Non-affine deformation of polystyrene nanocomposites leads to significant increase of local elastic properties

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Abstract

This paper presents an investigation of local elastic properties of polystyrene doped with a SiO\textsubscript{2} nanoparticle. The local elasticity is analyzed using the local density fluctuations at various length scales. A significant enhancement of local elastic properties of polystyrene was observed around the nanoparticle, and it was revealed that the additional stiffness has an exponential behavior with a typical length scale $R_0 \approx 1.4$ nm. At the same time, it was shown that the density and other structural properties of polystyrene at this distance from the nanoparticle surface are identical to those for the bulk polystyrene. The enhancement of the local elastic properties was attributed to the effect of non-affine deformations caused by the strong spatial fluctuations of polystyrene stiffness at the length scale below 1 nm. The effect was confirmed using the random matrix model with variable strength of disorder.

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Polymer nanocomposites have attracted significant attention due to their unique properties and enormous potential as future materials [1]. Experimental investigations have demonstrated that due to the nanometer-size inclusions, polymer nanocomposites could possess tailored mechanical, electrical, and thermal properties, as compared to the pure polymers [2–4]. Among many characteristics, the elastic properties of pure polymers and associated nanocomposites have historically attracted considerable attention [5–7]. It was established that polymer doping with nanoparticles even in small concentrations could lead to significant changes in the elasticity of the host material [8–11]. For example, it was shown that doping of polymethylmethacrylate with just 3 wt. % of SiO$_2$ nanoparticles may increase the storage modulus of the nanocomposite by 50 % [12].

It is well known that for a homogeneous elastic medium the classical elasticity theory defines the relation between local strain and local stress [13]. Applied to doped polymers, the Eshelby theory can then be used to determine the deformation of the nanoparticles and the surrounding medium caused by the macroscopic external stress [14], and the resulting overall stiffness of nanocomposites can be calculated using the Mori-Tanaka approach [15, 16]. However, this theory becomes inaccurate for small nanoparticles.

Elastic properties of nanocomposites can be described by the so-called three-phase model [17]. The model assumes that the structure of a polymer is perturbed around the nanoparticle, which results in an effective interface layer around the nanoparticle with intermediate elastic properties. Due to the large total surface area of a nanoparticle, the interfacial layer has a strong influence on the overall stiffness of the nanocomposite. However, the properties and the thickness of the interfacial layer are usually unknown and so far the three-phase model was used as a phenomenological model [18–22].

The present investigation considers an example of polystyrene doped with an amorphous SiO$_2$ nanoparticle and presents a study of local elastic properties around the nanoparticle. The results demonstrate a significant increase of polystyrene local elastic properties in a thick shell around the nanoparticle, where the internal structure of the polystyrene is not perturbed by the nanoparticle. The specific case study illuminates a general and versatile approach that can easily be adapted to study elastic properties of arbitrary nanocomposites. To elucidate the role of disorder in the studied system, we further utilize the random matrix model with variable strength of disorder [23].

The important property of a nanocomposite is the inhomogeneity of its constituents at a
microscopic length scale. The effect becomes especially significant for a polymer matrix since its constituent monomers have a much larger size than the individual atoms. Moreover, since polymers surrounding an embedded nanoparticle are often found in a glassy state, monomers’ disorder of positions and orientations makes the polymer matrix even more inhomogeneous.

The presence of the disorder leads to the so-called non-affine deformations under homogeneous external load. These deformations could not be described by a combination of local stretches or shears. Non-affine deformations play a crucial role in macroscopic elasticity properties and were observed in many disordered solids; examples include metallic glasses [24], polymer hydrogels [25], supercooled liquids [26], silica glass [27]. It was reported that the classical elasticity description breaks down below a length scale of tens of molecular sizes in Lennard-Jones glass [28]. Disorder in the polymer matrix also affects the influence of nanoparticles on the macroscopic elastic properties. It was particularly demonstrated recently that nanoparticles in the strongly disordered medium have a more significant influence on the macroscopic elastic properties than nanoparticles in an ordered matrix [29].

Two structures were considered in the present investigation: (i) a reference system of pure polystyrene, as illustrated in Fig. 1(a) and polystyrene doped with an amorphous SiO$_2$ nanoparticle, see Fig. 1(b). Pure polystyrene was modeled as a mixture of 216 polystyrene chains consisting of 120 monomers each inside a 17.25 nm$\times$17.25 nm$\times$17.25 nm simulation box. The interaction of coarse-grained polystyrene beads was described by the MARTINI potential [30, 31], consistent with earlier studies [31, 32]. After an extensive equilibration [32], an additional 200 ns long molecular dynamics (MD) simulation was carried out at 300 K with the use of NAMD 2.13 software [33]. The simulations assumed periodic boundary conditions with the NVT-statistical ensemble, where the temperature of the system was controlled through the Langevin thermostat with the damping coefficient of 1 ps$^{-1}$.

A single amorphous SiO$_2$ nanoparticle with a diameter of 3.6 nm was embedded into the equilibrated polystyrene matrix to model doped polystyrene. Accordingly, the simulation box was increased up to 17.285 nm$\times$17.285 nm$\times$17.285 nm to accommodate the nanoparticle and preserve the equilibrium density of the polystyrene matrix. An amorphous SiO$_2$ nanoparticle was constructed using the programs VMD [34], and MBN Studio [35] and embedded into the polystyrene matrix. The nanoparticle corresponds to polystyrene doping with a mass fraction of 1.6%, being consistent with the value typically used for nanocom-
FIG. 1. (a) Characteristic configuration of pure polystyrene inside the simulation box obtained after MD equilibration [32]. Polystyrene is modeled in a coarse-grained representation, where each styrene monomer is represented through 4 beads denoted as particles R1, R2, R3, and B in the inset. (b) An illustrative configuration of the system featuring an amorphous SiO$_2$ nanoparticle embedded into the polystyrene matrix.

posites [12]. The BKS-potential [36] was used to describe the interatomic interactions inside the nanoparticle and its interaction with the polystyrene matrix. The doped polystyrene was simulated for 280 ns using the same parameters as for pure polystyrene.

To understand the macroscopic elastic properties of nanocomposites, it is essential to study local elastic moduli around nanoparticles. There are several slightly different methods to define the local elastic moduli. For example, one can analyze stress or strain fluctuations by means of the fluctuation-dissipation theorem [37–41]. The relation between elastic moduli and stress fluctuations, however, contains the Born term, which relies on an involved analysis of the interaction potential between the constituents of the system [42]. On the other hand, the analysis of strain fluctuations requires knowledge of the MD trajectories only. It was reported that the analysis of strain fluctuations has slower convergence, which requires longer simulation time [43]. However, the actual simulation time is determined by a slow relaxation processes of polymers [32].

In this letter, we analyze the strain fluctuations of a polystyrene nanocomposite and determine its local elastic properties. In particular, we study the density fluctuations, which are more robust because they do not require the knowledge of the equilibrium positions of atoms.

Let us define the relative density of the system at the position $\mathbf{r}$ and the time instance $t$...
as
\[\xi(r, t) = \sum_i V_i \phi(r_i(t) - r),\] (1)
where \(r_i(t)\) characterizes the position of the \(i\)th particle, \(V_i\) is the average volume of the Voronoi-cell attributed to the \(i\)th particle, and the smoothing function \(\phi(r)\) is defined as
\[\phi(r) = \frac{1}{(2\pi w^2)^{3/2}} \exp \left(-\frac{r^2}{2w^2}\right).\] (2)

Here \(w\) represents the spatial scale of the smoothing function. The density \(\xi(r, t)\) in Eq. (1) is expected to be close to unity. Due to the thermal fluctuations, the density deviates from the average value, \(\langle \xi(r, t) \rangle_t\), where the deviation of density is then defined as
\[\delta\xi(r, t) = \xi(r, t) - \langle \xi(r, t) \rangle_t.\] (3)

Note that additional spatial fluctuations of \(\xi(r, t)\) in Eq. (1) may emerge due to the atomistic structure of the system. Such fluctuations may become important for the spatial scales \(w\) being much smaller than the characteristic distance between neighbor particles. However, we do not consider this special regime and are interested in the spatial scales where the thermal fluctuations dominate. It, therefore, follows that \(\langle \xi(r, t) \rangle_t \approx 1\), and \(\delta\xi(r, t)\) in Eq. (3) is caused by exclusively thermal fluctuations.

The thermal fluctuations of density allow determining the local elasticity modulus \(M\) as:
\[M(r) = \left(\theta_3^3(e^{-4\pi^2 w^2/L^2}) - 1\right) \frac{k_B T \langle \xi(r, t) \rangle_t^2}{L^3 \langle \delta\xi^2(r, t) \rangle_t},\] (4)
where \(\theta_3(x)\) is the third Jacobi theta-function, \(L\) defines the dimension of the simulation box, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature of the system. Equation (4) is derived in Appendix A using thermal equilibrium analysis of a reference isotropic homogeneous elastic body. For small spatial scales \(w \ll L\), Eq. (4) is simplified and reads as:
\[M(r) = \frac{1}{8\pi^{3/2} w^3} \frac{k_B T \langle \xi(r, t) \rangle_t^2}{\langle \delta\xi^2(r, t) \rangle_t}.\] (5)

The elasticity modulus \(M\) is known as P-wave modulus and determines the propagation velocity of longitudinal elastic waves as \(v_l = \sqrt{M/\rho}\), where \(\rho\) is the density. It is related to the bulk modulus \(K\), the Young modulus \(E\), and the shear modulus \(G\) as \(M = 3K(1 - \nu)/(1 + \nu) = E(1 - \nu)/(1 + \nu)(1 - 2\nu) = 2G(1 - \nu)/(1 - 2\nu)\), where \(\nu\) is the Poisson’s ratio, which for glassy polymers is usually close to 1/3.
FIG. 2. Spatial distribution of the elastic modulus $M(r)$ for pure polystyrene in the simulation box’s central plane with $z = 0$. Results are shown for the four considered spatial scales characterized through the parameter $w = 0.4, 0.8, 1.5$, and $2.5$ nm.

The smooth relative density $\xi(r,t)$ was computed during the MD simulation of bulk polystyrene and polystyrene with an embedded nanoparticle. Since the direct calculation of the convolution in Eq. (1) take enormous calculation time, we use the smooth histogram method described in Appendix B, which in the case of analysis of the thermal fluctuations almost does not increase the simulation time.

Figure 2 shows the computed elastic modulus $M(r)$ for bulk polystyrene obtained for different spatial scales $w$. One notes strong spatial fluctuations of the elastic modulus in the case of $w = 0.4$, while the spatial fluctuations decrease for the larger $w$-values. For a better representation of the actual length scale, we use the full width at half maximum (FWHM) of the smoothing function $\phi(r)$, which yields $w_{\text{FWHM}} = 2\sqrt{2\ln 2} \, w$. For $w = 0.4$ nm one obtains $w_{\text{FWHM}} = 0.92$ nm, the mean elastic modulus $\langle M(r) \rangle = 7.9$ GPa, and the FWHM of the elastic modulus fluctuations $\delta M_{\text{FWHM}} = 2.8$ GPa. The fluctuations of the elastic modulus are noticeably strong, and cannot be neglected at the given length scale. The fluctuations correspond specifically to the difference between the maximum and minimum values of $M(r)$.
FIG. 3. Spatial distribution of the elastic modulus $M(r)$ for polystyrene sample around a SiO$_2$ nanoinclusion (shown schematically with a circle) of 3.6 nm diameter. The elastic modulus distribution is computed for a plane that passes through the center of the sample at $z = 0$. Results are shown for the four considered spatial scales characterized through the parameter $w = 0.4$, 0.8, 1.5, and 2.5 nm.

observed in Fig. 2(a).

Figure 2(b) shows the results for $w = 0.8$ nm, where $w_{\text{fwhm}} = 1.88$ nm, $\langle M(r) \rangle = 9.0$ GPa, and $\delta M_{\text{fwhm}} = 1.3$ GPa. In that case, the relative fluctuations are smaller, being less than 20%, and furthermore decrease for larger spatial scales $w$. The result, therefore, demonstrates that the classical elasticity theory can only be applied at length scales that are significantly larger than $l_s \sim 1$ nm.

Figure 3 shows the elastic modulus $M(r)$ obtained for polystyrene with an embedded nanoparticle with a diameter of 3.6 nm. Far from the nanoparticle, one observes fluctuations of the elastic modulus $M(r)$ similarly as for bulk polystyrene, see Fig. 2. Inside the nanoparticle, the elastic modulus is significantly larger, corresponding to the typical values for SiO$_2$. It is, however, remarkable that the elastic modulus of polystyrene surrounding the nanoparticle is also noticeably larger than the corresponding bulk value. The relative
elastic modulus of polystyrene and the SiO$_2$ nanoparticle are analyzed in Fig. 4 as a function of distance from the nanoparticle center. A 10% enhancement of the elastic modulus is observed for distances up to 1 nm from the nanoparticle surface. This result is not significantly influenced by the smoothing length scale $w$, as evidenced in the inset to Fig. 4, which indicates that the observed enhancement of elastic modulus is not related to the smoothing of density fluctuations. Such elastic behavior is consistent with the description obtained from the three-phase model of the nanocomposite [17], however, it is important to discuss the nature of the enhanced elastic properties around the nanoparticle.

The cause of the enhancement in the elastic properties in the vicinity of the nanoparticle can be analyzed through evaluating the density $\rho(r) = \sum_i m_i \phi(r - r_i)$ separately for the nanoparticle and the polystyrene, as shown in Fig. 5. Here $m_i$ is the mass of $i$th coarse grain particle and $\phi$ is the smoothing function defined by Eq. (2). For the small smoothing value of $w = 0.1$ nm, one notes clear oscillations of polystyrene density caused by coordination shells of the polystyrene monomers around the nanoparticle. The oscillations vanish
for \( w = 0.4 \text{ nm} \), and the polystyrene density approaches its bulk value with a deviation of less than 1%. At the same time, Fig. 4 demonstrates a much larger deviation of \( M(R) \), which shows that the enhancement of \( M(R) \) near the nanoparticle is not directly related to the structural changes of the polymer in the vicinity of the nanoparticle. Other structural quantities also exhibit the same behavior near the nanoparticle and in the bulk polystyrene. Volumes of Voronoi cells around individual coarse-grain particles representing the polymer have homogeneous distribution except a narrow layer about 0.5 nm thick around the nanoparticle. Orientation of monomers is isotropic near the nanoparticle as well as in the bulk polystyrene. The detailed analysis of these quantities is presented in Appendix C.

In a strongly inhomogeneous medium, the local elastic properties are not completely determined by its local structure but depend on a large volume of the surrounding medium. Indeed, all atoms in the system tend to find new equilibrium positions for any applied macroscopic or microscopic stress. This deviation of equilibrium positions can be described by a continuous function \( u(r) \); however, at the nanometer length scale, each atom has an additional non-affine displacement \( u_{\text{na}} \). At the nanoparticle's surface, the non-affine displacements are suppressed because the nanoparticle is more homogeneous and stiffer than the surrounding polystyrene matrix, leading to different stiffness of the polystyrene matrix in the vicinity of the nanoparticle.

The inset in Fig. 4 shows that the additional stiffness of polystyrene has an exponential behavior \( M(R)/M_0 - 1 \sim \exp(-R/R_0) \) with \( R_0 = 1.4 \text{ nm} \), where the length scale \( R_0 \) determines the characteristic length scale of non-affine displacements. Indeed, for smaller length scales, strong fluctuations of local elastic properties can be observed, see Fig. 2.

The effect of disorder on local elastic properties around nanoparticles in an amorphous medium can be further quantified through the dimensionless random matrix model [23]. In that case, a dynamic matrix \( \mathcal{M} \) is introduced, which describes harmonic interactions between atoms of unit mass:

\[
\mathcal{M} = \mathcal{A} \mathcal{A}^T + \mu\mathcal{M}^{(0)}.
\]

The matrix \( \mathcal{A} \) describes random interaction between neighboring atoms and the matrix \( \mathcal{M}^{(0)} \) describes an ordered contribution in the dynamical matrix \( \mathcal{M} \). For simplicity, the random matrix model assumes that the deviation of atoms from their equilibrium position is described by the scalar quantities \( u_i \) [23]. In this simplified, so-called scalar model, the atoms are assumed to fluctuate only along one direction (e.g. in the \( z \) direction), such that
FIG. 5. Radial local density of the SiO$_2$ nanoparticle and the polystyrene (PS) matrix. The vertical dotted line marks the boundary of the nanoparticle. Solid and dashed lines show the density for $w = 0.1$ nm and $w = 0.4$ nm respectively. Inset shows a zoom for PS density around the nanoparticle.

$$r_i(t) = r_i^{eq} + u_i(t)e_z,$$

where $u_i$ is assumed to be much smaller than the interatomic distance.

For two neighboring atoms with indices $i$ and $j$, $A_{ij}$ is assumed to be a zero-mean Gaussian random number with unit variance and $M_{ij}^{(0)} = -1$. Other non-diagonal elements of both matrices in Eq. (6) are zero, while the diagonal elements obey the sum rules: $A_{ii} = \sum_{j \neq i} A_{ji}$, $M_{ii}^{(0)} = \sum_{j \neq i} M_{ji}^{(0)}$. The disorder in the system is controlled by the dimensionless parameter $\mu$, where $\mu \gg 1$ describes the regime with tiny fluctuations of the interaction between atoms; the other regime, $\mu \ll 1$ describes a strongly disordered amorphous material.

To model a disordered medium around the nanoparticle, consider a simple cubic lattice with the lattice constant $a_0$ and a small value of the parameter $\mu$. The nanoparticle is then described as a spherical region $R < R_{np}$ within the lattice with $\mu = \mu_{np} = 1$ inside that region. Within this model, the statistical properties of the disordered medium everywhere outside the nanoparticle are identical.

The radial dependence of the calculated elastic modulus $M(R)$ is presented in Fig. 6, which reveals the exponential dependence of the elastic modulus around the nanoparticle on distance from its center. In the case of a stronger disorder (characterized by the smaller values of $\mu$), one notes a more prominent dependence that is not strongly dependent on the
FIG. 6. Relative increase of the elastic modulus $M$ near the nanoinclusion in the random matrix model. Different colors represent different values of $w$. Dotted line shows the nanoinclusion size $R_{np} = 10a_0$. Solid lines show the exponential law $\sim \exp(-R/R_0)$ for the corresponding values of $\mu$. Inset shows the dependence of the fitted values of $R_0$ on the parameter $\mu$.

smoothing parameter $w$.

For each value of the parameter $\mu$, one can determine the length scale $R_0$ of the exponential decay of $M(R)/M_0 - 1 \sim \exp(-R/R_0)$, such that $R_0 \sim \mu^{-1/4}$, as shown in the inset to Fig. 6. The same scaling was observed for the Ioffe-Regel length $l_{IR} \sim \mu^{-1/4}$ in the random matrix model [23].

The performed investigation concludes that an exponentially decreasing induced elastic shell is formed around a nanoparticle embedded inside a soft polystyrene matrix. Such a shell increases the effective volume of nanoinclusions inside polymeric materials, which leads to an increase in the effect on the macroscopic elastic properties of nanocomposites.

The resulting elastic properties can approximately be modeled using the three-phase model with the interphase layer thickness $R_0 \approx 1.4$ nm. The observed enhancement of polystyrene’s elastic properties could not be explained by the deviation of its density and other structural properties. The result is consistent with a recent study for boehmite nanolayer in epoxy [46]. We conclude that this effect was caused by non-affine deformations of the polymer matrix, which is strongly inhomogeneous at the nanometer length scale. This conclusion was supported by the analysis within the random matrix model with
variable strength of disorder.

The presented results show that detailed elasticity maps at different length scales can be computed by the analysis of the density fluctuations, which can be performed on the fly during an MD simulation. The same analysis can be applied to study local elastic properties in various soft inhomogeneous mediums and liquids as well.

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APPENDICES

Appendix A: Density fluctuations and local elasticity modulus

Let us consider $L \times L \times L$ elastic cubic sample with periodic boundary conditions in the thermal equilibrium at a temperature $T$. Thermal fluctuations can be described by a displacement field

$$u(r) = \sum_q' \left[ a_q \sin(q \cdot r) + b_q \cos(q \cdot r) \right], \quad (A1)$$

where the wavevector $q$ is determined by the three integer numbers $(n_x, n_y, n_z)$ as $q_i = 2\pi n_i / L$ for $i = x, y, z$. Wavevectors $q$ and $-q$ define the same wave with $a_{-q} = -a_q$ and $b_{-q} = b_q$. Therefore, the summation is performed over half of the reciprocal space with non-equivalent wavevectors, which is denoted by prime in Eq. (A1). The wavevector $q = 0$ is excluded from the summation as it corresponds to a trivial translation of the system.

The deviation of the local density is defined as

$$\delta \rho(r_0) = \rho_0 \int \phi(r - r_0) \text{Tr} \hat{\varepsilon}(r) dr, \quad (A2)$$

where $\rho_0$ is the equilibrium density, $\phi(r)$ is the smoothing function defined by Eq. (2), and $\hat{\varepsilon}(r)$ is the strain tensor, which reads as

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) = \frac{1}{2} \sum_q' \left[ (a_q q_j + a_q q_i) \cos(q \cdot r) ight. \\
- \left. (b_q q_j + b_q q_i) \sin(q \cdot r) \right]. \quad (A3)$$

As a result, the deviation of the local density is $\delta \rho = \sum_q' \delta \rho_q$, where

$$\delta \rho_q = \rho_0 \left[ (a_q \cdot q) \cos(q \cdot r_0) \right. \\
+ \left. (b_q \cdot q) \sin(q \cdot r_0) \right] \exp \left( -\frac{w^2 q^2}{2} \right). \quad (A4)$$

To find the relation between the local density fluctuations and elastic moduli, consider a homogeneous isotropic elastic body as a reference. In that case, the elastic energy density is

$$\Pi(r) = \frac{1}{2} C_{ijkl} \varepsilon_{ij}(r) \varepsilon_{kl}(r), \quad (A5)$$
where the stiffness tensor is

\[ C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \tag{A6} \]

with \( \lambda \) and \( \mu \) being the Lamé parameters. The total elastic energy of the system is given as

\[ U = \int \Pi(r) d\mathbf{r} = \sum_q U_q, \]

where

\[ U_q = \frac{L^3}{4} \left[ (\lambda + \mu)(a_q \cdot \mathbf{q})^2 + (\lambda + \mu)(b_q \cdot \mathbf{q})^2 \right. \]

\[ + \mu (a_q^2 + b_q^2) \mathbf{q}^2 \]. \tag{A7} \]

The partition function of the system can be presented as

\[ Z = \prod_q Z_q, \]

where

\[ Z_q = \int \exp \left( -\frac{U_q}{k_B T} \right) d\mathbf{a}_q d\mathbf{b}_q = \frac{64\pi^3 k_B^3 T^3}{L^9 q^6 \mu^2 (\lambda + 2\mu)}. \tag{A8} \]

One finds that the mean of \( \delta \rho \) is zero, such that

\[ \langle \delta \rho \rangle = \sum_q \frac{1}{Z_q} \int \delta \rho_q \exp \left( -\frac{U_q}{k_B T} \right) d\mathbf{a}_q d\mathbf{b}_q = 0, \tag{A9} \]

The variance of \( \delta \rho \) is

\[ \langle \delta \rho^2 \rangle = \sum_q \frac{1}{Z_q} \int \delta \rho_q^2 \exp \left( -\frac{U_q}{k_B T} \right) d\mathbf{a}_q d\mathbf{b}_q \]

\[ = \frac{2k_B T \rho_0^2}{L^3 (\lambda + 2\mu)} \sum_q \exp \left( -w^2 q^2 \right). \tag{A10} \]

To carry out the summation in Eq. (A10), one applies the identity

\[ \sum_{n=-\infty}^{\infty} \exp \left( -\frac{4\pi^2 w^2 n^2}{L^2} \right) = \theta_3 \left( e^{-4\pi^2 w^2/L^2} \right), \tag{A11} \]

where \( \theta_3(x) \) is the third Jacobi theta-function. As a result, one obtains

\[ \langle \delta \rho^2 \rangle = \frac{k_B T \rho_0^2}{L^3 (\lambda + 2\mu)} \left( \theta_3^3 \left( e^{-4\pi^2 w^2/L^2} \right) - 1 \right). \tag{A12} \]

Therefore, the P-wave modulus \( M = \lambda + 2\mu \) can be found using the variance of the local density fluctuations as

\[ M = \frac{k_B T \rho_0^2}{L^3 \langle \delta \rho^2 \rangle} \left( \theta_3^3 \left( e^{-4\pi^2 w^2/L^2} \right) - 1 \right). \tag{A13} \]
Appendix B: Smooth histogram

To obtain the smooth relative density $\xi(r,t)$, one introduces the three-dimensional histogram

$$h_{ijk} = \sum_n \Phi_s(x_n/d - i)\Phi_s(y_n/d - j)\Phi_s(z_n/d - k),$$

(B1)

where $(x_n, y_n, z_n)$ are coordinates of the $n$th particle and $d = L/N_{\text{bins}}$ is the size of a sampling bin in each direction.

To obtain a smooth histogram, we recursively employ the convolution $\Phi_s(p) = \Phi_{s-1}(p) * \Phi_0(p)$, where $\Phi_0(p)$ is the standard box function, which is equal to 1 for $-1/2 < p < 1/2$ and zero otherwise. The resulting window function $\Phi_s(p)$ is $s - 1$ times differentiable and has the following important properties

$$\sum_i \Phi_s(p - i) = 1, \quad s \geq 0,$$

(B2)

$$\sum_i (p - i)\Phi_s(p - i) = 0, \quad s \geq 1,$$

(B3)

$$\sum_i (p - i)^2\Phi_s(p - i) = (s + 1)/12, \quad s \geq 2$$

(B4)

for any real value $p$. For $s \gg 1$ the window function $\Phi_s(p)$ is close to a Gaussian with the dispersion $(s + 1)/12$. However, the calculation time increases as $O(s^3)$. To obtain the best balance between the accuracy and the calculation time, one can employ $s = 4$ and make an additional Gaussian smoothing of $h_{ijk}$ with the dispersion $\sigma^2 = (w/d)^2 - (s + 1)/12$ using the Fast Fourier Transform method. In this case the window function is

$$\Phi_4(p) = \frac{1}{384} \begin{cases} 
(5 + 2p)^4, & -\frac{5}{2} < p \leq -\frac{3}{2}, \\
(5 + 2p)^4 - 5(3 + 2p)^4, & -\frac{3}{2} < p \leq -\frac{1}{2}, \\
96p^4 - 240p^2 + 230, & -\frac{1}{2} < p \leq \frac{1}{2}, \\
(5 - 2p)^4 - 5(3 - 2p)^4, & \frac{1}{2} < p \leq \frac{3}{2}, \\
(5 - 2p)^4, & \frac{3}{2} < p \leq \frac{5}{2}, \\
0, & \text{elsewhere},
\end{cases}$$

(B5)

which is smooth and close to a Gaussian with the dispersion 5/12. In the present study, we assume $N_{\text{bins}} = 100$, which is enough for the studied values of the smoothing parameter $w$. 

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FIG. 7. Distribution of the Voronoi volumes as a function of distance to the center of the nanoparticle. Different colors represent different types of the coarse-grain particles: B, R1, R2, R3. Solid and dashed lines show the result for the length scales $w = 0.1$ nm and $w = 0.4$ nm, respectively. The vertical dotted line indicates the boundary of the nanoparticle.

Appendix C: Structural properties of polystyrene around the nanoparticle

Here we study additional properties of polystyrene near the nanoparticle to show that the structural properties of the simulated polystyrene do not depend on the distance to the nanoparticle except for a very thin interfacial layer.

In addition to the density, we study the spatial distribution of individual Voronoi volumes around coarse-grain particles B, R1, R2, R3. For particles of type B, this spatial distribution has the following form

$$\langle V_B \rangle (R) = \frac{\langle \sum_{i \in \{B\}} V_i \phi(r_i - r) \rangle}{\langle \sum_{i \in \{B\}} \phi(r_i - r) \rangle}. \quad (C1)$$

Here the averaging is performed over the time $t$ and the coordinate $r$ for the given distance to the center of the nanoparticle $R = |r - r_{NP}|$. The smoothing function $\phi$ in Eq. (C1) defines the length scale $w$. Similar definitions for types R1, R2, R3 can also be adopted. The results of the calculated average Voronoi volumes are presented in Fig. 7 as a function of the distance to the center of the nanoparticle for $w = 0.1$ nm and $w = 0.4$ nm. One can observe the homogeneous distribution of Voronoi volumes for every type except a thin interphase layer around the nanoparticle.
FIG. 8. Anisotropy parameters of the orientation of monomers $\langle \cos \theta_1 \rangle$, $\langle \cos \theta_{12} \rangle$, and $\langle \cos^2 \theta_{123} \rangle$ as a function of the distance to the center of the nanoparticle. The vertical dotted line indicates the boundary of the nanoparticle. Horizontal gray lines indicate the average values for isotropic random orientation: 0, 0, and $1/3$, respectively.

The polymer structure also depends on the orientation of the monomers. For each monomer, we define the following vectors (see inset in Fig. 1(a)): the vector between the particle B on the polymer’s backbone and the central particle R1 in the monomer

$$\mathbf{r}_1 = \mathbf{r}_{R1} - \mathbf{r}_B,$$

the vector between the central particle R1 and side particle R2 in the monomer

$$\mathbf{r}_{12} = \mathbf{r}_{R2} - \mathbf{r}_{R1},$$

and the vector, which is normal to the triangle R1–R2–R3

$$\mathbf{n}_{123} = (\mathbf{r}_{R2} - \mathbf{r}_{R1}) \times (\mathbf{r}_{R3} - \mathbf{r}_{R1}).$$
The orientation of the monomer may be anisotropic due to the influence of the nanoparticle. If this anisotropy exists, its orientation depends on the vector between the monomer and the center of the nanoparticle $r_0 = r_{R1} - r_{NP}$. For each monomer, we find cosines of the angles between the vectors $r_1$, $r_{12}$, $n_{123}$ and the vector $r_0$:

$$\cos \theta_1 = \frac{r_1 \cdot r_0}{r_1 r_0},$$  \hspace{1cm} \text{(C5)}

$$\cos \theta_{12} = \frac{r_{12} \cdot r_0}{r_{12} r_0},$$  \hspace{1cm} \text{(C6)}

$$\cos \theta_{123} = \frac{n_{123} \cdot r_0}{n_{123} r_0}.$$  \hspace{1cm} \text{(C7)}

The corresponding average values represent the anisotropy of the monomer orientation:

$$\langle \cos \theta_1 \rangle(R) = \frac{\sum_{i \in \{R1\}} \cos \theta_1 \phi(r_i - r)}{\sum_{i \in \{R1\}} \phi(r_i - r)},$$  \hspace{1cm} \text{(C8)}

$$\langle \cos \theta_{12} \rangle(R) = \frac{\sum_{i \in \{R1\}} \cos \theta_{12} \phi(r_i - r)}{\sum_{i \in \{R1\}} \phi(r_i - r)},$$  \hspace{1cm} \text{(C9)}

$$\langle \cos^2 \theta_{123} \rangle(R) = \frac{\sum_{i \in \{R1\}} \cos^2 \theta_{123} \phi(r_i - r)}{\sum_{i \in \{R1\}} \phi(r_i - r)}. \hspace{1cm} \text{(C10)}$$

Here the averaging is performed over the time $t$ and the coordinate $r$ for the given distance to the center of the nanoparticle $R = |r - r_{NP}|$. In the third case we calculate the average of $\cos^2 \theta_{123}$ because the particles R2 and R3 are identical and the average of $\cos \theta_{123}$ is zero. The results are presented in Fig. 8 for two smoothing length scales $w = 0.1 \text{ nm}$ and $w = 0.4 \text{ nm}$. One observes that the calculated values are fluctuating near their values for isotropic random orientation: $\langle \cos \theta_1 \rangle \approx 0$, $\langle \cos \theta_{12} \rangle \approx 0$, and $\langle \cos^2 \theta_{123} \rangle \approx 1/3$.

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