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Stability and dynamics of crystals and glasses of motorized particles

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Many of the large structures of the cell, such as the cytoskeleton, are assembled and maintained far from equilibrium. We study the stabilities of various structures for a simple model of such a far-from-equilibrium organized assembly in which spherical particles move under the influence of attached motors. From the variational solutions of the many-body master equation for Brownian motion with motorized kicking we obtain a closed equation for the order parameter of localization. Thus, we obtain the transition criteria for localization and stability limits for the crystalline phase and frozen amorphous structures of motorized particles. The theory also allows an estimate of nonequilibrium effective temperatures characterizing the response and fluctuations of motorized assemblies.

A assemblies of molecular-size particles are seldom far from equilibrium owing to the relative strength of the thermal buffeting inherent at this scale. As we consider assemblies of larger and larger particles, the thermal forces become less capable of moving and reorganizing such assemblies. At the size scale of biological cells, objects are not rearranged just by equilibrium thermal forces but are moved about by motors or by polymerization processes that use and dissipate chemical energy(1). What are the rules that govern the formation of periodically ordered or permanently organized assemblies at this scale? Does the far-from-equilibrium character of the fluctuating forces due to motors and polymer assembly change the relative stability of different colloidal phases? These problems are not unique for intracellular dynamics but belong to an emerging family of nonequilibrium assembly problems ranging from driven particles (2), swarms (3), and jamming (4, 5) to microscopic pattern formation and mesoscopic self-organization (6, 7).

Motivated by these considerations, which may be relevant for the dynamics of the cytoskeleton (1, 8) and other far-from-equilibrium aggregation systems, we study a simple motorized version of the standard hard-sphere fluid often used to model colloids (9). Both motors and nonequilibrium polymer assemblies can convert the chemical energy of high-energy phosphate hydrolysis to mechanical motions, which one would ordinarily think would “stir” and hence destabilize ordered structures. We will show these systems, in some circumstances, may have an extended range of stability relative to those with purely thermal motions.

We adopt a stochastic description of the motions of a collection of motorized particles. The overdamped Langevin dynamics is \( \dot{\mathbf{r}}_i = \beta \mathbf{h}_i + \mathbf{q}(t) + \mathbf{u}_i \). Here, \( \dot{\mathbf{r}}_i \) is the position of the \( i \)th particle, \( \mathbf{h}_i = -\nabla_i U \) is the mechanical force that comes from the usual potential \( U(\mathbf{r}) = U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \sum_{ij} u(\mathbf{r}_{ij}) \) among particles. The random variable \( \mathbf{q}(t) \) vanishes on average and is Gaussian with \( \langle \mathbf{q}(t) \mathbf{q}(t') \rangle = 2D \delta_{t,t'} \delta(t - t') \). The motor term \( \mathbf{u}(t) = \sum_i f_i(t) \delta(\mathbf{r}_i - \mathbf{r}_m) \) is a time series of shot-noise-like kicks. Its properties depend on the underlying biochemical mechanism of the motors. The stochastic nature of the motors also leads to a master equation description (10, 11) for the dynamics of the probability distribution function \( \Psi \) of the particle configurations.
Eynik's nonhermitian variational formulation is similar to the Rayleigh–Ritz method in ordinary quantum mechanics but uses independent left and right state vectors. For isotropic kicking, we start with a Jastrow-like trial function

$$\Psi(\vec{q}) = \exp \left\{ -\sum_i \left[ \frac{\xi}{2} (\vec{q}_i - \vec{R}_i)^2 - \beta U(\vec{q}) \right] \right\}. \quad [2]$$

Similar to the quantum hard spheres (16), such a trial function avoids any singularities of $L_{FP}$ arising from the hard-sphere potentials $u_i(\vec{r}_i)$ between particles $i$ and $j$ used in this study. For simplicity, we set $\tilde{q}_i := \vec{r}_i - \vec{R}_i$ and a uniform $\xi := \xi$. The nonhermitian variational method implies for steady states that the second moment of $\tilde{q}$ satisfies the moment closure (17) equation:

$$\frac{\delta \langle q_i^2 \rangle}{\delta t} = \langle q_i^2 | L_{FP} + L_{NE} | \Psi \rangle = 0. \quad [3]$$

To effectively evaluate Eq. 3, we need to simplify the many-body integration $\int d\vec{q} \tilde{q}_i$ involving $\exp -\beta U(\vec{q})$. Here, we use cluster expansion (18, 19) to render the many-body Boltzmann factor a product of effective single-body terms by averaging over the neighbors’ fluctuations. We thus have $e^{-\beta U} = \Pi e^{-\beta u_i} = \Pi e^{-\beta \tilde{u}_i}$. Here, the original $u_i = \sum_{j \neq i} \tilde{u}_i$ depends on the many-body configuration, whereas $\tilde{u}_i$ depends on $\tilde{q}_i$ (and constant $\{\vec{R}_i\}$) only. In fact, we keep it to the harmonic order for consistency, i.e., $\tilde{u}_i = \beta^{-1} \langle q_i^2 \rangle$. Here, $\alpha$ is the effective spring constant from the mechanical feedback from neighbors. $\tilde{u}_i$ depends on its neighbors’ overall fluctuations controlled by $\tilde{q}$ and their mean position $\{\vec{R}_i\}$. In turn, the positions of the neighbors are controlled by the lattice spacing for crystals or radial distribution functions for glasses and ultimately by the nature of the structure and the particle density $n$. That is, for fcc lattice, we have $\alpha_{cr} = \alpha_{cr}(\tilde{q}, n)$ as the eigenvalues of the Hermite matrix constructed from the effective potential $\sum_{j \neq i} v(\vec{R}_j; \tilde{q})$. Here, $v(\vec{R}_j; \tilde{q}) = \ln(1 + \text{erf}[\vec{R}_j; \tilde{q}]) - \frac{3}{2} \text{erf}[\vec{R}_j; \tilde{q}] + \frac{1}{2} \text{erf}^2[\vec{R}_j; \tilde{q}]$ and the sum of $\vec{R}_j$ is over the 12 nearest-neighbor positions of the origin of a fcc lattice

$$\left[ \begin{array}{c} \text{with lattice spacing} \left( \frac{4}{\sqrt{n}} \right) \end{array} \right].$$

For glasses (20, 21), we replace the summation over discrete crystalline neighbor location with a mean-field average over the first shell of the pair-distribution function of the hard-sphere liquids, $\alpha_{g}(\tilde{q}, n) = \frac{1}{2} \sum_{n, q} \alpha_{g}(n, R, n) \text{Tr} v(\vec{R}; \tilde{q})$. For numerical work, we take $g(R, n)$ as the Verlet and Weisz’s corrected radial-distribution function (22).

After some calculations, we obtain the steady-state many-body probability-distribution function as a product of localized Gaussians of the form $\exp[-\alpha(\vec{R} - \vec{R})^2]$ with $\alpha$, the final localization strength, satisfying two equations:

$$\alpha = \tilde{\alpha} + \alpha (\tilde{\alpha}, n) \quad [4]$$

$$6D \frac{\tilde{\alpha}}{\alpha} + \kappa \sigma L(\tilde{\alpha}) \times \left( \frac{\pi}{\alpha} \right)^{-3/2} = 0. \quad [5]$$

The first and second terms of Eq. 5 come from $\langle q_i^2 | L_{FP} | \Psi \rangle / \langle 1 | \Psi \rangle$ and $\langle q_i^2 | L_{NE} | \Psi \rangle / \langle 1 | \Psi \rangle$, respectively. The integral $\sigma L(\tilde{\alpha}) := \int d\vec{q} \tilde{q}^{2} (\tilde{\alpha} + \kappa \tilde{\alpha})^{1/2} \exp (-\alpha \tilde{q}^{2} + \lambda \tilde{q} - \kappa \tilde{\alpha})$ can be further expressed as explicit but complicated analytical formulas with incomplete Gamma functions. Thus, using Eq. 6 in Eq. 5, we finally derive the order parameter for localization, $\alpha$, in a closed form with parameters $\tilde{\alpha}, \kappa, s, s', n, \beta$. When $\kappa = 0$, we have $\tilde{\alpha} = 0$ and the equilibrium equation $\alpha = \alpha(\tilde{\alpha}, n)$, which returns to the self-consistent phonon solution (18–21, 23). A nonzero solution $\tilde{\alpha}$ of Eq. 5 is only obtained at sufficiently high density, i.e., for $n > n_c$. For low density, the system cannot support stable localized vibrations and is in the fluid phase with $\tilde{\alpha} = 0$. An instability density $n_c$ separates these two phases. This phase transition is first-order-like, characterized by a discontinuous jump of $\tilde{\alpha}$.

We calculated $n_c$, as a function of two independent parameters, $s$ and $s', n(s, s')$ for various $\kappa, D$, and $\ell$. An important dimensionless ratio $\Delta := \kappa \ell^2 / D$ measures the strength of chemical versus thermal noise. For an actin polymer solution (1), we can relate the effective kicking rate to the speed of nonequilibrium polymerization. Here, $\ell$ is the monomer size $0.01 \mu m (\mu = 10^{-6})$. The treadmill concentration is $\kappa_{tr} = 0.17 \mu M$. The chemical reaction rates of the barbed and pointed ends of actin are $k_1 = 11.6 \mu M^{-1} s^{-1}$ and $k_{-1} = 1.3 \mu M^{-1} s^{-1}$, respectively. The diffusion constants of rod are given by the Kirkwood equation (24). This equation relates the diffusion to solvent viscosity, $\eta$, and gives the translational diffusion constants: $D_1 = k_B T \ln(L/d)/(2\pi\eta L)$ and $D_2 = D_1/2$. With the typical length of the actin filaments, $L = 20 \mu m$, and typical width, $d = 10^{-5} \mu m$, an estimate of the hydrodynamic diffusion along the rod gives $D_0 = 0.1 \mu m^2 s^{-1}$. Thus, for a dilute solution of typical actin filaments, $\Delta \sim 10^{-1}$. However, in vivo, the actin monomer concentration is kept much higher than $\kappa_{tr}$ (with the help of capping proteins that prevent actin filaments from growing longer). Also, the viscosity of the cell medium is higher than $\eta$ of pure water because of the presence of other macromolecular components. These components lower the effective diffusion constant and raise the value of $\kappa$; therefore, they could push $\Delta$ above 1. The limit $\Delta \rightarrow 0$ corresponds to entirely motorized motion.

The resulting densities $n_c(s, s')$ are shown in Figs. 1 and 2. Fig. 1 shows some 1D plots that come from vertical slices of $n_c$ for several special cases. Fig. 2 shows the 2D view of the critical surfaces $n_c$ for variety of parameters. For the case shown with $\Delta = 1$, $s(s')$ (which is the only $n$-dependent part of $\alpha$) drops to zero, but we still have a nonzero solution $\tilde{\alpha} = \tilde{\alpha}$ for a corner of $(s, s')$ space. In the opposite corner we stopped searching for
solutions when \( n_c \) approached the maximum packing density \( \sqrt{\pi} \).

Thus we have three distinct regions.

As seen from these figures, kicking noise does not always destabilize the structures. Instead, the localized phases have an enlarged stability range when \( s + s' > 1 \). When \( s' = 1 - s \), the same stability limits are obtained as in the equilibrium thermodynamic theory. Both the frozen disordered glass and the ordered fcc lattice can be stabilized by kicking motors. The motor effects on the fcc lattice are more pronounced. The fcc ordered fcc lattice can be stabilized by kicking motors. The feedback procedure, we first obtain the mapping from a hard-sphere model to an effective harmonic potential \( \alpha = \alpha(\hat{a}) \).

Here, \( \alpha \) depends on the steady-state probability distribution of its neighbors. Conversely, \( \alpha \) can be viewed as the final effective spring constant of a kicking particle in an harmonic potential of \( \hat{a} \). Next, we numerically solve \( \tilde{\alpha} = \alpha(\tilde{a}) \) from single-particle master equations by using a variational method based on the square hermitianized operator \( (1/2) \) with single-particle trial functions. The two sets of operations are iterated to obtain a pair of self-consistent results \( (\alpha, \tilde{a}) \). The critical density predicted by this self-consistent squared hermitian variational method agrees very well with results from the nonhermitian variational method. The difference of instability density is \( <0.1\% \) when \( \Delta < 1 \). The corresponding critical \( \tilde{\alpha} \) is also similar. The two methods do give different results when \( \Delta \gg 1 \).

For persistent kicking, the trial functions have to be modified. Each localized particle now has a distribution of locations of the form \( \tilde{\alpha}(\tilde{a}, \tilde{r}) = \tilde{a} \). Here, \( \tilde{a} \) is an off-center shift vector parallel to \( \tilde{a} \). We must consider the effects of the variational parameter \( b \) on \( \alpha \) along with the direct changes of \( \tilde{a} \). The additional decrease of \( \alpha \) arises from the distortion of the structures caused by always kicking in the same directions. We model the distortion effect of persistent kicking on the pair distributions by replacing each initial position with a dispersed distribution. For the crystal, this means the initial neighboring position of \( \tilde{r} \) is replaced by an average over positions \( \tilde{R} + \tilde{b} \hat{n} \) with \( \hat{n} \) is an arbitrary unit direction. Likewise, the radial distribution function of the glass case is broadened from the initial \( g_{b=0}(\tilde{r}) \) to

\[
g_b(\tilde{r}) = \int g_{b=0}(\tilde{r}) \left( \frac{1}{4\pi R^2} \right) \delta(|\tilde{r}' - \tilde{r}| - b) d\tilde{r}'.
\]

In this case, an additional normalization of the first peak enforces the condition \( g = 0 \) for \( r < 1 \).

For persistent kicking, \( s \) has similar effects on \( \tilde{a} \), as were found for the isotropic case. The shift \( b \) agrees quite well (within several percentages for the practical range of parameters) with the estimate \( k\epsilon/2\alpha D \) based on a small \( \epsilon \) expansion of the master equation. The resulting displacement amplitude \( b \) is large enough to distort the stable structure so that any increased stability that may arise from kicking (if any) is now very modest, as shown in Fig. 3.

Since the kicking noise enlarges the stability region in the isotropic case with \( s + s' > 1 \), we wondered whether susceptible kicking may sometimes actually decrease the effective temperature of this nonequilibrium system. An effective temperature can be defined by the fluctuation–dissipation relation even for far-from-equilibrium situations like the motorized crystal (25). The ratio of the thermal temperature to the effective temperature is also called the fluctuation-dissipation theorem violation factor. The effective temperature can be computed by comparing the fluctuations of a motorized particle with its response to an external force. \( T^{\text{eff}} \) depends on the frequency or time duration, the absolute time (in the case of an aging system), and even possibly on the choice of the observable itself. To compute the needed time-dependent quantities, we solve the time-dependent master equations for nonhermitian operators, again using a Gaussian ansatz characterized now with dynamic first and second moments.
For illustration, we carry out the analysis of the dynamics for the 1D symmetric case in a harmonic potential \( \alpha x^2 \) with \( s = s' \). Thus, \( \dot{L}_{PE} \psi = D \dot{\alpha} x^2 \psi - \beta [\dot{\psi} B \theta (x) \psi] \) and

\[
\dot{L}_{NE} \psi(x) = \frac{\kappa}{2} \phi (x - \ell) e^{\alpha(x - \ell)} + \frac{\kappa}{2} \phi (x + \ell) e^{\alpha(x + \ell)}
\]

with \( \alpha(x, \ell) = -2s \alpha \ell - s \alpha \ell^2 \). The parameters in the Gaussian ansatz

\[
\psi(x, m(t)) = (2\pi \hbar \gamma(t))^{-1/2} \exp \left( \frac{- (x - m(t))^2}{2\hbar(t)} \right)
\]

where \( m_1 = m = m_2 \) satisfies the time-dependent dynamics described by a set of differential equations with \( \kappa(t) = \kappa \exp(-s \alpha t^2) / \hbar(t) \) and \( m_1 = 2D \alpha m_2 = \kappa(t) \exp(2s \alpha t^2) \ln \sinh(2s \alpha t m_1) - 2 \kappa(t) \exp(2s \alpha t^2) \ln \sinh(2s \alpha t m_2) + 2 s \alpha m_2 \ln \sinh(2s \alpha t m_2) \).

To obtain the Green's function, \( G(x, t'; t, 0) \), \( m_1(t) \), and \( m_2(t) \) must satisfy the equations above with the initial conditions \( m_1(0) = x' \) and \( m_2(0) = x'' \). We denote \( \tilde{m}(t; x') \), \( \tilde{m}(t; x'') \) for this pair solution of the differential equation. Green's function's correlation and response are given by \( C(t) = \int dx' \tilde{m}(t; x') \dot{\psi}^*(x', m^*) \). Here, \( \ast \) denotes the steady-state value, and the response to a pulse is \( R(t) = \int dx' \left( \dot{\psi} B \theta (x') \psi(x', \dot{m}(t; x')) \right) \).

Combining these yields the effective temperature:

\[
T_{eff}(t) = -\frac{\beta}{R(t)} \left[ 1 + \frac{\kappa(t)^2}{2} \exp(2s \alpha t^2 m_2^*) \right]
\]

For long times, \( m_1 \to 0 \), \( \sinh(2s \alpha t m_1) \to \sinh(2s \alpha t m_2) \), and \( m_2 \to m_2^* \). At this limit, we find the value of the ratio exactly same as the short time limit. Therefore,

\[
T_{eff}(t = 0) = T_{eff}(t = \infty) = 1 + \frac{\kappa(t)^2}{2} \exp(2s \alpha t^2 m_2^*)
\]

Yet for intermediate times, the ratio is not constant and differs from either limiting value. In general, \( T_{eff} > T_{th} \), i.e., the system is “hotter” although chemical noise apparently enlarges the stability range of the localized phase.

We have studied the stability and dynamics of localized nonequilibrium structures of motorized particles. The nonequilibrium noise from kicking motors sometimes increases the effective spring constant and enlarges the mechanical stability range of both crystal and frozen glass structures. We see that for systems like the cytoskeleton, nonequilibrium noise may speed up the dynamics without sacrificing structural stability. This model can be further developed to include anisotropy of the particles or under other types of nonequilibrium noise or driven forces. Besides taking this solid-state viewpoint, one can also study the transition from the liquid side by mode-coupling theory, a problem for future studies.

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