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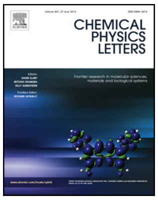

Indirect interacting force between nanoparticles within athermal polymers: A Langevin dynamics study

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ABSTRACT

Using molecular dynamics (MD) simulations, we have measured the indirect interacting force between surface-separated nanoparticles (NPs) within athermal polymers. Our simulations confirm the existence of repulsion between NPs with separation beyond the range of attractive forces. We demonstrate that both attractive and repulsive forces are monotonically strengthened by increasing polymer concentration and/or enlarging the size of NPs. The indirect interacting force as function of separation between NPs has no dependence on polymer chain length for semi-dilute polymers. Moreover, we have calculated the radial distribution functions of monomers surrounding NPs, the density profiles appear to corroborate the measured forces.

1. Introduction

Adding nanoparticles (NPs) within polymers is of extensive interests in the study of polymer physics and the practical applications of polymer based nanomaterials [1–5]. The physical properties of polymer-NP composites can be significantly improved as a result of intentionally controlling the equilibrium distribution of NPs [6–10]. Dispersion of NPs is thought to be the prerequisite for taking advantages of NPs' performance characteristic originated from their nano-scale size effect [11–14]. On the other hand, it is interesting to construct hierarchically distributed aggregation of NPs with desired structure, through tuning the macroscopic conditions of polymer-NP composites [3,15]. In general, system of polymer-NP composites involves various entropic and enthalpic effects [16–20], which enrich the interacting mechanism between different elements of polymer-NP composites. The intricate interplay between entropy and enthalpy, and its influence on the local distribution of polymer segments, is always hard to be directly detected and distinguished in experimental and theoretical studies [21–24].

The local conformation of polymer segments at the surface of NPs appears to be disturbed owing to the stretching of NPs to polymer chains [11,12]. In order to minimize the total disturbance of NPs to polymers, indirect interacting force is induced between surface separated NPs. This kind of force gives strong effect on the static and dynamical behaviors of polymer-NP composites, like the spontaneous structure formation, phase separation, or flocculation. Thereby, the indirect force is in high demand to be understood in detail. A quantitative calculation of the indirect interacting force between nanoscale particles, under varied conditions, is still absent. More insights into the physics understanding of the complicated behaviors of polymer-NP composites can be gained by computational studies. It is available to isolate individual interactions using MD simulations. In the present work, a MD simulation based calculation model is proposed to study the mutual indirect interacting force and the corresponding physics for NPs in athermal polymers.

2. Simulation method

In our simulations, polymer chains are modeled using a bead-spring model without explicit twisting or bending potential, i.e. the bonds are freely rotating and freely jointed within the limits set by excluded volume interactions with nearby monomers. The connectivity between monomers is enforced by a finite extensible nonlinear elastic (FENE) potential [25], defined as

$$U_{\mathrm{FENE}}(r) = -0.5\kappa {R_0}^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right], r < R_0, \qquad (1)$$

where $\kappa = 30\epsilon_0/{\sigma_M}^2$ is the spring constant, $\epsilon_0 = 1$, and $R_0 = 1.5\sigma_M$ being the maximum pair length to prohibit the interaction of chains. Here, $\sigma_M = \sigma_0 = 1$ stands for the monomer size, and $\sigma_{NP} = 3$ represents the NP size. The NP-monomer and monomer–monomer

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interactions were modeled as truncated and shifted Lennard–Jones (LJ) potentials

$$U_{\mathrm{LJ}}(r) = 4\epsilon_0 \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6} - \left(\frac{\sigma_{ij}}{r_c}\right)^{12} + \left(\frac{\sigma_{ij}}{r_c}\right)^{6} \right], r < r_c, \tag{2}$$

where σ_{ij} stands for the mean size of the two particles (ith and jth) involved in the pair interaction. $\sigma_{ij} = \sigma_M$ and $\sigma_{ij} = (\sigma_{NP} + \sigma_M)/2$ for pairs of monomer–monomer and pairs of monomer-NP, respectively. The strength of the NP-monomer and monomer–monomer interactions is fixed at $\epsilon_0 = 1$. The parameter r_c is the cut-off distance. It is easily verified that without any cutoff this potential has a minimum at $r_{\min} = 2^{\frac{1}{6}}\sigma_{ij}$ with the depth $U_{LJ}(r_{min}) = -\epsilon_0$. In turn, once a cutoff $r_c = 2^{\frac{1}{6}}\sigma_{ij}$ is implemented, the attractive contribution to this potential is eliminated, i.e. $U_{\mathrm{LJ}}(r) = 0$ when $r > r_c$, and in this way athermal monomer–monomer interactions are simulated. Note that there is no direct interaction between NPs when they are surface separated with each other.

In this work, the LJ system of units is used. It is defined using a model polymer with a LJ pair potential, featuring a bead size $\sigma_M = 1$ (one length unit), a potential depth $\epsilon_0 = 1$ (one energy unit) and a mass $m = 1$ (one mass unit). The temperature is then normalized to that energy unit using a Boltzmann constant $k_B = 1$, and the time unit is $\tau_{LJ} = d(m/\epsilon)^{1/2}$, which is the oscillation time of a monomer inside the LJ potential, at small amplitudes so that the harmonic approximation is valid. The equation of motion for the displacement of a particle (monomer or NP) with index i is given by the Langevin equation [26,27]:

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\nabla U_i - \zeta \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i\,, \tag{3}$$

where $m_i = 1$ for monomers and $m_i = (\frac{\sigma_{NP}}{\sigma M})^3$ for NPs, $\mathbf{r}_i$ is the position of the ith particle, and U_i is the total conservative potential energy acting on the ith particle. The quantity $\mathbf{F}_i$ is a random external force without drift and a second moment proportional to the temperature and the friction constant ζ. In our simulations, the temperature $T = 1$, a time-step $\Delta t = 0.001\tau_{LJ}$, and the friction coefficient $\zeta = \tau_{LJ}^{-1}$ were implemented.

Every simulation was carried out at constant temperature in a cubic box with size $d = 30$. The boundary conditions in all directions are periodic. Throughout the Letter, the volume ratio $\eta = N_{\mathrm{Monomer}}\pi\sigma_M^3/6d^3$ was used to define the polymer concentration, N_{Monomer} being the number of monomers inside system. All simulations started from a phase in which polymers were distributed fairly homogeneously inside the system. In our simulations, each system was relaxed by a simulation of 10^7 timesteps (corresponding to 5×10^4 LJ-times), followed by 3×10^7 time-steps (1.5×10^5 LJ-times) of data acquisition, during which a trajectory of 2000 conformations was stored for the subsequent data analysis.

3. Force calculation

In calculating the indirect force, there are two NPs included in the system. One NP was fixed at the origin while the second one was restricted with freedom in only one dimension and attached via a stiff harmonic potential $f_{\mathrm{spring}}(r) = -k(r - r_0)$ with $k = 150$, r_0 denotes the natural length of this spring potential. The harmonic potential is the only direct interaction between the two NPs, enforcing a well defined average distance $\bar{r}$ over a large number of timesteps for each choice of r_0. The average distance $\bar{r}$ was then used to measure the effective forces acting on the two NPs with separation larger than the diameter of NPs. More specifically, the equation

$$f_{\mathrm{spring}}(\bar{r}) + f(\bar{r}) = 0 \tag{4}$$

has to hold, where $f(r)$ denotes the indirect force induced by surrounding polymers. A positive value of $f(r)$ indicates an repulsion between the NPs. In the opposite, NPs are attracted to each other when $f(r)$ is negative. In Eq. (4) we have expressed the forces as function of the average distance, instead of using ensemble-averaged forces. Since fluctuations about r_0 remained very small, both approaches delivered identical results within the accuracy achieved in the simulations. Note that we set the energy unit to $k_BT = 1$ in Eq. (4) and in the following. In the simulations, we have generated the array of indirect force $(\bar{r}, f(\bar{r}))$, in which the value of r_0 was varied in separated systems.

4. Results and discussion

For NPs mixed within athermal polymers, their equilibrium state is fully decided by entropic effects. In order to maximize the conformational entropy of polymers at the hard surface of NPs, there is indirect interacting force induced between surface separated NPs. As can be seen in Figure 1, attractive force is observed between NPs when their surface separation is as large as about one monomer diameter or even smaller. The indirect attractive force is at its maximum value when the NPs are just surface contacted with each other. Increasing polymer concentration strengthens the attractive force observed at short separations between NPs. The measured indirect attracting force is in accordance with previous theoretical and experimental works which show that NPs are pushed together by polymer chains without preferred NP-monomer enthalpic interaction [28,29]. Interestingly, repulsive forces are seen as well for the two NPs at further separations beyond the range of attractive forces. The value of repulsive force is much weaker compared to that of attractive force, however, it is still clearly visible. This indicates that, for NPs mixed within concentrated polymers, they have to firstly across a repulsion barrier before jumping into an aggregated phase. In our simulations, monomers are regarded as hard spheres. The hard-sphere like monomers contributes to the repulsive forces between NPs when their surrounding polymers are overlapped. In this case, monomers cannot interpenetrate into each other due to the hard-sphere like repulsion between them. The repulsive forces are enlarged as well by increasing polymer concentration. It has also been shown in Figure 1 that the interacting range of repulsive forces shifts to a further separation between NPs as lowering the polymer concentration. Correspondingly, the interacting range of attractive forces is extended to a further separation between NPs. Note that

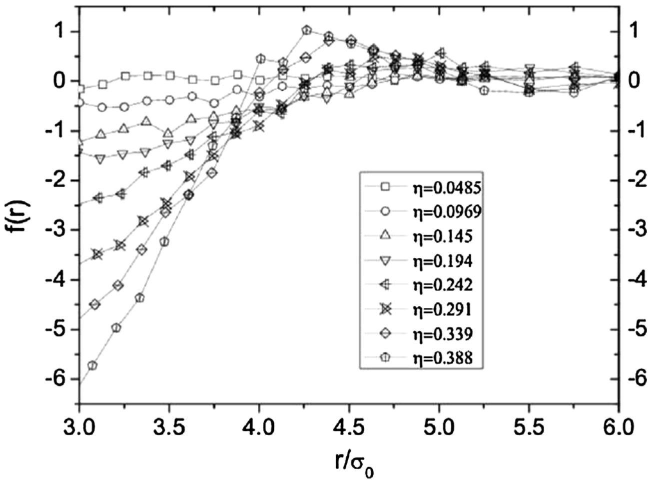

Figure 1. Indirect interacting force, $f(r)$, between pair NPs within polymer matrix as function of the mass-center separation, r, between the NPs at different polymer concentrations. Here, $\sigma_{NP} = 3\sigma_M$ and $L_c = 64$.