Solvent vapor annealing block copolymer nanocomposite films: a dynamic mean field approach

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I. IMPLEMENTATION DETAILS

In this section, we present some additional details of our implementation, such as the discretized equation of motion used to integrate both the particle positions and the rotational dynamics of the grafted nanoparticles.

A. Discretized equation of motion

In order to achieve stable trajectories and accurate thermodynamic properties efficiently, we adopt the discretization scheme of the Langevin equation of motion presented by Grønbech-Jensen and Farago (GJF)[1]. Here, we used the Störmer-Verlet form of GJF scheme, which updates the particle position at current time step according to the particle positions at the previous two time steps without an explicit dependence on the particle velocity. Briefly, the discretized Langevin equation for the polymer segment, $\mathbf{r}_{k,s}(t)$, is given as

$$\mathbf{r}_{k,s}(t_n) = 2 b \, \mathbf{r}_{k,s}(t_{n-1}) - a \, \mathbf{r}_{k,s}(t_{n-2}) + b \, \delta t^2 [\mathbf{f}_{k,s}^{(b)}(t_{n-1}) + \mathbf{f}_{k,s}^{(nb)}(t_{n-1})] + \frac{b \, \delta t}{2} [\theta_{k,s}(t_n) + \theta_{k,s}(t_{n-1})],$$
(1)

where δt is the time step, and the superscripts (b) and (nb) refer to the bonded and nonbonded forces, respectively, and a and b are two integration parameters with the definition given below

$$a = \frac{1 - \frac{\delta t}{2Dm_{k,s}}}{1 + \frac{\delta t}{2Dm_{k,s}}},\tag{2}$$

$$b = \frac{1}{m_{k,s} + \frac{\delta t}{2D}},\tag{3}$$

where the $m_{k,s}$ and D are the mass and diffusion coefficient of segment (k, s), respectively. Similar to the Euler-Maruyama discretization used in the derivation of the mean-field equations (Eqs. 12 and 13 in the main text) this discretization scheme for predicting the particle positions at time t only depends on the noise history. Thus, repeating the derivation presented in Fredrickson and Orland[2] leads to same simplifications under a dynamic mean-field approximation. In the current study, the mass of polymer segments is set as the unit value while for nanoparticles the mass is taken as the volume $V_P = \frac{4\pi R_P^3}{3}$ times the bulk segment density ρ_o . The Gaussian random variable $\theta_{k,s}(t_n)$ used in the above equations has the following statistics

$$\langle \theta_{k,s}(t_n) \rangle = \mathbf{0},$$
(4)

$$<\theta_{k,s}(t_n)\theta_{k',s'}(t_{n'})>=\frac{2\delta t}{D}\delta_{n,n'}\delta_{k,k'}\delta_{s,s'}.$$
(5)

B. Rotational dynamics of anisotropic components

The grafted polymers are harmonically bonded to fixed grafting sites on the nanoparticle surfaces and thus impose torques on the particles, which requires evolving the rotational dynamics. However, stochastic integration of the angular displacements is not additive on orthogonal coordinates, and we cannot simply evolve the Euler angles to capture the rotational dynamics. To solve the issue in a concise way, we use quaternions to describe the orientation of the nanoparticles. Each nanoparticle is associated a quaternion (**q**), a vector with four components and a unit norm ($\sum_{\alpha=0}^{3} q_{\alpha}^2 = 1$). The angular displacements can be shown to become continuous increments in the four coordinates of the quaternion. This quaternion description can be conveniently converted to the Euler angles using

$$[\phi, \theta, \psi] = \begin{bmatrix} \tan_2^{-1}(2q_1q_3 - 2q_0q_2, 2q_2q_3 + 2q_0q_1) \\ \cos^{-1}(q_3^2 - q_2^2 - q_1^2 + q_0^2) \\ \tan_2^{-1}(2q_1q_3 + 2q_0q_2, -2q_2q_3 + 2q_0q_1) \end{bmatrix}^T.$$
(6)

Now, the orientation of the nanoparticle can be determined via the rotational motions defined by the Euler angles, $[\phi, \theta, \psi]$. First, the nanoparticle is rotated about z-axis with angle ψ followed by a rotation the x-axis by θ . Finally, a rotation about the z-axis with angle ϕ is applied. Note that the subscript "2" on the $\tan^{-1}(x, y)$ function indicates the arctangent calculated so that the resulting angle can lie within any of the four quadrants; this is implemented in the $\tan^{-1}(x, y)$ function in common programming languages.

To efficiently capture the dynamics of quaternions, we adopted a new quaternion-based rotational Brownian dynamics algorithm[3]. In the algorithm, the quaternion associated with the i^{th} nanoparticle obeys the modified Brownian dynamics with the equation,

$$\mathbf{q}^{i}(t_{n}) = \mathbf{q}^{i}(t_{n-1}) + \mu_{r} \mathbf{BAT}^{i}(t_{n-1}) \delta t + \mathbf{B}\theta^{q}_{i}(t_{n}) + \lambda_{q^{i}} \mathbf{q}^{i}(t_{n-1}),$$
(7)

where μ_r is the rotational mobility and inversely proportional to the nanoparticle moment of inertia, $V_P \rho_o R_P^2$, λ_{q^i} is a Lagrange multiplier that maintains the unit norm of the quaternion,

and $\theta_i^q(t_n)$ is the stochastic process vector with the following statistics

$$\langle \theta_i^q(t_n) \rangle = \mathbf{0},\tag{8}$$

$$<\theta_i^{q_\alpha}(t_n)\theta_j^{q_\beta}(t_{n'})>=2\mu_r\delta t\delta_{n,n'}\delta_{i,j}\delta_{\alpha,\beta}.$$
(9)

Here, A and B are two rotational matrices associated with the quaternion with the forms

$$\mathbf{A} = \begin{bmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2q_1q_2 + 2q_0q_3 & 2q_1q_3 - 2q_0q_2 \\ 2q_1q_2 - 2q_0q_3 & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2q_2q_3 + 2q_0q_1 \\ 2q_1q_3 + 2q_0q_2 & 2q_2q_3 - 2q_0q_1 & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{bmatrix},$$
(10)
$$\mathbf{B} = \frac{1}{2\mathbf{q}^4} \begin{bmatrix} q_0 & -q_1 & -q_3 \\ q_1 & q_0 & q_2 \\ q_2 & q_3 & -q_1 \\ q_3 & -q_2 & q_0 \end{bmatrix}.$$
(11)

The torque applied on the i^{th} nanoparticle, $\mathbf{T}^{i}(t_{n})$, directly comes from the harmonic bonding between the grafted chain-ends and the graft sites on the nanoparticle surface and has the form as the following

$$\mathbf{T}^{i}(t_{n}) = 3 \sum_{k=1}^{N_{g}} [\mathbf{r}_{g,k}^{i}(t_{n}) - \mathbf{r}_{i,c}(t_{n})] \times [\mathbf{r}_{k}(0,t_{n}) - \mathbf{r}_{g,k}^{i}(t_{n})],$$
(12)

where $\mathbf{r}_k(0, t_n)$ is the position of the zeroth segment in k^{th} grafted chain harmonically bonded to the k^{th} graft site, $\mathbf{r}_{g,k}^i(t_n)$, fixed on the surface of i^{th} nanoparticle whose center is located at the position, $\mathbf{r}_{i,c}(t_n)$.

The rotational dynamics of the nanoparticles can be implemented in to the DMFT framework as the following manner. First, both the bonded and the non-bonded forces are calculated for the nanoparticles. Meanwhile, The torques are also calculated for each nanoparticle based on the current configuration. Subsequently, the quaternions are updated using the aforementioned Brownian dynamics scheme. Next, the position of the nanoparticles is evolved forward to a new configuration according to the GJF scheme. Then, the updated quaternions are used to determine the Euler angles and subsequently the orientation of the nanoparticles at the new configuration. Finally, the coordinates of the graft sites are updated according to the new orientation of the nanoparticles. We note that the graft sites only serve as bonding sites and do not contribution to any non-bonded interactions.

II. THE GJF INTEGRATION SCHEME

In the main text, we have shown that the DMFT approach captures the thermodynamic fluctuations, and at least for the simple regularized Edwards model, converges equilibrium properties more efficiently than either complex Langevin field-theoretic simulations or dissipative particle dynamics (DPD) as implemented in LAMMPS. Here we compare the effects of the GJF discretization scheme.



FIG. 1. (Left) Effect of using the GJF discretization scheme in the DMFT method with C = 10and B = 0. The MSD calculations shown in the right were all performed in a system with C = 3, B = 10 and a time step size fixed at $D\delta t = 0.002$.

Figure 1 shows the improvement in the accuracy of our simulations as a function of the time step size that is achieved when using the GJF algorithm in place of the EM discretization. The GJF scheme permits time steps that are approximately 80 times larger than the Euler-Maruyama scheme in the DMFT method. Interestingly, we can even use approximately 4 times larger time steps than the LAMMPS implementation of DPD, which further improves the efficiency of the DMFT method over the DPD comparison made in Figure 2b in the main text. Thus, not only is the DMFT approach more efficient per time step, but it also allows for larger time steps.

Figure 1b compares various choices of the monomer diffusivity in the GJF scheme on the dynamics of the system to the EM scheme; the time axis is nondimensionalized by the long-time diffusivity of the polymer chains. The GJF scheme that we implemented is based on a Störmer-Verlet (SV) algorithm, which we chose because it does not specifically involve the velocities and velocity fields need not be introduced into the dynamic partition function that we employ. There are deviations at short times relative to the diffusion time of the polymer because the GJF method does not assume overdamped dynamics as in the EM scheme, so large choices for the parameter D leads to ballistic motion on short times. Choosing a smaller D = 0.1 leads to dynamics that are comparable to the overdamped EM scheme, though we would still expect a transition to ballistic behavior on times shorter than we measured.

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