Effective Interactions in Active Brownian Suspensions

T. F. F. Farage, P. Krimminger, and J. M. Brader

1Department of Physics, University of Fribourg, CH-1700 Fribourg, Switzerland
2Theoretische Physik II, Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

Active colloidal particles in suspension are currently the subject of considerable attention, due largely to their ability to model self-organisation phenomena in biological systems, but also as a new branch of fundamental research in nonequilibrium statistical mechanics: assemblies of active colloids are intrinsically out-of-equilibrium systems. In contrast to their passive counterparts, active colloids undergo both solvent induced Brownian motion and a self-propulsion which requires a continual consumption of energy from the local environment. Several idealized experimental model systems have been developed, such as catalytic Janus particles, colloids with artificial flagella and light activated particles. The understanding of active systems has been further aided by the development of simple theoretical models, which aim to capture the essential physical mechanisms and which have been used to study e.g. bacteria, cells or filaments in the cytoskeleton.

Active particles are characterised by a persistent motion, which can lead to ‘self trapping’ dynamics and a rich variety of related collective phenomena. Even the simplest models of active spherical particles with purely repulsive interactions can display the phenomenon of motility-induced phase separation (MIPS). In many respects, MIPS resembles the equilibrium phase separation familiar from passive systems with an attractive component to the interaction potential (e.g. the Lennard-Jones potential). This apparent similarity has motivated several recent attempts to map an assembly of active colloids onto a passive equilibrium system, interacting via an effective attraction (usually taken to be a very short range sticky-sphere potential). Despite the intuitive appeal of mapping to an equilibrium system, there exists no systematic theoretical approach capable of predicting an effective equilibrium potential directly from the bare interactions.

Our current understanding of MIPS has largely been gained through either simulation or phenomenological theory. The phenomenological theory is based on an equation for the coarse-grained density, featuring a local speed and a local orientational relaxation time. Although the precise relationship between these one-body fields and the interparticle interaction potential remains to be clarified, some progress in this direction has been made. On a more microscopic level, it has recently been shown that a general system of active particles does not have an equation of state, due to the influence of the confining boundaries, however, one can be recovered for the special case of active Brownian spheres.

Here we report a first-principles theory for systems of active Brownian spheres, which demonstrates explicitly how an effective many-body interaction potential is induced by activity. An appealing feature of this approach is that intuition gained from equilibrium can be used to understand the steady-state properties of active systems. The required input quantities are the passive (‘bare’) interaction potential, the rotational diffusion coefficient and the particle propulsion speed. The theory generates as output the static correlation functions and phase behaviour of the active system. For a repulsive bare interaction, activity generates an attractive effective pair potential, thus providing an intuitive explanation for the MIPS observed in simulations. For an attractive bare potential, we find that increasing activity first reduces the effective attraction, consistent with the experiments of Schwarz-Linek et al., before leading at higher activity to the development of a repulsive potential barrier. We speculate that this barrier may be related to the reentrant phase behaviour observed in simulation by Redner et al.

The paper will be structured as follows: In we specify the microscopic dynamics and describe how to eliminate orientational degrees of freedom. From the resulting coarse-grained, non-Markovian Langevin equation we derive a Fokker-Planck equation for the positional degrees of freedom, from which we identify an effective pair potential. In we employ the effective pair potential in an equilibrium integral equation theory and investigate the structure and phase behaviour of both repulsive and attractive bare potentials. In the former case we predict MIPS, whereas in the latter case phase separation is suppressed by activity. Finally, in we discuss our findings and provide an outlook for future research.
I. THEORY

A. Microscopic dynamics

We consider a three dimensional system of $N$ active, interacting, spherical Brownian particles with spatial coordinate $r_i$ and orientation specified by an embedded unit vector $p_i$. Each particle experiences a self propulsion of speed $v_0$ in its direction of orientation. Omitting hydrodynamic interactions the particle motion can be modelled by the overdamped Langevin equations

$$\dot{r}_i = v_0 p_i + \gamma^{-1} F_i + \xi_i, \quad (1)$$
$$\dot{p}_i = \eta_i \times p_i, \quad (2)$$

where $\gamma$ is the friction coefficient and the force on particle $i$ is generated from the total potential energy according to $F_i = -\nabla_i U_N$. The stochastic vectors $\xi_i(t)$ and $\eta_i(t)$ are Gaussian distributed with zero mean and have time correlations $\langle \xi_i(t) \xi_j(t') \rangle = 2D_i\delta_{ij}\delta(t-t')$ and $\langle \eta_i(t) \eta_j(t') \rangle = 2D_i\delta_{ij}\delta(t-t')$, where $D_i$ and $D_D$ are the translational and rotational diffusion coefficients.

Equations (1) and (2) are convenient for simulation, but are perhaps not the most suitable starting point for developing a first-principles microscopic theory. For a homogeneous system, averaging over the angular degrees of freedom generates a coarse-grained equation

$$\dot{\chi}_i(t) = \gamma^{-1} F_i(t) + \xi_i(t) + \chi_i(t), \quad (3)$$

where $\chi_i(t)$ is a Markov process with zero mean and where the time correlation function is given by

$$\langle \chi_i(t) \chi_j(t') \rangle = \frac{v_0^2}{3} e^{-2D_i|t-t'|}\delta_{ij}. \quad (4)$$

The average in (4) is over both noise and initial orientation. The distribution of $\chi_i(t)$ is Gaussian to a good approximation. This point and further technical details of the coarse graining are discussed in Appendix B. Equation (3) provides a mean-field level of description, which deviates from the exact equations (1) and (2) by neglecting the coupling of fluctuations in orientation and positional degrees of freedom.

The Langevin equation (3) describes a non-Markovian process, which approximates the stochastic time evolution of the positional degrees of freedom. The persistent motion of active particles is here encoded by the exponential decay of the time correlation (1), with persistence time $\tau_p = (2D_r)^{-1}$. For small $\tau_p$, the time correlation becomes $\langle \chi_i(t) \chi_j(t') \rangle = 2D_r\delta_{ij}\delta(t-t')$ and the dynamics reduce to that of an equilibrium system with diffusion coefficient $D_i + D_{D_a}$, where $D_{D_a} = v_0^2/(6D_r)$. This limit is realized when $\tau_p$ is shorter than the mean free time between collisions, i.e. in a dilute suspension. To treat finite densities requires an approach which deals with persistent trajectories. With this aim, we adopt (3) as the starting point for constructing a closed theory.

B. Fokker-Planck equation

A stochastic process driven by colored noise, such as that described by equation (3), is always non-Markovian. Consequently, it is not possible to derive an exact Fokker-Planck equation for the time evolution of the probability distribution. Nevertheless, an approximate Fokker-Planck description capable of making accurate predictions can usually be found. The approximate Fokker-Planck equation implicitly defines a Markov process which best approximates the process of physical interest (although precisely what constitutes the ‘best’ approximation remains a matter of debate). From the extensive literature on this subject (see [24–26] and references therein) has emerged a powerful method due to Fox [27, 28], in which a perturbative expansion in powers of correlation time is partially resummed using functional calculus. The resulting Fokker-Planck equation is most accurate for short correlation times (‘off white’ noise) and for one-dimensional models makes predictions in good agreement with simulation data [26].

We now consider applying the method of Fox [27, 28] to equation (3). This approach consists of first formulating the configurational probability distribution as a path (functional) integral and then making a time-local, Markovian approximation to this quantity. Technical details of the method are given in Appendix B. Fox’s approach was originally developed to treat one-dimensional problems [27, 28], however the generalization to three dimensions is quite straightforward. This enables us to directly obtain the following Fokker-Planck equation

$$\partial_t \Psi(r^N, t) = -\sum_{i=1}^{N} \nabla_i \cdot J_i(r^N, t), \quad (5)$$

where $\Psi(r^N, t)$ is the configurational probability distribution. Within the generalized Fox approximation the many-body current is given by

$$J_i(r^N, t) = -D_i(r^N) \left[ \nabla_i - \beta F_i^{\text{eff}}(r^N) \right] \Psi(r^N, t), \quad (6)$$

where $\beta = (k_B T)^{-1}$. The diffusion coefficient is given by

$$D_i(r^N) = D_i + D_{D_a} \left( 1 + \frac{\tau \nabla_i \cdot \beta F_i(r^N)}{1 - \tau \nabla_i \cdot \beta F_i(r^N)} \right), \quad (7)$$

where we have defined a dimensionless persistence time, $\tau = \tau_p D_i/d^2$. The effective force is given by

$$F_i^{\text{eff}}(r^N) = \frac{1}{D_i(r^N)} \left( F_i(r^N) - k_B T \nabla_i D_i(r^N) \right), \quad (8)$$

where $D_i(r^N) = D_i(r^N)/D_i$ is a dimensionless diffusion coefficient. Either in the absence of interactions or in limit of large $D_r$ the diffusivity (7) reduces to $D_i + D_{D_a}$ and the effective force becomes $D_i F_i(r^N)/(D_i + D_{D_a})$. In this diffusivity limit the system behaves as an equilibrium system at effective temperature $T_{\text{eff}} = T(1 + D_{D_a}/D_i)$. 
For weakly persistent motion, $\tau \to 0$, equations [3] to [8] become exact and the theory provides the leading order correction to the diffusion approximation. However, the Fox approximation goes beyond this by including contributions to all orders in $\tau$. Indeed, detailed studies of one-dimensional systems have demonstrated good results over a large range of $\tau$ values [20]. The only caveat is that the condition $1 - \tau \nabla^2 \beta F^a; > 0$ must be satisfied [27] [28]. The range of accessible $\tau$ values thus depends upon the specific form of the bare interaction potential.

Within our stochastic calculus approach, the effective many-body force [8] emerges in a natural way from the coarse grained Langevin equation [3]. The more standard route (adopted in all attempts made so far [20] [29]) to approach this problem is to derive from the Markovian equations [1] the exact Fokker-Planck equation for the joint distribution of positions and orientations, $P(r^N, \rho^N, t)$. However, coarse graining strategies based on integration of $P$ over orientations generate intractable integral terms. By starting from [3] we are able to circumvent these difficulties. As we shall demonstrate below, our effective force accounts for several important collective phenomena in active systems.

C. Effective pair potential

In the low density limit we need only consider isolated pairs of particles. In this limit [3] reduces to an equation of motion for the radial distribution function, $g(r, t) \equiv \Psi(r, t)/\rho_t^2$, where $\rho_t$ is the bulk density. This equation of motion, the pair Smoluchowski equation, is given by

$$\partial_t g(r, t) = -\nabla \cdot \mathbf{j}(r, t),$$

where $r = |r_{12}|$ is the particle separation and $\nabla = \nabla_{r_{12}}$. The pair current is given by

$$\mathbf{j}(r, t) = -2D(r)g(r, t) \left[ \nabla \ln g(r, t) - \beta \mathbf{F}^{\text{eff}}(r) \right],$$

where the radial diffusivity

$$D(r) = D_t + D_a \left( 1 - \frac{\tau \nabla^2 \beta u(r)}{1 + \tau \nabla^2 \beta u(r)} \right),$$

interpolates between the value $D_t$ at small separations, where $u(r)$ is strongly repulsive, and $D_t + D_a$ at large separations. The effective interparticle force is given by

$$\mathbf{F}^{\text{eff}}(r) = \frac{1}{D(r)} \left[ \mathbf{F}(r) - k_BT \nabla D(r) \right],$$

where the bare force is related to the pair potential by $\mathbf{F}(r) = -\nabla u(r)$. The symmetry of the two-body problem can be exploited to calculate from [12] an effective interaction potential

$$\beta u^{\text{eff}}(r) = \int_r^\infty \, dr' \left( \frac{\beta F(r')}{D(r')} - \frac{\partial}{\partial r'} \ln D(r') \right),$$

where $F(r) = |\mathbf{F}(r)|$. We have thus identified an effective interaction pair potential, which requires as input the bare potential and the activity parameters $\tau$ and $D_a$.

FIG. 1: Activity induces effective attraction. Passive potential $\beta u(r) = r^{-12}$. (a) Increasing $Pe$ (in steps of 8) from 0 to 40 generates an effective interparticle attraction. Points indicate the potential minima. (b) Radial distribution function, $g(r)$, from simulation (points) and theory (lines) for $\rho_b = 0.5$ and $Pe = 0$ to 20 (in steps of 4). Curves are shifted vertically for clarity. (c) As in (b), but focusing on larger separations for $Pe = 4$ (squares), 12 (circles) and 20 (diamonds). Inset: position of the first peak in $g(r)$ as a function of $Pe$. (d) Spinodals for $\tau = 0.045$ (dot-dashed) to 0.065 (long dashed) in steps of 0.005.

II. RESULTS

A. Motility-induced phase separation (MIPS)

To illustrate how activity can generate an effective attraction in a passively repulsive system we consider the non-specific potential $\beta u(r) = r^{-12}$. In Fig.1(a) we show the evolution of the effective potential [13] for fixed $\tau$ as a function of the dimensionless velocity $Pe = u_0 d/D_t$. For $Pe \gtrsim 10$ the effective potential develops an attractive tail. As $Pe$ is increased the potential well deepens, the minimum moves to smaller separations and the radius of the soft repulsive core decreases. These trends are consistent with the intuitive picture that persistent motion drives soft particles into one another (the soft core radius reduces) and that they remain dynamically coupled (‘trapped’) for longer than in the corresponding passive system. Within our equilibrium picture the trapping is accounted for by the effective attraction.

For systems at finite density the pair potential [13] is an approximation, because three- and higher-body interactions will play a role (see equation [3]). However, for simplicity we henceforth employ the pair potential [13] for all calculations, as we anticipate that this will provide the dominant contribution. Although corrections to this assumption can be made, they obscure the physical picture and come at the expense of a more complicated theory. The validity of the pair potential approximation...
is very well described. Further comparison for other parameter values (not shown) suggests that (13) combined with the SMSA theory provides an accurate account of the asymptotic decay of pair correlations.

In Fig.1 we show the spinodal lines mapping the locus of points for which the static structure factor, $S(q) = (1 - \rho_b c(q))^{-1}$, diverges at vanishing wavevector. Simulations have shown that MIPS is consistent with a spinodal instability [12]. As $\tau$ is decreased the critical point moves to higher values of $Pe$ and to slightly higher densities. When compared with the spinodal of a standard Lennard-Jones system (e.g. the black curve in Fig.2b) the critical points in Fig.1 lie at rather higher values of $\rho_b$. This suggests that typical coexisting liquid densities for MIPS will be larger than those found in equilibrium phase separated systems, as has been observed in simulation [12] [14].

B. Suppression of phase separation

We next consider the influence of activity on a Lennard-Jones system, $\beta u(r) = 4\varepsilon (r^{-12} - r^{-6})$. For a phase-separated passive system, recent experiments and simulations have demonstrated that increasing $Pe$ first suppresses the phase separation [16] and then leads to higher $Pe$ to a reentrant MIPS [14]. Schwarz-Linek et al. have argued that the suppression of phase separation at lower to intermediate $Pe$ occurs in their system because particle pairs bound by the attractive (depletion) potential begin to actively escape the potential well, and that this can be mimicked using an effective potential less attractive and shorter-ranged than the bare potential [16].

To investigate these phenomena we set $\varepsilon = 1.4$, which ensures a phase separated passive state [31], and consider the evolution of the effective potential as a function of $Pe$. In Fig.2a we show that as $Pe$ is increased from zero to the value 18 both the depth and range of the effective potential reduce significantly, consistent with the expectation of Schwarz-Linek et al. [16]. Spinodals within this range of $Pe$ values, identifying where the static structure factor diverges at zero wavevector, are shown in Fig.2b. As $Pe$ is increased the critical point moves to higher values of $\varepsilon$ (cf. Figs.1 and 3 in Ref.[16]). A passively phase-separated system will thus revert to a single phase upon increasing the activity. To examine this behaviour in more detail we show in Fig.2c the trajectory of the critical point in the $(Pe, \varepsilon)$ plane. Above the line there bulk densities for which phase separation occurs.

In order to test the predicted trajectory of the critical point we have performed Brownian dynamics simulations at a bulk density $\rho_b = 0.4$, which lies close to the critical density [31], for various values of $\varepsilon$ and the $Pe$ values 5, 8 and 10. Visual inspection of the simulation snapshots reveals the existence of voids in the particle configurations corresponding to a phase separated state (see Figs.2a and 3 for snapshots). This visual impression can be made more quantitative by calculating the radial distribution

---

**FIG. 2:** From active suppression of phase separation to a cluster phase. Passive potential $\beta u(r) = 4\varepsilon (r^{-12} - r^{-6})$ with $\varepsilon = 1.4$. (a) Effective potential [13] for $\tau = 0.025$ and $Pe = 0$ (black), 4, 8, 12 (red broken lines) and 20, 28, 36 (blue). Inset: zoom of the repulsive peak for $Pe = 20$, 28, 36. (b) Spinodals for $Pe = 0$, 4, 8, 12. Increasing $Pe$ increases $\varepsilon_{\text{crit}}$, the critical value of $\varepsilon$. (c) $\varepsilon_{\text{crit}}$ as a function of $Pe$ (black full line) and the locus of points for which the repulsive peak of $\beta u_{\text{eff}}$ takes the value 0.1 (red dashed) and 0.05 (blue dot-dashed). Open (closed) circles indicate points where BD simulation find a mixed (phase-separated) state (see figure 3). Arrow indicates path taken in (a). (d) Theory (lines) and simulation (symbols) data (shifted for clarity) for $g(r)$ at $\varepsilon = 0.5$, $\rho_b = 0.3$ for $Pe = 0$ (black), 12 (blue) and 20 (green). Dotted lines indicate peak positions.
FIG. 3: Simulated phase separation. (a) Snapshot of a mixed system at $t/\tau_B = 40$, $Pe = 8$, $\varepsilon/(k_B T) = 1.5$. (b) Snapshot of a phase separating system at the same time and $Pe = 8$, $\varepsilon = 2.5$. (c) The radial distribution function, $g(r)$, for $\varepsilon = 1.5$ (black curve), 2 (blue curve), and 2.5 (green curve). (d) As in (c) but focusing on larger distances. From the snapshots together with the long range behaviour of the $g(r)$ we can distinguish between a mixed and a phase separated system. The slow decay to the asymptotic value of unity, as shown in (d), indicates phase separation.

function. Phase separating states generate a very characteristic slow decay of $g(r)$ (Figs. 3c and 3d) which provides a useful indicator. The open circles in Fig. 2 represent mixed states, whereas closed circles indicate phase separated statepoints. The phase boundary predicted by the theory is highly consistent with the simulation data.

C. Cluster phase

Returning to Fig. 2, we find that for $Pe > 18$ the effective potential develops a repulsive barrier, which grows in height (see inset) with increasing $Pe$, while the potential minimum becomes deeper. It is well-known that potentials with a short-ranged attraction and long-ranged repulsion (SALR potentials) exhibit unusual equilibrium phase behaviour, including clustering and microphase-separation [32, 33]. Although the attractive component of the potential may favour phase separation, the long range repulsion destabilises distinct liquid and gas phases and causes them to break up into droplets or clusters. This represents a non-spinodal type of phase transition, characterized by a divergence in the structure factor at finite wavevector. The appearance of a repulsive barrier in the effective potential suggests that a similar mechanism may be at work in passively attractive systems subject to high $Pe$ activity.

In Fig. 2, we show the locus of points where the effective potential peak height attains a given value (we choose 0.05 and 0.1 for illustration). When these ‘isorepulsion curves’ are viewed together with the critical point trajectory the resulting phase diagram is very similar to that obtained by Redner et al. in their simulation study of two-dimensional active Lennard-Jones particles (cf. figure 1 in Ref. [14]). However, a detailed study of the connection between the potential barrier and high $Pe$ clustering goes beyond the scope of the present work.

III. DISCUSSION

In summary, we have shown that systems of active spherical Brownian particles can be mapped onto an equilibrium system interacting via an effective, activity-dependent many-body potential. The only required inputs are the bare potential, thermodynamic statepoint and the parameters specifying the state of activity. Our theory captures the phenomenon of MIPS in repulsive systems and provides first-principles predictions for the activity dependence of the pair correlations, in very good agreement with Brownian dynamics simulation. As far as we are aware there exists no other approach capable of predicting from the microscopic interactions the pair correlation functions of an active system. Further insight into the steady state particle distribution could in principle be obtained by investigating the three-body correlations. These could be obtained by employing the effective potential in a higher-order liquid state integral equation theory (see e.g. [31] and references therein).

For passively attractive systems the theory rationalizes the experimental finding [10] that increasing activity can suppress passive phase separation. We find that as $Pe$ is increased from zero to intermediate values the minimum of the effective potential becomes less deep, thus weakening the cohesion of the liquid phase. To the best of our knowledge there is currently no alternative theoretical explanation of phase-transition suppression in active suspensions. It is an appealing aspect of our theory that the suppression of passive phase separation follows naturally from the same approach which yields activity-induced attraction for repulsive potentials. For high values of $Pe$ the appearance of a repulsive barrier in the effective potential suggests that the reentrant phase separation observed in simulations [14] may be interpreted using concepts of equilibrium clustering in SALR potential systems. This will be a subject of future detailed investigations. It is known that care must be exercised when analysing SALR potentials, as traditional liquid state theories can prove misleading [33].

A key step in our development is the Fox approximation [27], which yields an effective Markovian description of the coarse-grained equation (4). Making a Markovian approximation automatically imposes an effective equilibrium, however, we are aware that there exist certain
situations for which this breaks down \[10,19\]. Establishing more clearly the range of validity of our approach, as well as its possible extensions, will be the subject of ongoing study. However, it is already clear that going beyond the Markovian approximation will be very challenging. Indeed, such a step may not even be desirable. Any kind of non-Markovian description would lead inevitably to a loss of the effective equilibrium picture and the physical intuition associated with it. It thus seems likely that practical improvements to the present approach will retain the Markovian description while seeking to optimize, or improve upon, the Fox approximation for certain classes of bare potential. Very recently, Maggi et al. have employed an alternative approach to treating stochastic processes driven by Ornstein-Uhlenbeck noise \[35\]. A comparison of their approach with the Fox method employed here would be very interesting.

With a view to further applications of our approach, we note that there has recently been considerable interest in active suspensions at very high densities \[36–39\]. We thank Yaouen Fily, Ronald Fox and Paolo Grigolini et al. for helpful correspondence. Funding provided by the Swiss National Science Foundation. PK thanks the Eiltenetzwerk Bayern (ENB) and Matthias Schmidt for financial support.

### Acknowledgments

**Appendix A: Coarse-grained Langevin equation**

Equation (2) describes the orientational diffusion of an active particle. The corresponding conditional probability distribution function \( \Upsilon(\mathbf{p}, t | \mathbf{p}_0, t_0) \), where \( t > t_0 \), obeys a Fokker-Planck equation which can be obtained by usual techniques \[40\].

\[
\frac{\partial}{\partial t} \Upsilon(\mathbf{p}, t | \mathbf{p}_0, t_0) = D_r R^2 \Upsilon(\mathbf{p}, t | \mathbf{p}_0, t_0), \tag{A1}
\]

where \( R \equiv (\mathbf{p} \times \nabla_p) \) is the intrinsic angular momentum differential operator. Eq. (A1) describes nothing but a diffusion process on the unit sphere. This problem is well-known when studying, e.g., dielectric relaxation in polar liquids \[11,12\]. In spherical coordinates, (A1) becomes

\[
\frac{1}{D_r} \frac{\partial}{\partial t} \Upsilon(\Omega, t | \Omega_0, t_0) = \frac{1}{\sin^2 \vartheta} \left[ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{\partial^2}{\partial \varphi^2} \right] \Upsilon(\Omega, t | \Omega_0, t_0), \tag{A2}
\]

where we have defined \( \Omega \equiv (\vartheta, \varphi) \).

Assuming that \( \Upsilon \) and its derivatives are continuous on the sphere \[45\], we expand the probability distribution function \( \Upsilon \) in spherical harmonics

\[
\Upsilon(\Omega, t | \Omega_0, t_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm}(t | \Omega_0, t_0) Y_{lm}(\Omega), \tag{A3}
\]

where \( Y_{lm} \) are the spherical harmonics and \( A_{lm} \) are coefficients encoding the initial condition. We also recall that spherical harmonics are eigenvectors of the operator \( R^2 \) (in spherical coordinates), namely that

\[
R^2 Y_{lm} = -l(l+1)Y_{lm}. \tag{A4}
\]

Inserting (A3) in (A2) and using (A4) we obtain

\[
\sum_{l,m} \frac{\partial}{\partial t} A_{lm}(t | \Omega_0, t_0) Y_{lm}(\Omega) = -D_r \sum_{l,m} l(l+1) A_{lm}(t | \Omega_0, t_0) Y_{lm}(\Omega). \tag{A5}
\]

Multiplying both sides of (A5) by \( Y_{lm}^* \) (\( \Omega \)), integrating over solid angle and using the orthogonality property, \( \int d\Omega Y_{lm}^*(\Omega) Y_{lm}(\Omega) = \delta_{m,m'} \delta_{l,l'} \), yields

\[
\frac{\partial}{\partial t} A_{lm}(t | \Omega_0, t_0) = -D_r l(l+1) A_{lm}(t | \Omega_0, t_0), \tag{A6}
\]

which has the solution

\[
A_{lm}(t | \Omega_0, t_0) = e^{-D_r l(l+1)(t-t_0)} a_{lm}(\Omega_0), \tag{A7}
\]

where the \( a_{lm} \) are a new set of coefficients. The probability distribution is thus given by

\[
\Upsilon(\Omega, t | \Omega_0, t_0) = \sum_{l,m} e^{-D_r l(l+1)(t-t_0)} a_{lm}(\Omega_0) Y_{lm}(\Omega). \tag{A8}
\]
The initial condition,
\[ \mathbf{Y}(\Omega, t_0 | \Omega_0, t_0) = \delta(\Omega - \Omega_0), \]

(A9)

together with the completeness relation of the spherical harmonics,
\[ \delta(\Omega - \Omega_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}(\Omega) Y_{lm}^*(\Omega_0), \]

(A10)

allows the missing coefficients to be identified,
\[ a_{lm}(\Omega_0) = Y_{lm}^*(\Omega_0). \]

(A11)

The conditional probability distribution is now fully determined as
\[ \mathbf{Y}(\Omega, t | \Omega_0, t_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} e^{-D_{l}|t-t_0|} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega). \]

(A12)

As \( t \to \infty \) only the terms with \( l = 0 \) survive. The steady-state distribution function is thus given by
\[ \mathbf{Y}_{eq}(\Omega) = \lim_{t \to \infty} \mathbf{Y}(\Omega, t | \Omega_0, t_0) = (4\pi)^{-1}. \]

(A13)

The conditional and equilibrium distributions, (A12) and (A13), respectively, can be used to coarse-grain the exact Langevin equations (A1) and (A2). The approach taken is to consider the orientation vector \( \mathbf{p}_i(t) \) attached to particle \( i \) as a stochastic variable and to provide its full statistical characterization. In spherical coordinates the orientation vector is given explicitly by
\[ \mathbf{p}(t) = (p_x(t), p_y(t), p_z(t))^T = (\cos \varphi(t) \sin \vartheta(t), \sin \varphi(t) \sin \vartheta(t), \cos \vartheta(t))^T, \]

(A14)

where \( \varphi \) and \( \vartheta \) are the azimuthal and polar angles respectively. Using (A13) we have that
\[ \langle p_z(t) \rangle = \int d\Omega \mathbf{Y}_{eq}(\Omega) \cos \vartheta = 0, \]

(A15)

together with analogous results for the \( x \) and \( y \) components
\[ \langle p_x(t) \rangle = 0 = \langle p_y(t) \rangle. \]

(A16)

Defining the new stochastic variable by \( \mathbf{\chi}_i(t) \equiv v_0 \mathbf{p}_i(t) \), its first moment is thus given by
\[ \langle \mathbf{\chi}_i(t) \rangle = v_0 \langle \mathbf{p}_i(t) \rangle = \mathbf{0}. \]

(A17)

Calculation of the equilibrium correlation matrix requires the conditional probability distribution function given by (A12). For example, for the \( zz \) component, we obtain
\[
\langle p_z(t)p_z(t_0) \rangle = \int d\Omega_0 \cos \vartheta \cos \vartheta_0 \mathbf{Y}(\Omega, t | \Omega_0, t_0) \mathbf{Y}_{eq}(\Omega_0)
= \frac{1}{3} \int d\Omega \int d\Omega_0 \sum_{l,m} e^{-D_{l}|t-t_0|} \times \nonumber
\times Y_{10}^*(\Omega) Y_{lm}(\Omega_0) Y_{10}(\Omega_0) Y_{lm}^*(\Omega_0)
= \frac{1}{3} e^{-2D_{l}|t-t_0|}, \]

(A18)

where we have expressed the cosine functions in terms of spherical harmonics, \( Y_{10} = \sqrt{3/(4\pi)} \cos \vartheta = Y_{10}^* \), and used the orthogonality property. Calculations for the \( xx \) and \( yy \) components are performed in the same spirit. We thus obtain
\[ \langle p_x(t)p_x(t_0) \rangle = \frac{1}{3} e^{-2D_{l}|t-t_0|} = \langle p_y(t)p_y(t_0) \rangle, \]

(A19)

whereas off-diagonal components of the correlation matrix are all zero. We can thus conclude that
\[ \langle \mathbf{\chi}_i(t)\mathbf{\chi}_j(t') \rangle = v_0^2 \langle \mathbf{p}_i(t)\mathbf{p}_j(t') \rangle = \frac{v_0^2}{3} e^{-2D_{l}|t-t'|} \delta_{ij}. \]

(A20)

It has been shown [3] that the probability distribution function (A12) can be well approximated by an expression which generalizes the planar Gaussian function to the sphere. The new noise function \( \mathbf{\chi}_i(t) \) is thus approximately Gaussian distributed with zero mean and exponentially decaying correlations. The coarse-grained Langevin equation (A1) thus describes a stochastic process with additive colored-noise.

Appendix B: Approximate Fokker-Planck equation

To derive from (A1) an approximate Fokker-Planck equation we apply the functional calculus methods of Fox [27]. We address the one-dimensional case before generalizing to higher dimension. Consider the stochastic differential equation
\[ \dot{x}(t) = F(x) + g(x) \mathbf{\chi}(t), \]

(B1)

where \( F(x) \) and \( g(x) \) may be nonlinear functions in \( x \). If \( g(x) = 1 \), the process is then called additive, otherwise it is called multiplicative. The noise function \( \mathbf{\chi}(t) \) is by definition Gaussian distributed with zero mean. Its second moment determines whether it is a white or colored noise. As we are interested here in the case of additive colored noise we set \( g(x) = 1 \).

In the framework of functional calculus, the Gaussian nature of \( \mathbf{\chi}(t) \) is expressed by the following probability distribution functional,
\[ P[\mathbf{\chi}] = N e^{-\frac{1}{2} \int ds \int ds' \mathbf{\chi}(s)\mathbf{\chi}(s') K(s-s')}, \]

(B2)

where the function \( K \) is the inverse of the \( \mathbf{\chi} \) correlation function and the normalization constant is expressed by a path integral over \( \mathbf{\chi} \),
\[ N^{-1} = \int D[\mathbf{\chi}] e^{-\frac{1}{2} \int ds \int ds' \mathbf{\chi}(s)\mathbf{\chi}(s') K(s-s')} \]

(B3)

The first and second moments of \( \mathbf{\chi} \) are given by
\[ \langle \mathbf{\chi}(t) \rangle = 0, \]

(B4)

\[ \langle \mathbf{\chi}(t)\mathbf{\chi}(s) \rangle = C(t-s). \]

(B5)
Recalling that the functional derivative may be defined according to
\[ \frac{\delta I[\phi]}{\delta \phi'(t')} = \left. \frac{d}{d\lambda} I[\phi(t) + \lambda \delta(t - t')] \right|_{\lambda = 0}, \]
we now derive two useful identities. The first concerns the functional derivative of the probability distribution functional,
\[ \frac{\delta P[\chi]}{\delta \chi(t)} = \frac{\delta N}{\delta \chi(t)} e^{-\frac{1}{2} \int ds \int ds' \delta(s') \delta(s) \chi(s') K(s - s')} + N \frac{\delta}{\delta \chi(t)} e^{-\frac{1}{2} \int ds \int ds' \delta(s') \delta(s) \chi(s') K(s - s')} = -P[\chi] \int dsK(t - s) \chi(s), \]
where, using (B6) and (B4), it can be easily shown that \( \frac{\delta N}{\delta \chi(t)} = 0 \). The second identity demonstrates the inverse relation between the functions \( K \) and \( C \). The second functional derivative of \( P[\chi] \) yields
\[ \frac{\delta^2 P[\chi]}{\delta \chi'(t') \delta \chi(t)} = P[\chi] \left\{ \int ds' \int dsK(t' - s') K(t - s) \chi(s') \chi(s) - K(t - t') \right\}, \]
where use of (B7) has been made. Using (B8) and (B5) together with the normalization \( \int D[\chi] P[\chi] = 1 \), leads to
\[ 0 = \int D[\chi] \frac{\delta^2 P[\chi]}{\delta \chi'(t') \delta \chi(t)} = \int ds' K(t' - s') \int dsK(t - s) C(s - s') - K(t - t'), \]
which implies that
\[ \int dsK(t - s) C(s - s') = \delta(t - t'). \]
The solution to the stochastic process described by (B11), namely the probability distribution functional for \( x(t) \), is given by the formal expression
\[ P(y, t) = \int D[\chi] P[\chi] \delta(y - x(t)). \]
Taking the time derivative of (B11) yields
\[ \frac{\partial}{\partial t} P(y, t) = -\frac{\partial}{\partial y} [F(y) P(y, t)] - \frac{\partial}{\partial y} \int D[\chi] \delta(y - x(t)) P[\chi] \chi(t). \]
The product \( P[\chi] \chi(t) \) appearing in the second term can be rewritten in the following way
\[ P[\chi] \chi(t) = P[\chi] \int ds \delta(t - s) \chi(s) = -\int ds' C(t - s') \frac{\delta P[\chi]}{\delta \chi(s')}, \]
where we have used (B10) and (B7). Inserting (B13) back into the second term of (B12) and integrating by parts gives us
\[ \int D[\chi] \delta(y - x(t)) P[\chi] \chi(t) = -\int ds' C(t - s') \int D[\chi] \left( \frac{\partial}{\partial y} \delta(y - x(t)) \right) \frac{\delta x(t)}{\delta \chi(s')} P[\chi], \]
which serves as the exact starting point for Fox’s approximation scheme [27].
In order to progress further we need to calculate \( \delta x(t)/\delta \chi(s') \). Applying the functional derivative with respect to \( \chi(t') \) on (B1) yields a first-order differential equation,
\[ \frac{d}{dt} \frac{\delta x(t)}{\delta \chi(t')} = F(x) \frac{\delta x(t)}{\delta \chi(t')} + \delta(t - t'), \]
the solution of which is
\[ \frac{\delta x(t)}{\delta \chi(t')} = \int_0^t ds e^{\int_s^t ds' F'(x(s))} \Theta(t - s'), \]
where \( \Theta \) is the Heaviside step function, which we define here as follows
\[ \Theta(t - s') = \begin{cases} 1, & t > s' \\ \frac{1}{2}, & t = s' \\ 0, & t < s'. \end{cases} \]
Using (B16) in (B14) we can rewrite (B12) in an alternative form
\[ \frac{\partial}{\partial t} P(y, t) = -\frac{\partial}{\partial y} [F(y) P(y, t)] + \frac{\partial^2}{\partial y^2} \left\{ \int_0^t ds' C(t - s') \int D[\chi] P[\chi] e^{\int_s^t ds' F'(x(s))} \delta(y - x(t)) \right\}, \]
which already begins to resemble a Fokker-Planck-type equation. However, because of the non-Markovian nature of \( \int_0^t ds' F'(x(s)) \) appearing in the exponential of (B17), it is apparent that a reduction of this term to an expression containing \( P(y, t) \) is not possible. An approximation is required.

The colored noise of interest here is characterized by an exponentially decaying correlation function (A17). In the literature on non-Markovian processes the time-correlation functions are generally noted as follows
\[ C(t - s) = \frac{D}{\tau} e^{-|t-s|/\tau}, \]
with a diffusion coefficient \( D \) and a correlation time \( \tau \). In order to retain some coherence with the existing literature we will here employ the standard notation of (B18).
and only use the relation of the parameters in (B18) to those of (A20) at the end of the calculation.

Returning to (B17), we first perform a change of variable, \( t' \equiv t - s' \), in the time-integral,
\[
\int_0^t ds' C(t-s')e^{\int_s^t ds' F'(x(s))} = \int_0^t dt' C(t')e^{\int_{t_0}^{t'} ds' F'(x(s))},
\]
and then expand the time integral over \( F' \) in terms of \( t' \),
\[
\int_{t-t'}^t ds F'(x(s)) \approx F'(x(t))t' - F''(x(t))\dot{x}(t)t'^2/2.
\]
Neglecting the \( t'^2 \) term in (B20) enables the integral in (B19) to be evaluated
\[
\int_0^t ds' C(t-s')e^{\int_s^t ds' F'(x(s))} \approx \int_0^t dt' C(t')e^{\int_{t_0}^{t'} ds' F'(x(s))} \approx \frac{D}{1 - \tau F'(x(t))},
\]
where we used (B18), and the second approximation results from assuming a sufficiently large \( t \). We can finally put (B21) back into (B17) to obtain an approximate Fokker-Planck equation,
\[
\frac{\partial}{\partial t} P(y,t) = -\frac{\partial}{\partial y} [F(y)P(y,t)] + D \frac{\partial^2}{\partial y^2} \left( \frac{1}{1 - \tau F'(y)} P(y,t) \right).
\]
This is Fox’s result for the approximate Fokker-Planck equation corresponding to the non-Markovian process (B1). Eq. (B22) implicitly defines a Markovian process, which approximates the non-Markovian process of physical interest. However, the question of whether this represents the best approximation remains a subject of debate. We note that equation (B22) has also been derived by Grigolini et al. [26] using alternative methods which do not make any assumptions of a short correlation time.

The one-dimensional Fokker-Planck equation (B22) can be generalized without much difficulty to describe a three-dimensional system of \( N \) particles. The dynamics of interest is described by the stochastic equation (3). We now adapt the standard notation used above to that employed in the main text, namely \( P(y,t) \rightarrow \Psi(r,N,t) \), \( \tau \rightarrow \tau_B = 1/(2D_r) \) and \( D \rightarrow v_B^2/3 \), and recall that \( D_a = v_B^2/(6D_r) \) and \( \zeta^{-1} = \beta D_r \) for the friction coefficient in (4). Making the appropriate replacements enables us to write the three-dimensional generalization of (B22)
\[
\frac{\partial}{\partial t} \Psi(r,N,t) = -\sum_{i=1}^{N} \nabla_i \cdot D_t \left[ \beta F_i(r,N) - \nabla_i \right] \Psi(r,N,t) - \sum_{i=1}^{N} \nabla_i \left[ -D_a \nabla_i \left( \frac{1}{1 - \frac{D_a}{2D_r}} \frac{\beta F_i(r,N)}{2D_r} \Psi(r,N,t) \right) \right].
\]
A simple rearrangement of terms in (B23) leads directly to equations (15-18) in the main text.

Appendix C: Integral equation theory

To calculate the steady-state radial distribution function, \( g(r) \), from the effective pair potential (13) we employ an equilibrium liquid state integral equation developed by Madden and Rice [30]. This soft mean-spherical approximation (SSMA) exploits the Weeks-Chandler-Anderson splitting of the pair potential [47] into attractive and repulsive contributions, \( u(r) = u_{\text{rep}}(r) + u_{\text{att}}(r) \), where the repulsive part is given by
\[
u_{\text{rep}}(r) = \begin{cases} u(r) - u(r_{\text{min}}) & r < r_{\text{min}} \\ 0 & r > r_{\text{min}} \end{cases}
\]
and the attractive part is given by
\[
u_{\text{att}}(r) = \begin{cases} u(r) & r > r_{\text{min}} \\ u(r_{\text{min}}) & r < r_{\text{min}} \end{cases}
\]
where \( r_{\text{min}} \) is the position of the potential minimum. The total correlation function, \( h(r) = g(r) - 1 \), is related to the shorter range direct correlation function, \( c(r) \), by the Ornstein-Zernike equation (38)
\[
h(r) = c(r) + \rho_b \int dr' h(|r - r'|)c(r').
\]
The SSMA approximation is given by the closure relation
\[
c(r) = (1 - e^{\beta u_{\text{rep}}(r)})g(r) - \beta u_{\text{att}}(r).
\]
For the Lennard-Jones potential the closure relation (C4) has been shown to provide results for \( g(r) \) which are superior to both Percus-Yevick (PY) and Hypernetted Chain (HNC) theories [30]. Moreover, the SSMA theory predicts a true spinodal line in the parameter space, namely a locus of points for which the static structure factor, \( S(k) = (1 - \rho_b S(k))^{-1} \), diverges at vanishing wavevector. This behaviour is a consequence of the assumed asymptotic form of the direct correlation function, \( c(r) \sim -\beta u_{\text{att}}(r) \). Other standard integral equation theories, such as PY and HNC, do not exhibit a complete spinodal line, but rather a region within which the theory breaks down (‘no solutions region’) [49].

Appendix D: Brownian Dynamics Simulations

In order to benchmark our theoretical predictions we perform Brownian dynamics simulations of \( N \) particles, randomly initialized without overlap. The system is confined to a periodic cubic box, the size of which is determined by the number density according to \( L^3 = N/\rho_b \), where \( L \) is the side length. The Langevin equations of motion, (1) and (2), are integrated via a standard Brownian dynamics scheme [50] with a constant time step of \( \delta t/\tau_B = 10^{-5} \). Both the translational and rotational noise are Gaussian random variables with a standard deviation of \( \sigma_t = (2D_B T)^{1/2} \) and \( \sigma_r = (2D_r T)^{1/2} \), respectively.
For the soft repulsive potential to be considered in this work, $\beta u(r) = r^{-12}$, we employ $N = 2000$ particles. The potential is truncated and shifted at $r_{\text{cut}}/d = 2$. To provide good statistics for the static quantities the simulations are carried out for $10^6$ time steps, sampling every 1000 steps, which is equivalent to a total run time of $t_{\text{tot}}/\tau_B = 10$ and a sampling rate of $\tau_B/t_{\text{sample}} = 100$.

For the second system we will consider, the Lennard-Jones system, $\beta u(r) = 4\epsilon (r^{-12} - r^{-6})$, we simulate a larger system of 5000 particles. The integration time of the equations of motion is the same as in the repulsive system, as is the cut-off radius. In this case, the runtime is $10^7$ and the particle positions are sampled every $10^4$ steps.