leqslant N\leqslant800$ [Fig. 4(b)]. However, when λ becomes very large, although P_{ring} is still almost 1 when the number of particles in a cluster is low, P_{ring} starts decreasing rapidly with an increase in the cluster size [Fig. 4(b)]. Let us first focus on the ring cluster production features when the dipole-dipole interactions are not very strong. In the case of two particles, the interactive potential energy becomes lowest when they contact each other in such a way that two dipole moment vectors line up in the same direction (*nose-to-tail* contact). When the number of particles is greater than 3, however, the internal potential energy of a ring becomes lower than that of a chain [1]. As N increases, the diameter of a ring increases and the dipole moment vectors of adjacent particles can be lined up in the same direction. As a result, ring clusters predominate more and more from the point of view of potential energy with an increase in N. However, once the ring perimeter becomes much greater

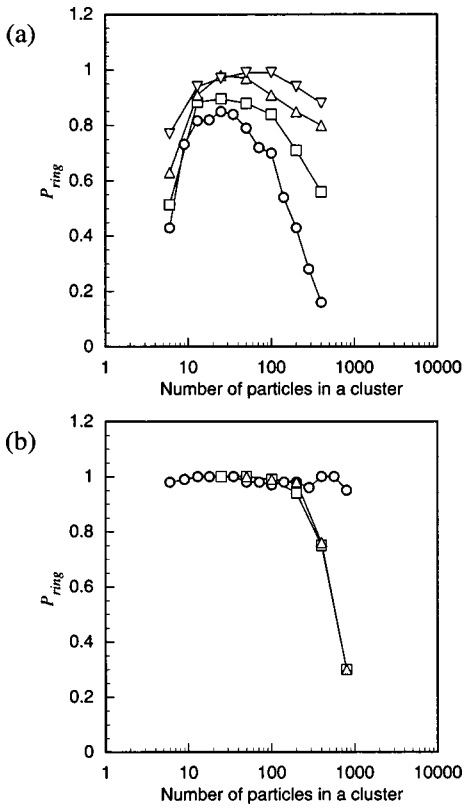

FIG. 4. Dependence of the probability of ring clusters being produced, P_{ring}, on the control parameter λ and the cluster size N. (a) ○, λ=5; □, λ=5.5; △, λ=6; ▽, λ=7. (b) ○, λ=10; □, λ=50; △, λ=100.

than the effective length of the interparticle potential energy, the energy difference between rings and open chains becomes constant and therefore forming a ring cluster does not give any extra advantage from the point of view of potential energy. From the point of view of entropy, on the other hand, forming ring clusters is disadvantageous. The entropy difference between ring and chain clusters becomes greater as the number of particles increases. The ring formation characteristics as shown in Fig. 4(a) can be explained qualitatively by the above energy vs entropy competitions. Let us carry out more quantitative analysis. Suppose clusters are composed of N particles. The probability of ring clusters being produced, P_{ring}, is evaluated as follows:

$$P_{ring}(\lambda,N)\approx\left[1+\frac{\Omega_{NR}(N)}{\Omega_R(N)}\exp\{-\lambda[\overline{\varepsilon}_{NR}(N)-\overline{\varepsilon}_R(N)]\}\right]^{-1}, \tag{1}$$

where $\Omega_R(N)$ and $\Omega_{NR}(N)$ are, respectively, the total number of ring clusters and that of nonring clusters. $\lambda\overline{\varepsilon}_R(N)$ and $\lambda\overline{\varepsilon}_{NR}(N)$ are the mean energies of rings and nonrings, which are nondimensionalized by kT. Since λ is not very large, we approximate $\lambda\overline{\varepsilon}_R(N)$ and $\lambda\overline{\varepsilon}_{NR}(N)$ by the potential energies of a ring and a chain as obtained by Jund *et al.* [21]:

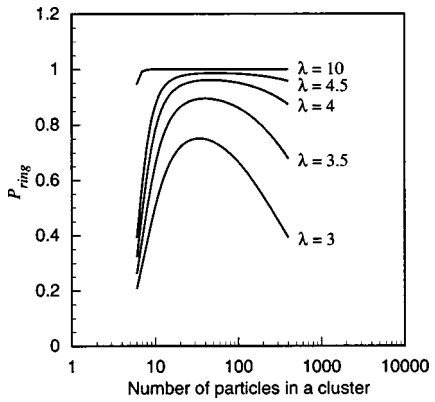

FIG. 5. Dependence of P_{ring} on λ and N obtained analytically by Eqs. (1)–(3).

$$\lambda[\overline{\varepsilon}_{NR}(N)-\overline{\varepsilon}_R(N)]\approx-2.4\lambda(N-1)+\frac{2.4\lambda N}{4}\left\{3+\cos\left(\frac{2\pi}{N}\right)\right\}. \tag{2}$$

We also employ a two-dimensional random walk model [22] for estimating $\Omega_{NR}(N)/\Omega_R(N)$ as follows:

$$\frac{\Omega_{NR}(N)}{\Omega_R(N)}\approx\frac{\exp\{-(N-1)\}-\exp[-r_c^2/(N-1)d^2]}{\exp[-r_c^2/(N-1)d^2]-\exp[-1/(N-1)]}, \tag{3}$$

where r_c is the cutoff radius used for defining a ring. The dependence of P_{ring} on λ and N obtained by Eqs. (1)–(3) is shown in Fig. 5. The above semiquantitative analysis explains very well the P_{ring} features for $\lambda\leqslant 10$ obtained by the present numerical analysis, despite the rough estimation (see Fig. 4). This means that Eq. (1) is basically correct in relatively weak interaction cases.

When λ is very large, as we mentioned, P_{ring} is still almost 1 for small N, but decreases rapidly with an increase in N [see Fig. 4(b)]. In this region, the probability of the production of clusters that are composed of a chain with one or two rings attaching to the end(s) increases (see Figs. 2 and 3). What is more, different types of clusters as shown in Fig. 6 are created. When the dipole-dipole interaction is strong and the number of particles in a cluster is large, some parts, which we call internal chains, tend to stick to each other in a cluster in the following two ways: either (a) two internal chains are stuck in parallel, in which case the dipole moments in the two chains are directed in an antiparallel direction [see Fig. 6(a)], or (b) internal chains are stuck in a staggered way, in which case the dipole moments in the two chains are pointing in the same direction [see Figs. 6(a) and 6(b)]. In the experiment carried out by Wen *et al.* [4], such structures as illustrated in Fig. 6 were clearly observed. Note that the value of the control parameter λ was as large as 1.69×10^6 in the above experiment.

Finally, we investigate the connectivity between particles in clusters to clarify the cluster structures more precisely. We define the connectivity N_c as the total number of contact points in a cluster minus $N-1$, which is the number of contact points in a simple chain composed of N particles, where

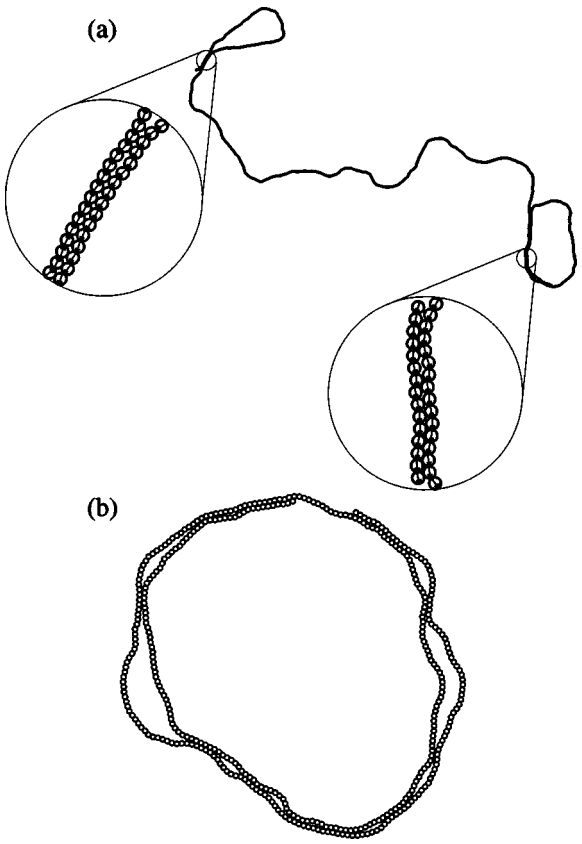

FIG. 6. Complex structures created when both λ and N are large. (a) $\lambda=50$, $N=800$; (b) $\lambda=50$, $N=400$.

the same cutoff radius r_c is used for defining the particle-particle contact. Therefore, for example, $N_c=0$ and 1, respectively, in the case of a simple chain and a simple ring. The dependence of the mean connectivity $\langle N_c\rangle$ on λ and N is shown in Fig. 7. When $\lambda\leqslant 10$, $\langle N_c\rangle$ is less than or equal to 1 since either simple ring or chain clusters are mostly created in such relatively weak interaction cases, whereas when $\lambda=50$ and 100, $\langle N_c\rangle$ increases rapidly once N exceeds the critical values. In other words, complex structures such as those shown in Fig. 6 are created only when the dipole-dipole interactions are strong and the cluster size is large. The above features can be understood if we consider the effective interactive energy between two chains, which are placed either in parallel or in a staggered way. In both cases, the effective potential energy between two chains becomes lower with an increase in the number of particles included in each chain. The energy is lowered, for instance, by approximately $250kT$ in the parallel case and by $500kT$ in the staggered case by increasing the number of particles in each chain from 5 to 20 in the case of $\lambda=100$. Chain-chain connections, however, occur only when λ is large, since entropy is reduced with an increase in the number of connecting points. As a result, the internal chain-chain connections as shown in Fig. 6 are created only when both λ and N are large [see also Figs. 4(b) and 7]. According to Fig. 7, the critical

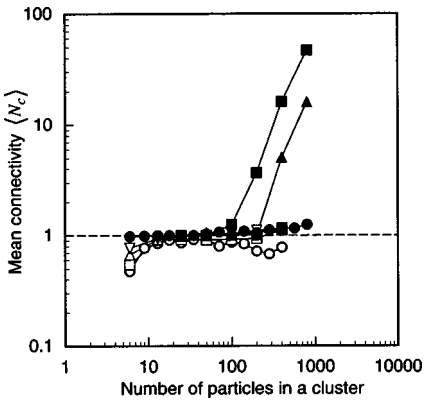

FIG. 7. Dependence of the mean connectivity $\langle N_c\rangle$ on λ and N. ○, $\lambda=5$; □, $\lambda=5.5$; △, $\lambda=6$; ▽, $\lambda=7$; ●, $\lambda=10$; ■, $\lambda=50$; ▲, $\lambda=100$.

cluster size at which the mean connectivity starts increasing rapidly is shorter when λ is 50 than when λ is 100. This relation between the critical cluster size and λ may be understood if we also consider the internal energy loss caused by the bending of the flexible chains in the formation of the complex structures shown in Fig. 6. The internal energy is reduced by an increase in the number of connecting points as we showed above, but the energy loss caused by the bending of the chains increases at the same time. Therefore, the curvature of the chains should be as small as possible from the point of view of the reduction of the energy loss caused by the distortion of chains. The energy loss increases with an increase in λ. As a result, the critical cluster size becomes shorter when λ is 50 than when λ is 100 from the point of view of internal energy.

In summary, we investigated the structures of isolated clusters composed of ferromagnetic particles, based on a flexible chain model, by the configurational-bias Monte Carlo method. Although the cluster size distributions cannot be obtained by this analysis, we can see the details of cluster structures and the probability of the creation of different types of clusters. The computational time is also reduced quite remarkably by employing the present method, compared to the conventional numerical methods. This approach can easily be extended to three-dimensional analysis of cluster structures. We believe that the equilibrium structures of clusters under various conditions can be analyzed systematically and efficiently by applying the present method in combination with the conventional methods.

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[1] P. G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).
[2] G. Helgesen, A. T. Skjeltorp, P. M. Mors, R. Botet, and R. Jullien, Phys. Rev. Lett. **61**, 1736 (1988).
[3] G. Helgesen and A. T. Skjeltorp, J. Appl. Phys. **69**, 8277 (1991).
[4] W. Wen, F. Kun, K. F. Pál, D. W. Zheng, and K. N. Tu, Phys. Rev. E **59**, R4758 (1999).
[5] C. F. Hayes, J. Colloid Interface Sci. **52**, 239 (1975).
[6] V. F. Puntes, K. M. Krishnan, and A. P. Alivisatos, Science **291**, 2115 (2001).
[7] L. N. Donselaar, P. M. Frederik, P. Bomans, P. A. Buining, B. M. Humbel, and A. P. Philipse, J. Magn. Magn. Mater. **201**, 58 (1999).
[8] F. Gazeau, E. Dubois, J.-C. Bacri, F. Boué, A. Cebers, and R. Perzynski, Phys. Rev. E **65**, 031403 (2002).
[9] J. E. Weber, A. R. Goñi, D. J. Pusiol, and C. Thomsen, Phys. Rev. E **66**, 021407 (2002).
[10] R. W. Chantrell, A. Bradbury, J. Popplewell, and S. W. Charles, J. Appl. Phys. **53**, 2742 (1982).
[11] J. J. Weis, Mol. Phys. **93**, 361 (1998).
[12] J. M. Tavares, J. J. Weis, and M. M. Telo da Gama, Phys. Rev. E **65**, 061201 (2002).
[13] H. Morimoto and T. Maekawa, Int. J. Mod. Phys. B **13**, 2085 (1999).
[14] H. Morimoto and T. Maekawa, J. Phys. A **33**, 247 (2000).
[15] M. A. Osipov, P. I. C. Teixeira, and M. M. Telo da Gama, Phys. Rev. E **54**, 2597 (1996).
[16] A. Yu. Zubarev and L. Yu. Iskakova, Phys. Rev. E **65**, 061406 (2002).
[17] T. Tlusty and S. A. Safran, Science **290**, 1328 (2000).
[18] P. Pincus, Science **290**, 1307 (2000).
[19] D. Frenkel, G. C. A. M. Mooij, and B. Smit, J. Phys.: Condens. Matter **4**, 3053 (1992).
[20] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic, San Diego, CA, 1996).
[21] P. Jund, S. G. Kim, D. Tománek, and J. Hetherington, Phys. Rev. Lett. **74**, 3049 (1995).
[22] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).