Diffusion and Relaxation Dynamics in Cluster Crystals

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For a large class of fluids exhibiting ultrasoft bounded pair potentials, particles form crystals consisting of clusters located in the lattice sites, with a density-independent lattice constant. Here we present an investigation on the dynamic features of a representative example of this class. It is found that particles can diffuse between lattice sites, maintaining the lattice structure, through an activated hopping mechanism. This feature yields finite values for the diffusivity and full relaxation of density correlation functions. Simulations suggest the existence of a localization transition which is avoided by hopping, and a dynamic decoupling between self- and collective correlations.

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The investigation of large-scale structural and dynamic properties of complex fluids can be facilitated by coarse-graining intramolecular fast degrees-of-freedom. By following this procedure, each macromolecule is represented as a single particle interacting with any other through an effective ultrasoft pair potential.\footnote{Generalized exponential models (GEM), \(v(r) = \epsilon \exp(-(r/\sigma)^m)\), constitute a class of such effective bounded interactions. The cases \(m \leq 2\) and \(m > 2\) belong, respectively, to the so-called \(Q^+\) and \(Q^-\) classes for which the Fourier transform, \(\tilde{v}(q)\), of \(v(r)\) is, respectively, positive definite or oscillating around zero.}

According to a general criterion based on a mean-field density functional theory,\footnote{For a large class of fluids exhibiting ultrasoft bounded pair potentials, particles form crystals consisting of clusters located in the lattice sites, with a density-independent lattice constant. Here we present an investigation on the dynamic features of a representative example of this class. It is found that particles can diffuse between lattice sites, maintaining the lattice structure, through an activated hopping mechanism. This feature yields finite values for the diffusivity and full relaxation of density correlation functions. Simulations suggest the existence of a localization transition which is avoided by hopping, and a dynamic decoupling between self- and collective correlations.} systems belonging to the \(Q^+\) class display reentrant crystallization in the density-temperature plane.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

Generalized exponential models (GEM), \(v(r) = \epsilon \exp(-(r/\sigma)^m)\), constitute a class of such effective bounded interactions. The cases \(m \leq 2\) and \(m > 2\) belong, respectively, to the so-called \(Q^+\) and \(Q^-\) classes for which the Fourier transform, \(\tilde{v}(q)\), of \(v(r)\) is, respectively, positive definite or oscillating around zero. Depending on the values of \(\rho, T,\) and \(\sigma\), systems belonging to the \(Q^+\) class do not yield reentrance but rather a monotonically freezing line beyond which the system forms cluster crystals.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

Previous theoretical and computational investigations of the GEM model for \(m > 2\) have focused on structural and thermodynamic properties.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

The investigation of large-scale structural and dynamic properties of complex fluids can be facilitated by coarse-graining intramolecular fast degrees-of-freedom. By following this procedure, each macromolecule is represented as a single particle interacting with any other through an effective ultrasoft pair potential.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

The dynamics of these crystals have not been studied to-date and their particular form of self-organization suggests that the former must be different from that of atomic solids with single site occupancy. The purpose of this Letter is to investigate the novel features arising in the dynamics of such cluster crystals in general. We find that particles diffuse between lattice sites through an activated hopping mechanism, without breaking the lattice structure, resulting in finite values for the diffusivity and full relaxation of self-correlation functions. We establish the existence of a localization transition which is avoided by hopping and is distinct for self- and density-density correlations. Therefore, an unusual decoupling between self- and collective dynamics is observed, the latter exhibiting a lower transition temperature than the former.

Particles in the simulated system interact through a GEM potential with \(m = 8\), which is cut-off at a distance \(r_c = 1.5\sigma\). The particle mass \(m_p\), energy scale \(\epsilon\), and particle diameter \(\sigma\) are set to one. In the following, energy, temperature, density, time, distance, and wavevector will be given respectively in units of \(\epsilon, \epsilon/k_B, \sigma^{-3}, \sigma(m_p/\epsilon)^{1/2}, \sigma\), and \(\sigma^{-1}\). We investigate dynamic features of the cluster crystals, in a wide range of temperature \(T\), deep inside the region of stability of the fcc-phase.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

Due to the large values of \(\rho\), investigation of relaxation dynamics in the present system is computationally more demanding than for standard model systems with unbounded interactions as, e.g., Lennard Jones mixtures, which are typically studied at \(\rho \sim 1.0\). For this reason Newtonian dynamics simulations have been carried out instead of Brownian dynamics, which would yield a much slower relaxation.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

Fig. 1 shows the \(T\)-dependence of the mean squared displacement for densities \(\rho = 2.0\) and \(\rho = 7.0\). The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).} as \(\rho^{-1/2}\). Rescaling time as \(\rho^{1/2} t\) causes a collapse of the curves at short times and confirms the above result that was derived on the basis of statics.\footnote{The initial ballistic regime corresponds to oscillations around lattice sites whose period scales, according to \(2 \sigma \sqrt{3}/q_\ast\), with \(q_\ast\) the wavevector for which \(\tilde{v}(q)\) shows its first minimum. The obtained value is \(a = 1.8571325\). The distance between nearest-neighbor lattice sites is \(a_{\text{nn}} = a/\sqrt{2} = 1.313191\).}

Short-time motion is dictated, thus, by \(\rho\) alone whereas long-time diffusion by \(\rho/T\), as we will shortly demonstrate. After the ballistic regime, a plateau arises characterizing the temporary trapping of the particles within the clusters. At long times, the particles reach the diffusive regime (\(\langle \Delta r^2(t) \rangle \sim t\)) at all the investigated temperatures, reaching distances of at
least one particle diameter from their initial position. The fcc structure remains stable in the whole time window of the simulation. Therefore, particles move between neighboring clusters, modifying thus the clusters’ initial identity but leaving unaffected their average population $n_c$.

Fig. 2 displays an illustrative example of the time evolution of the van Hove self-correlation function, $G_s(r,t)$. The discrete nature of the motion between clusters centered around distinct lattice sites is evidenced by the succession of peaks arising in $G_s(r,t)$. With increasing time, the height of the first peak progressively decreases and new peaks of increasing intensity located at larger distances arise. From integration of $G_s(r,t)$ for the longest represented $t$ it is found that more than a 80% of the particles are located at distance $r > 0.5d_{nn}$ from their initial position, i.e., they have moved to different lattice sites.

Though a detailed characterization of jumps between lattice sites is beyond the scope of this Letter, it is worth commenting some interesting features of $G_s(r,t)$. Arrows in Fig. 2 indicate distances between $n$th nearest-neighbor lattice sites, $\sqrt{n}d_{nn}$, where $n = 1, 2, 3,$ and 4. The two first sharp maxima after the initial peak match such distances for $n = 1$ and 3. The pronounced minimum at $r \equiv 1.4d_{nn}$ matches the case $n = 2$. Given two consecutive jumps connecting three distinct lattice sites 1, 2, 3 for which $d_{12} = d_{23} = d_{nn}$, it is easy to see that the four allowed angles between both jumps, 60°, 90°, 120°, and 180° yield, respectively, $d_{13}/d_{nn} = 1, \sqrt{2}, \sqrt{3},$ and 2. The presence of a marked minimum for $r/d_{nn} = \sqrt{2}$ and a sharp maximum for $r/d_{nn} = \sqrt{3}$ suggests a preferential directionality for the motion between neighboring sites with low and high probability for angles of, respectively, 90° and 120° between consecutive jumps.

Fig. 3 shows for a typical configuration at $\rho = 5.0$ and $T = 0.667$ a map of the local potential energy $U$ on a $[001]$ lattice plane, for a configuration at $\rho = 5.0$ and $T = 0.667$. Darker colors represent lower energies (see legend) and are centered around lattice sites.

Fig. 4 shows the distribution of local potential energy, $\rho g(U)$, vs. rescaled energy, $U/\rho$, at different densities. (a): results considering all the volume in the simulation box; (b): results by computing $U$ only at lattice sites.
The approximations involved in deriving Eq. (1) with some numerical coefficient $U$ of the problem, $\langle t \rangle \propto \rho$ and vanishing for $E < 0$, with $\beta = (k_B T)^{-1}$. The probability $P_\rho(\Delta U)$ to have $E > \Delta U$ can be calculated as $P_\rho(\Delta U) = e^{-\beta E}[(\beta \Delta U)^2/2 + \beta \Delta U + 1]$. Once $E > \Delta U$, the particle hops to the neighboring site. We can now translate $P_\rho(\Delta U)$ into a ‘waiting time’ $\tau_w$ that particles typically spend on a given lattice site before hopping to the next one, which scales as $\tau_w \sim 1/P_\rho(\Delta U)$. If we observe any given particle for a number of timesteps $N_{t_s} \gg 1$, there will only be a fraction $N_{\text{hop}} \sim P_\rho(\Delta U)N_{t_s}$ of them for which the particle will hop, its motion being a random walk of step size $\ell \sim \sigma$. Hence, measured in the natural units of the problem, $\langle \Delta r^2(t) \rangle$ will scale as $P_\rho(\Delta U)\tau_w$.

By using $\Delta U \approx 2.3\rho$ (see above) we obtain

$$D = \gamma_0 \left[ (2.3\rho/T)^2/2 + 2.3\rho/T + 1 \right] e^{-2.3\rho/T},$$

with some numerical coefficient $\gamma_0$ of order unity. Theory predicts, thus, that $D$ depends solely on the ratio $\rho/T$. The approximations involved in deriving Eq. (1) above become more accurate as $\rho$ grows, for which case the polydispersity in the cluster population is reduced and all sites can be treated as identical harmonic wells. The results shown in Fig. 5 fully corroborate this treatment. The diffusivity can be very well described by the law of Eq. (1) above and, indeed, for sufficiently high densities all data points collapse on a single curve, where $D$ is expressed as a function of the ratio $\rho/T$. This is a dynamical generalization of the scaling properties previously found for statics.

Finally, we discuss the self- and density-density correlators of wavevector $q$, respectively defined as $F_s(q, t) = N^{-1}\langle \sum \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) ] \rangle$, and $F(q, t) = \langle \rho_j(t)\rho^*_j(0) \rangle / \langle \rho_j(0)\rho^*_j(0) \rangle$, where $\rho_j(t)$ is defined as $\rho_j(t) = \sum \exp[i\mathbf{q} \cdot \mathbf{r}_j(t) ]$. Fig. 6 shows, for $\rho = 2.0$ and for a fixed wavevector $q = 4.0$ not probing the lattice structure, the $T$-dependence of $F_s(q, t)$ and $F(q, t)$. After the first microscopic decay, both correlators exhibit a plateau, whose duration increases with decreasing $T$. As usually found in systems displaying slow relaxation, the presence of this plateau indicates a temporary freezing of such correlations. Strong density oscillations related with intracluster motion are observed at the crossover between the microscopic and plateau regimes. At long times self-correlations relax and decay to zero. This is also true for density-density correlations if $q$ does not match any wavevector probing the lattice structure. On the contrary, and consistently with the observed stability of the fcc lattice, density-density correlations for $q$ belonging to the reciprocal lattice are permanently frozen, and there is no signature of a final decay of the plateau, which remains flat (not shown) up to the limit of the simulation window.

An ideal (i.e., without intervening hopping events) localization transition to a non-ergodic (‘glassy’) phase can be defined by a jump from zero to a finite value (non-ergodicity parameter) of the long-time limit of dynamic correlators. Hence, at the transition point the non-ergodicity parameter is equal to the...
plateau height. This quantity progressively increases with decreasing temperature in the non-ergodic phase. The presence of hopping events can, in principle, restore ergodicity at temperatures below the ideal transition, leading to final relaxation of correlators [17]. Still, the existence of an avoided ideal transition can still be identified by the increase of the plateau height. Now we investigate features of such a transition in the present system. As shown in Fig. 6, \( F(q, t) \) and \( F(q, t) \) exhibit a rather different behaviour at the intermediate plateau regime. The plateau height, \( F_q^p \), for \( F(q, t) \) increases with decreasing \( T \) [see inset in panel (a)]. This feature is observed for all wavevectors and suggests the existence of a localization transition for self-motions. Fig. 7 shows the \( q \)-dependence of \( f_q^p \) for \( q = 2.0 \) at the same temperatures of Fig. 6. The increasing width of \( f_q^p \) with decreasing \( T \) indicates a progressive decrease of the localization length [17]. However, in contrast to the standard behavior in crystal states, and similarly to relaxation in supercooled fluids, hopping events move the particles beyond the localization length and ergodicity for self-motions is restored, yielding final relaxation of \( F(q, t) \).

The inset in Fig. 6(b) shows that, in the same \( T \)-range of the latter data, the plateau height, \( f_q \), for \( F(q, t) \) stays constant, contrary to the case of \( f_q^p \). This behavior is observed for all \( q \)-values, except for those probing the lattice structure, for which a progressive increase of the plateau is observed with decreasing \( T \) (not shown). An increase of \( f_q \) for \( q \) not probing the lattice structure is only observed at much lower \( T \) [see data for \( T = 0.070 \) in Fig. 6(b)]. Though for these low-\( T \) values the system cannot be equilibrated and aging effects are observed at long times (not shown), such effects do not affect the behavior of \( F(q, t) \) at intermediate times, where the plateau regime arises. Results in Fig. 6(b) show that the localization transition occurs at lower \( T \) for out-of-lattice collective correlations than for self-correlations, i.e., there is a dynamic decoupling between self- and collective relaxation. These results resemble dynamic features of plastic crystals, where molecules are constrained to vibrate around lattice positions, but can perform full rotations leading to relaxation of out-of-lattice collective correlations (in the present case cluster deformation is an additional mechanism). However, contrary to the case of plastic crystals, activated hopping restores ergodicity of translational motions and leads to finite diffusivity and full decay of self-correlators.

Results for \( f_q \) (excluding \( q \)-values probing the lattice structure) above its localization transition (i.e., \( T \)-independent) are shown in Fig. 7 for the investigated densities. The approximate scaling behavior of \( f_q \) is consistent with a common lattice constant for all the densities. Since \( n_c \propto \rho \), the major effect of increasing \( n_c \) on \( F(q, t) \) is a rescaling of \( \rho_q \), which is canceled after normalization of \( F(q, t) \). The smaller width of \( f_q \) as compared to \( f_q^p \) indicates a much weaker localization for collective than for self-motions.

In summary, we have investigated slow dynamics in the cluster crystal phase of a representative model of macromolecules in solution interacting through effective ultrasoft bounded potentials. The obtained major features are a full change of the initial identity of the clusters through particle hopping between lattice sites, and dynamic decoupling between self- and collective out-of-lattice correlations.

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