Depletion Forces in Nonequilibrium

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The concept of effective depletion forces between two fixed big colloidal particles in a bath of small particles is generalized to a nonequilibrium situation where the bath of small Brownian particles is flowing around the big particles with a prescribed velocity. In striking contrast to the equilibrium case, the nonequilibrium forces violate Newton's third law; they are nonconservative and strongly anisotropic, featuring both strong attractive and repulsive domains.

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Colloidal mixtures are excellent model systems to study fundamental questions of equilibrium and nonequilibrium phase transitions with important physical applications, such as protein crystallization [1] as well as gel and glass formation [2]. One of the reasons for the pivotal role of colloids as model systems lies in the fact that their interactions can be tailored [3]. In the theoretical description of colloidal mixtures, the concept of the effective interaction has proved to be of paramount importance in advancing our understanding of how to steer the properties of these complex systems [4]. It stems from integrating out the coordinates of the small particles, reducing thereby the number of statistical degrees of freedom considerably [5,6]. This approach has been successfully applied to colloid/polymer mixtures [7–9], to binary colloidal mixtures [10,11], and to charged suspensions [12]. The most widely known effect is the depletion attraction in strongly nonadditive systems, such as the Asakura-Oosawa model [7] pertaining to colloids and nonadsorbing ideal polymer coils. This attraction is entropic; i.e., it scales with the thermal energy k_BT and results from a depletion zone of polymer between a pair of nearly touching colloidal particles, which causes an imbalance of the osmotic pressure of the polymers acting on the colloidal surface. While the range of the depletion attraction is typically associated with the radius of gyration of the polymers, its attractive depth is fixed by the polymer concentration, so that both the range and the depth are in principle tunable.

The crucial limitation of the concept of effective interactions is that it works, strictly speaking, only in thermodynamic equilibrium and can thereafter be applied for the calculations of static quantities, such as correlation functions and free energies (resulting in phase diagrams). In this Letter, we investigate whether and how the effective interaction can be applied also in *nonequilibrium steady-state situations*. In order to be as transparent as possible, we study a minimal model of nonequilibrium for two fixed big colloidal particles in a quiescent viscous solvent which are exposed to a flowing bath of small Brownian particles. The latter ones are ideal, in full analogy to the equilibrium case of the Asakura-Oosawa model, and hydrodynamic interactions mediated by the solvent are neglected. Despite its simplicity, the model is realized in colloidal mixtures with weakly interacting depletants (which justifies the assumed ideality) which have a small physical volume fraction with well-separated excluded volumes of the big and small particles (which justifies neglecting hydrodynamic interactions). Examples include strongly asymmetric highly charged suspensions with a small physical volume fraction [13] and sterically stabilized colloidal particles in a bath of thin rods [14] or polymer coils [15,16]. Our situation is different from the classical hydrodynamic problem of two fixed spheres in a Stokes flow of a viscous incompressible fluid, [17–19] in which the force vanishes for zero flow. More importantly, the physical origin of the depletion forces is the high osmotic compressibility of the bath particles complementary to the incompressibility of the viscous fluid mediating hydrodynamic interactions. It is only for high volume fractions of the small particles that the solvent flow field will be significantly distorted by the presence of the big spheres, in which case hydrodynamic interactions will strongly affect our findings.

Based on a standard Smoluchowski approach and on Brownian dynamics computer simulations in nonequilibrium, we show that the effective force can be generalized in a straightforward way to a stationary nonequilibrium state. The results for the effective force, however, differ from the corresponding equilibrium case both qualitatively and quantitatively. First of all, the nonequilibrium force field (as a function of the mutual distance between the particles) is nonconservative and violates Newton's third law, implying that the concept of an effective interaction potential does not hold in nonequilibrium. Second, when the small particles are brought to flow, the equilibrium depletion attraction gets strongly anisotropic favoring an alignment of the colloidal pair along the flow direction. Conversely, there is mutual effective repulsion between the colloidal pair perpendicular to the drift direction of the bath due to a compression of the small

particles between the colloids. Furthermore, the range of the depletion interaction in the drifting case is larger than that in equilibrium.

Equilibrium depletion forces can be measured in real colloidal samples with high accuracy [14–16,20,21]. Our predictions in nonequilibrium can be tested in experiments of binary colloidal mixtures as well. A drifting bath is generated either by gravity [22,23] or by an electric or magnetic field [13], and the big particles can be fixed by optical tweezers [21,24]. The measurement of the relative displacement with respect to the tweezer's position of the big particles provides direct access to the effective nonequilibrium forces.

In our theoretical model we consider two fixed big particles in a bath of small Brownian particles that drift with velocity $\mathbf{v} = v\hat{\mathbf{z}}$. The bath has a bulk number density ρ_0. While there is no interaction between the bath particles, the interaction between the big and small particles is described with an exponential, spherically symmetric potential $V(\mathbf{r})$ given by

$$V(\mathbf{r}) = V(r) = V_0 \exp[-(r/\sigma)^n],$$

where $\mathbf{r}$ is the vector separating the bath particle with the center of the colloid, r is the magnitude of $\mathbf{r}$, and $V_0 = 10k_BT$. In this work we focus on an exponent $n = 6$, on one hand to deal with a well-defined "hard" interaction radius of the colloidal sphere, σ, on the other hand to circumvent numerical inconveniences due to huge forces at $r = \sigma$ for high exponents n.

In what follows, we first discuss a theoretical Smoluchowski approach for a single driven colloid. Adopting a dynamical superposition approximation (DSA), we then address the case of two colloids and afterwards we compare the theoretical predictions arising from the DSA with Brownian dynamics (BD) computer simulations, finding good agreement between the two approaches. In detail, for the case of a *single* big colloidal particle, the Smoluchowski equation [19] for the steady-state density field $\rho(\mathbf{r})$ of the bath particles reads as $\vec{\nabla} \cdot \mathbf{j}(\mathbf{r}) = 0$ with the current density field $\mathbf{j}(\mathbf{r})$ composed of

$$\mathbf{j}(\mathbf{r}) = \frac{\Gamma}{\beta}\vec{\nabla}\rho(\mathbf{r}) + \Gamma\rho(\mathbf{r})\vec{\nabla}V(\mathbf{r}) + \mathbf{v}\rho(\mathbf{r}),$$

where $\beta = 1/k_BT$ is the inverse thermal energy and Γ is the mobility of the bath particles in the solvent. As the problem possesses azimuthal symmetry, these equations can be readily numerically solved in cylindrical coordinates yielding a density profile $\rho^{(1)}(\mathbf{r} - \mathbf{R}, \mathbf{v})$ of the bath particles around one big colloid with $\mathbf{R}$ denoting the position of the colloid. The resulting drift velocity field $\mathbf{j}(\mathbf{r})/\rho(\mathbf{r})$ is inhomogeneous approaching the imposed $\mathbf{v}$ for large distances from the colloid.

Spatial homogeneity dictates that $\rho^{(1)}$ depends only on the difference $\mathbf{r} - \mathbf{R}$. The force $\mathbf{F}_d$ acting on the big particle due to the drifting bath is then obtained as $\mathbf{F}_d = -\int d^3r \rho^{(1)}(\mathbf{r})\vec{\nabla}V(|\mathbf{r}|)$.

In the presence of two colloids, the corresponding quantity of interest is the bath density profile $\rho^{(2)}(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2; \mathbf{v})$ that depends on the locations $\mathbf{R}_i$ of the colloids ($i = 1, 2$) and parametrically on the velocity $\mathbf{v}$. In this case, the numerical solution of the Smoluchowski equation is more difficult such that a direct particle-resolved computer simulation is more appropriate. However, let us motivate a simple superposition approximation. As the bath particles are noninteracting, in the case of thermodynamic equilibrium, $v = 0$, $\rho^{(2)}(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2; 0)$ can be exactly factorized as the product of the density fields $\rho^{(1)}(\mathbf{r} - \mathbf{R}_i; 0)$ divided by ρ_0. In what follows, we employ the same factorization ansatz also for the nonequilibrium situation, $v \neq 0$, introducing the *dynamical superposition approximation* [25]:

$$\rho^{(2)}(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2; \mathbf{v}) \approx \rho^{(1)}(\mathbf{r} - \mathbf{R}_1; \mathbf{v})\rho^{(1)}(\mathbf{r} - \mathbf{R}_2; \mathbf{v})/\rho_0. \quad (1)$$

The corrections to the DSA when inserted into the Smoluchowski equation are of the order of $\vec{\nabla}\rho^{(1)}(\mathbf{r}, \mathbf{R}_1, \mathbf{v}) \cdot \vec{\nabla}\rho^{(1)}(\mathbf{r}, \mathbf{R}_2, \mathbf{v})$ and of $\vec{\nabla}\rho^{(1)}(\mathbf{r}, \mathbf{R}_1, \mathbf{v}) \cdot \vec{\nabla}V(\mathbf{r} - \mathbf{R}_2)$ [respectively, $\vec{\nabla}\rho^{(1)}(\mathbf{r}, \mathbf{R}_2, \mathbf{v}) \cdot \vec{\nabla}V(\mathbf{r} - \mathbf{R}_1)$]. All these terms are products of gradients of factors of which the one is an $\mathbf{R}_1$ quantity and the other is an $\mathbf{R}_2$ quantity. For small $\mathbf{v}$, these factors are confined close to the surface of the colloids such that their product is very

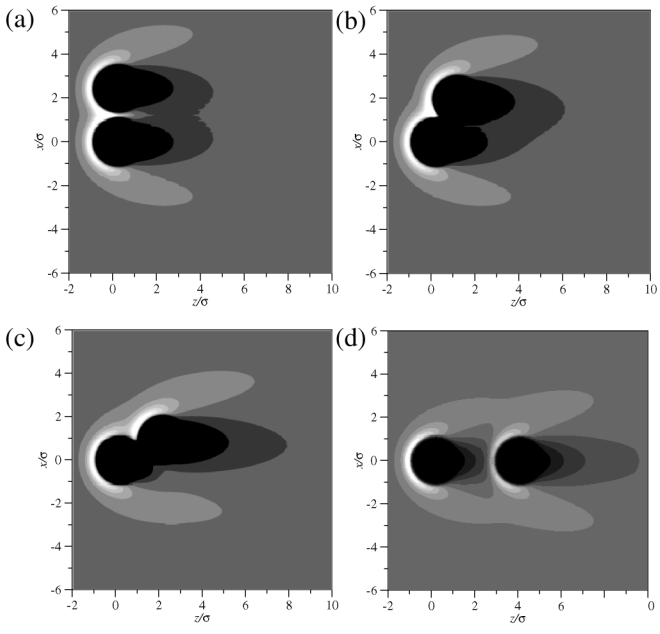

FIG. 1. Steady-state contour density fields ($v^* = 5$) of noninteracting Brownian particles, driven around two stationary colloidal spheres, on the x-z plane where the centers of the spheres are located. The distributions are obtained from the superposition approximation, Eq. (1). Bright regions show high densities while low density regions are plotted dark. One colloid is placed at the origin, $\mathbf{R}_1 = 0$, and the position $\mathbf{R}_2$ of the other one is (a) $\mathbf{R}_2/\sigma = (2, 0, 0)$, (b) $\mathbf{R}_2/\sigma = (1.5, 0, 1)$, (c) $\mathbf{R}_2/\sigma = (1, 0, 2)$, and (d) $\mathbf{R}_2/\sigma = (0, 0, 4)$.

small for two distant colloids. Hence the DSA is justified for small $\mathbf{v}$ and two distant colloids. Results from the DSA are shown in Fig. 1, where we plot the density distribution in the x-z plane, on which the centers of both colloids are located. The profiles are plotted for four different relative positions of the two colloids and for a dimensionless drift velocity $v^* = 5$, defined as $v^* = \beta\sigma v/\Gamma$. The density profiles are strongly anisotropic and show long-ranged low-density regions in the wake region behind the spheres. The extension of the concept of the effective interaction to a steady-state nonequilibrium situation can now be performed via the definition of the effective *force* which is a statistical average over the forces of the small bath particles exerted onto the big ones [5]. Generalizing to a steady-state average in nonequilibrium, the effective force reads as [26]

$$\mathbf{F}_i = -\int d^3r \rho^{(2)}(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2; \mathbf{v}) \vec{\nabla}_{\mathbf{R}_i} V(|\mathbf{R}_i - \mathbf{r}|). \quad (2)$$

The force has been calculated in theory by employing the DSA, Eq. (1), for various different configurations of the colloids and drift velocities, including the equilibrium case, $v = 0$, in which the results are exact. In this way, a comparison between the static and dynamic depletion force $\mathbf{F}_{\mathrm{depl},i}$ acting on the ith particle can be obtained. The latter is defined as the force $\mathbf{F}_{\mathrm{depl},i} = \mathbf{F}_i - \mathbf{F}_\mathrm{d}$, where $\mathbf{F}_\mathrm{d}$ is the drift force acting on a single big particle

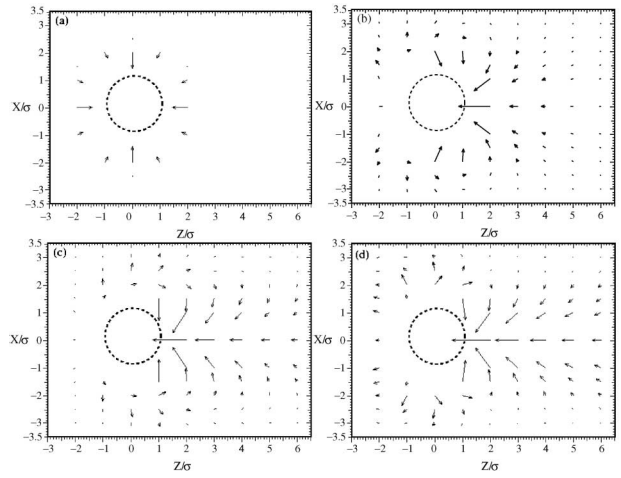

FIG. 2. The depletion force $\mathbf{F}_{\mathrm{depl},2}$ (arrows) acting on colloid 2, when colloid 1 is placed at the origin (dashed circle), as the Brownian bath particles drift from the left to the right with speed v^*. Forces are plotted in the X-Z plane where the centers of the colloids are located. Results are shown for drift velocities (a) $v^* = 0$ (equilibrium), (b) $v^* = 1$, and (c) $v^* = 5$. The results in (a)–(c) are calculated theoretically from Eqs. (1) and (2). Plot (d) shows the force for $v^* = 5$ resulting from BD computer simulations. Different scales for the length of the vectors are used for different values of v^*. The magnitude of the force vector located at $(X, Z) = (0, 2)$ is $\beta F\sigma = 1.22$ in (a), 2.38 in (b), 8.04 in (c), and 9.16 in (d). Furthermore, $\rho_0 = 1/\sigma^3$.

($\beta F_\mathrm{d}\sigma = 2.96$ for $v^* = 1$ and $\beta F_\mathrm{d}\sigma = 11.76$ for $v^* = 5$). We accompanied the DSA with standard BD simulations [27], in which the Langevin equations for each bath particle are solved iteratively. Here, the bath particles are driven by an external force $\mathbf{v}/\Gamma$ for a prescribed flow velocity $\mathbf{v}$. The box lengths in all simulations were $L_x = L_y = 10\sigma$ and $L_z = 20\sigma$ and $N = 2000$ particles were simulated, applying periodic boundary conditions in all directions.

Results for the averaged force field acting on a colloid placed at the position $\mathbf{R}_2$ away from another colloid at the origin ($\mathbf{R}_1 = 0$) are depicted in Fig. 2. A comparison between Figs. 2(c) and 2(d) (DSA vs BD simulation) shows that the former captures the features of the nonequilibrium depletion force quantitatively, even for drifting speeds as large as $v^* = 5$. Whereas for the case of equilibrium, Fig. 2(a), we obtain spherically symmetric *attractive* depletion forces, the dynamical depletion force shows new qualitative features: First, as is clear from inspection of Fig. 2, the dynamical depletion forces violate Newton's third law. Second, the violation of the "action = reaction" principle implies a nonconservative force. Indeed, if a putative depletion potential V_depl existed in the dynamical case at hand, translational invariance of space (which is not broken by the steady flow) would imply $V_\mathrm{depl} = V_\mathrm{depl}(\mathbf{R}_1 - \mathbf{R}_2)$. As $\mathbf{F}_{\mathrm{depl},i} = -\vec{\nabla}_{\mathbf{R}_i} V_\mathrm{depl}(\mathbf{R}_1 - \mathbf{R}_2)$, $i = 1, 2$, this would have the consequence $\mathbf{F}_{\mathrm{depl},1} = -\mathbf{F}_{\mathrm{depl},2}$. Third, the depletion force shows strong anisotropy, becoming attractive as the colloid starts positioning itself "behind" the one at the origin and its magnitude (in the attractive case) and its range are vastly larger for $v \neq 0$ than in equilibrium.

In order to better quantify the features of the depletion force in nonequilibrium, we show in Fig. 3 plots of the projected depletion force at fixed $X = 0$ (particles fully aligned along the flow direction) and at fixed $Z = 0$ (particles fully aligned perpendicular to the flow direction). The depletion force exhibits a *repulsive barrier* in the X direction due to compression of the small particles between the colloids, in qualitative difference to the

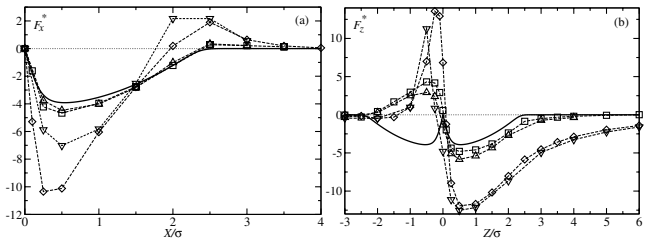

FIG. 3. Depletion forces as in Fig. 2, but now we plot the projection of the the depletion force $F_x^*(X) = \beta\sigma\mathbf{F}_{\mathrm{depl},2} \cdot \hat{\mathbf{X}}$ for fixed $Z = 0$ in the X direction (a) and the projection of the depletion force $F_z^*(Z) = \beta\sigma\mathbf{F}_{\mathrm{depl},2} \cdot \hat{\mathbf{z}}$ for fixed $X = 0$ in the Z direction. The solid line is the exact result for $v^* = 0$ and the symbols are results from the DSA for $v^* = 1$ (squares) and $v^* = 5$ (diamonds), as well as simulation results for $v^* = 1$ (triangles up) and $v^* = 5$ (triangles down).

purely attractive equilibrium case $v = 0$. In the Z direction, on the other hand, there is much stronger attraction for $Z > 0$ due to a long low-density region in the wake of the colloids but a marked repulsive barrier for $Z < 0$. Furthermore, the range of the depletion force is significantly larger than in equilibrium. Notice that we show forces also for the case of overlapping colloids [26]. The drift force F_d on a pair of *completely* overlapping spheres, i.e., $\mathbf{R}_1 = \mathbf{R}_2$, is obviously the same as that acting on a single sphere, such that per sphere, $F_i = F_d/2$ and $F_{depl}(i) = -F_d/2$, for both $i = 1, 2$. We can finally deduce from Fig. 3 that the computer simulation results are in good quantitative agreement with the theory up to drifting speeds of $v^* = 5$, except for overlapping and almost touching colloidal spheres.

In conclusion, we have generalized the depletion concept to a simple nonequilibrium situation of two big particles in a Brownian flow of small ideal particles. The effective forces averaged in the steady state are strikingly different from those in equilibrium: they are strongly anisotropic with both attractive and repulsive domains and violate Newton's third law, in strong resemblance to the so-called "social forces" that have been applied extensively in the modeling of pedestrian and automotive traffic flows [28].

Although the present study has focused on noninteracting bath particles, the extension to interacting ones can be carried out within the framework of the recently proposed dynamical density functional theory [29]. We expect that interaction effects will weaken the strength of the dynamical depletion forces, as they will tend to smoothen out regions of spatial inhomogeneity of the bath density that give rise to these forces in the first place. Finally, we remark that the strong attractive forces tending to align the colloids in the direction of the incoming flow can be regarded as precursors of the laning transition that has been analyzed recently for concentrated colloidal mixtures [30].

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