Dynamics of patchy particles in and out of equilibrium

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We combine particle-based simulations, mean-field rate equations, and Wertheim’s theory to study the dynamics of patchy particles in and out of equilibrium, at different temperatures and densities. We consider an initial random distribution of non-overlapping three-patch particles, with no bonds, and analyze the time evolution of the breaking and bonding rates of a single bond. We find that the asymptotic (equilibrium) dynamics differs from the initial (out of equilibrium) one. These differences are expected to depend on the initial conditions, temperature, and density.

I. INTRODUCTION

The possibility of synthesizing novel materials with enhanced physical properties from the spontaneous self-assembly of colloidal particles is among the most popular challenges of Soft Condensed Matter [1–6]. Functionalized colloidal particles with patches on their surfaces (patchy particles) are promising candidates for the individual constituents, as they allow control of both the valence (number of neighboring particles) and the local structure [7–17]. Equilibrium studies of patchy particle systems revealed rich phase diagrams depending on temperature and density, and in novel ways on the number and type of patches [12, 18, 19]. However, the potential application of these predictions may be compromised, as the feasibility of assembling the new phases is seriously hampered by the kinetic barriers that emerge from the complex particle-particle correlations [20–30]. Thus, understanding the dynamics towards thermodynamically stable (equilibrium) structures is vital to tackle this challenge.

Previous studies attempted to relate the out of equilibrium dynamics to the dynamics at equilibrium [31–33]. The idea is to describe the dynamics as a balance between breaking and forming individual bonds, where the rates for each process are considered time invariant. Since the overall bond probability should converge to the rates for each process are considered time invariant.

II. MODEL AND SIMULATIONS

Following previous works [28, 34, 35], we model the patchy particles as three-dimensional spheres, with three patches equally distributed on their surfaces. The core-core interaction is described by a (repulsive) Yukawa-like potential, \( V(r) = \frac{\epsilon}{r} \exp(-k [r - \sigma]) \), where \( \sigma \) is the effective diameter of the interacting particles, \( A/k = 0.25k_B T \) is the interaction strength and \( k/\sigma = 0.4 \) is the inverse screening length. The patch-patch interaction is described by an attractive pairwise potential \( V_C(r_p) = -\epsilon \exp\left[-(r_p/\xi)^2\right] \), where \( \epsilon \) is the interaction strength, \( \xi = 0.1\sigma \) is the size of the patch, and \( r_p \) the distance between patches [36].

To resolve the individual trajectories of the particles, we perform particle-based simulations using the velocity Verlet scheme of the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [37]. We integrate the Langevin equations of motion for the translational and rotational degrees of freedom, respectively,

\[
m \dot{\vec{v}}(t) = -\nabla_r V(\vec{r}) - \frac{m}{\tau_r} \vec{v}(t) + \sqrt{\frac{2mk_B T}{\tau_r}} \vec{f}_r(t),
\]

and

\[
I \dot{\vec{\omega}}(t) = -\nabla_\theta V(\theta) - \frac{I}{\tau_\omega} \vec{\omega}(t) + \sqrt{\frac{2I k_B T}{\tau_\omega}} \vec{f}_\theta(t),
\]

where, \( \vec{v} \) and \( \vec{\omega} \) are the translational and angular velocities, \( m \) and \( I \) are the mass and moment of inertia of each
patchy particle, \( V(\cdots) \) is the pairwise potential, \( \tau_t \) and \( \tau_r \) are the translational and rotational damping times, and \( \bar{f}_t(t) \) and \( \bar{f}_r(t) \) are stochastic terms taken from a random distribution of zero mean. The damping time for the translational motion is \( \tau_t = m/(6\pi\eta R) \), and the damping time for the rotational motion is \( \tau_r = 10\tau_t/3 \), in line with the Stokes-Einstein-Debye relation for spheres [38].

Simulations are performed for a three-dimensional system of linear size \( L = 16 \), in units of the particle diameter \( \sigma \), averaged over 20 samples, starting from a random (uniform) distribution of non-overlapping particles. The density \( \rho \) is the number of particles per unit volume. We consider five different densities, namely, \( \rho = \{0.128, 0.16, 0.2^{0.3} \} \) in units of \( 1/\sigma^3 \), and four different temperatures: \( T = \{0.075, 0.1, 0.125, 0.15\} \) in units of \( k_B T \).

III. RESULTS

The dynamics evolves through a sequence of bonding and breaking events. The simplest approach to describe this dynamics is through a (mean-field) rate equation for the bonding probability \( p_b(t) \), which corresponds to the fraction of bonded patches in the infinite size limit. Accordingly,

\[
p_b(t) = -k_{br} p_b(t) + \rho f k_{bo} [1 - p_b(t)]^2,
\]

where \( p_b(t) \) stands for the time derivative, \( t \) for time in units of the Brownian time, \( f \) for the valence, \( \rho \) for the number density, and \( k_{br}, k_{bo} \) for the breaking and bonding rates of a single bond, respectively. As discussed in Refs. [33, 39], Eq. (3) can be derived from a generalized Smoluchowski set of equations, accounting for both aggregation and fragmentation of loopless clusters of particles of functionality \( f \) (i.e. \( f \) patches), under the assumptions that all patches are identical, the diffusion coefficient is the same for all clusters, and all patches are unbonded at \( t = 0 \). If, for simplicity, we consider that \( k_{br} \) and \( k_{bo} \) are time invariant and depend on temperature and density only then,

\[
p_b(t) = p_\infty \left( \frac{1 - \exp(-\Gamma t)}{1 - p_\infty^2 \exp(-\Gamma t)} \right),
\]

where \( p_\infty = \lim_{t \to \infty} p_b(t) \). At equilibrium, \( \dot{p}_b(t) = 0 \), and the net rates of bonding and breaking are necessarily the same. Thus,

\[
\Gamma = k_{br} \frac{1 + p_\infty}{1 - p_\infty} = f \rho k_{bo} \frac{1 - p_\infty^2}{p_\infty}.
\]

Clearly, \( p_\infty \) depends only on the ratio \( k_{br}/k_{bo} \) and is simply the bond probability under equilibrium conditions, as discussed below. The value of \( \Gamma \) (and thus the individual values of \( k_{br} \) and \( k_{bo} \)) may be estimated from a fit of Eq. (4) to numerical data for \( p_b(t) \) obtained from particle-based simulations.

Werthemeir’s theory is the most successful thermodynamic perturbation theory for associating fluids with short-ranged, anisotropic interactions (see e.g. [40]). Within this equilibrium theory, the bonding free energy, treated as a perturbation over that of a reference fluid, is found to be a function of the equilibrium bonding probability, \( p_{b,eq} \), which in turn depends on the number density, the functionality \( f \), the interaction potential between the
patches $V_G$, and the reference fluid, and it is the solution of
\[ f \rho \Delta = \frac{p_{b,eq}}{(1 - p_{b,eq})^2}; \tag{6} \]
where
\[ \Delta = \frac{1}{(4\pi)^2} \int d\hat{r} \int d\hat{r}_1 \int d\hat{r}_2 (\exp[-\beta V_G(r_p)] - 1) g_{ref}(r). \tag{7} \]
Here, $g_{ref}(r)$ is the pair correlation function of the reference fluid, $\hat{r}$ is the vector between the centers of the two particles participating in the bond, and $\hat{r}_i$ is the unit vector that defines the position of the bonded patch on particle $i$ relative to the center of that particle. In order to proceed we replaced the soft-core repulsion $V_G(r)$, by the repulsion of hard spheres with a temperature dependent diameter $d$, obtained through the Barker-Henderson approximation. Thus, $g_{ref}(r)$ is given by $g_{HS}(r = d, \rho)$, the contact value of the pair correlation function of a system of hard spheres of diameter $d$ and number density $\rho$ (see e.g., Ref. [34]). $\Delta$ is now rewritten as,
\[ \Delta = g_{HS}(r = d, \rho) G(T, \alpha, \delta), \tag{8} \]
where $\alpha = \xi/\sigma$ and $\delta = (1 - d/\sigma)$. $G(T, \alpha, \delta)$ is the integral of the Mayer function of the patch-patch interaction $V_G$ over the bond volume (see Ref. [34] for further details).

Since $p_{b,eq} = p_\infty$, Eqs. (3) and (6), imply that at equilibrium the breaking and bonding rates satisfy,
\[ \Delta = \frac{k_{bo}}{k_{br}}, \tag{9} \]
consistent with the fact that both Eqs. (3) and (6) may be derived from the Flory-Stockmayer size distribution of clusters [39, 41]. It is also known that the equilibrium mean-field relation breaks down in the limit where a strongly connected gel is formed [31]. Note that, both the dynamics and the equilibrium descriptions, neglect patch-patch correlations.

In order to assess the validity of the rate equations we compared, in Fig. 4, the time evolution of the bonding probability $p_b(t)$ of a single bond, obtained from the particle-based simulations (symbols) and a least squares fit of Eq. (4) (solid lines). Clearly, the rate equation Eq. (4) captures the behaviour of $p_b(t)$ accurately. In addition, this procedure provides estimates of $\Gamma$ and $p_\infty$, which through Eq. (3) yield estimates of the breaking and bonding rates, $(k_{br}, k_{bo})$, over a wide range of temperatures and densities. As shown in Fig. 2 we find a remarkable agreement between $p_\infty(\rho, T)$ obtained from the fit and $p_{b,eq}(\rho, T)$ obtained from Wertheim’s theory. The observed deviations at the lowest simulated temperature may be due to the approximations required to calculate $\Delta$, as the mapping of the reference system to a system of hard spheres with an effective diameter, or the fact that, at high densities and low temperatures a gel is formed.

As discussed above, it is possible to estimate the temperature dependence of the effective rates $k_{br}$ and $k_{bo}$, from $\Gamma$ (Fig. 1), as shown in Fig. 3. We see that $k_{br}$ follows an exponential decay with $1/T$, as expected for a thermal activated (Arrhenius) process, with no significant dependence on the density. Following Arrhenius’ work, we expect that $k_{br} \sim \langle \exp(\beta V_G) \rangle$, where $\beta = (k_B T)^{-1}$ and $\langle \cdots \rangle$ stands for an ensemble average over different bonds. From Wertheim’s theory, Eq. (8), $G(T) = \langle \exp(-\beta V_G) \rangle$, and we expect $k_{br} \sim G(T)$. The solid line in Fig. 3(a) corresponds to $aG(T)^{-1}$, where $a$ is a constant adjusted to fit the numerical data. One
and thus the energy barrier is equal to the energy of the bond (\(E_b\)) for the patch-patch interaction. In those systems, the decreasing function of \(T\). We note that most other studies between the line and the numerical data. This re-
sees that the lower the temperature, the better the agreement. The solid lines in (a) and (d), and the symbols in (a) and (c) have the same meaning as in Fig. 3.

![FIG. 5. Temperature and density dependence of the asymptotic value of the rate of bond breaking (\(k_{br}^*\)) and bonding (\(k_{bo}^*\)) of a single bond. Rate of bond breaking of a single bond as a function of (a) the inverse temperature and (b) density, at different densities and temperatures, respectively. Rate of bonding of a single bond as a function of (c) temperature and (d) density, at different densities and temperatures, respectively.](image)

sees that the lower the temperature, the better the agreement between the line and the numerical data. This result indicates that \(k_{br} = F(T)G(T)^{-1}\), where \(F(T)\) is a decreasing function of \(T\). We note that most other studies of patchy particles consider a square well potential for the patch-patch interaction. In those systems, the energy barrier is equal to the energy of the bond \((E_b)\) and thus \(k_{br}(T) \approx \exp(\beta E_b)\), since \(E_b\) is the same for all bonds. 

At equilibrium \(k_{bo} = k_{br}\Delta\) and thus \(k_{bo} \approx g_{HS}(\tau = d, \rho)F(T)\). Under these conditions, since the dependence on \(T\) is only through \(F(T)\), the bonding rate of a single bond should decrease with temperature, as shown in Fig. 3(c). In Fig. 3(d) we plot the dependence of \(k_{bo}\) on density at different temperatures. The solid line is proportional to \(g_{HS}\), showing that the density dependence is well described by \(g_{HS}\). Note that, the rate of bonding should depend on the diffusion coefficient of the particles, which sets the time scale for two particles in solution to collide, and thus increases with temperature. However, as time is rescaled by the Brownian time, this effect is not apparent in the results.

For simplicity, in line with previous works, we considered that the rates \(k_{br}\) and \(k_{bo}\) are indeed constant, i.e. time independent. Particle-based simulations allow us to measure these rates and evaluate this assumption. To that end, we measured the number of new and broken bonds over intervals of 5000 iteration steps (between 0.075 and 0.15 in Brownian time, depending on the temperature) and estimated \(k_{br}(t)\) and \(k_{bo}(t)\). Fig. 4 illustrates the time dependence of these rates, at different temperatures and \(\rho = 0.25\). We find that both rates increase with time and saturate at long times. However, while \(k_{br}\) saturates rapidly at times of the order of the Brownian time, \(k_{bo}\) takes up to one order of magnitude longer to saturate. The lower the temperature the longer the time it takes to saturate. In the same figure, we also plotted the effective rates estimated from the fit discussed above (horizontal lines). It is clear that the asymptotic values of these rates are significantly different from the effective rates obtained from the fit. In Fig. 5 we plot the asymptotic values of these rates, \(k_{br}^*\) and \(k_{bo}^*\) as a function of temperature and density (computed from an average over the long-time regime of \(k_{br}(t)\) and \(k_{bo}(t)\) - see Fig. 4). While, the qualitative dependence of these rates on \(T\) and \(\rho\) is consistent with that obtained from the fits (see Fig. 3), the values are significantly different. Nevertheless, their ratio is the same, as expected Wertheim’s theory [3] and [4], with \(p_\infty = p_\infty^{eq}\). Finally, Eq. (9) with \(\Gamma\) obtained using the asymptotic values of \(k_{br}^*\) and \(k_{bo}^*\) from the numerical simulations does not fit the data of Fig. 4(not shown). This clearly suggests that the out of equilibrium dynamics is different from that at equilibrium, at least in three dimensions, and that the effective rates describing the initial dynamics are different from those that describe the dynamics at equilibrium.

**IV. CONCLUSIONS**

We combined Langevin particle-based simulations, mean-field rate equations, and Wertheim’s equilibrium theory to study the dynamics of patchy particles both in and out of equilibrium. By analyzing the dependence of the rate of breaking and forming a single bond, at different temperatures and densities, we have shown that the dynamics at equilibrium is different from that towards equilibrium (out of equilibrium). In particular, for initial systems of randomly distributed particles with no bonds, both rates are systematically higher at equilibrium. However, since the asymptotic value of the fraction of bonded patches depends on the ratio of the two rates, it can be estimated both from the dynamics and the equilibrium theory.

We have focused on the non-percolative regime (high temperature and low density). At low temperatures and high densities, percolation is expected to occur and thus collective effects will definitely affect the dynamics [3]. Assumptions such as negligible patch-patch correlations and independence of the diffusion coefficient of the cluster size are no longer valid. In that regime, we expect differences between the equilibrium and out of equilibrium dynamics to be more significant and the validity of the mean-field approach compromised.

This work highlights the relevance of out of equilibrium studies. It was shown previously that, under certain conditions, the dynamics depends strongly on the initial configuration [28, 34]. Here, we have considered only initially unbonded particles. The difference between the
equilibrium and out of equilibrium dynamics is expected to depend also on the initial conditions. This difference is expected to impact most strongly on the rate of bonding, as different kinetic pathways will correspond to different mechanisms of bond formation. Notwithstanding, in the limit of very strong patch-patch correlations, even the bond breaking dynamics may be affected by collective effects.

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