The concept of effective depletion forces between two fixed big colloidal particles in a bath of small particles is generalized to a non-equilibrium 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 non-equilibrium forces violate Newton’s third law, are non-conservative and strongly anisotropic, featuring both strong attractive and repulsive domains.

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FIG. 1: Steady-state contour density fields of non-interacting 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. (11). Bright regions show high densities while low density regions are plotted dark. One colloid is placed at the origin, $R_1 = 0$, and the position $R_2$ of the other one is: (a) $R_2/\sigma = (2, 0, 0)$; (b) $R_2/\sigma = (1.5, 0, 1)$; (c) $R_2/\sigma = (1, 0, 2)$; (b) $R_2/\sigma = (0, 0, 4)$. In this figure, the bath particles drifting from the left to the right with a speed $v^* = 5$.

fixed by optical tweezers [21, 22]. The measurement of the relative displacement with respect to the tweezer’s position of the big particles provides direct access to the effective non-equilibrium forces.

In our theoretical model we consider two fixed big particles in a bath of small Brownian particles that drift with velocity $v = v\hat{z}$. The bath has a bulk number density $\rho_0$. 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 $V(r)$ given by

$$V(r) = V(r) = V_0 \exp \left[ -\left( r/\sigma \right)^n \right],$$

where $r$ is the vector separating the bath particle with the center of the colloid, $r$ is the magnitude of $r$ 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 diameter of the colloidal sphere, $\sigma$, 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 $\rho(r)$ of the bath particles reads as $\vec{\nabla} \cdot \vec{j}(r) = 0$ with the current density field $\vec{j}(r)$ composed of

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

where $\beta = 1/k_BT$ is the inverse thermal energy and $\Gamma$ 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.

Let us define the resulting density profile of the bath particles around one big colloid as $\rho^{(1)}(r - R; v)$ with $R$ denoting the position of the colloid. Spatial homogeneity dictates that $\rho^{(1)}$ depends only on the difference $r - R$. The force $\vec{F}_d$ acting on the big particle due to the drifting bath is then obtained as $\vec{F}_d = -\int d^3 r \rho^{(1)}(r) \vec{\nabla} V(|r|)$.

In the presence of two colloids, the corresponding quantity of interest is the bath density profile

FIG. 2: The depletion force $\vec{F}_{depl,2}$ (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 Brownian Dynamics 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, $\rho_0 = 1/\sigma^3$. 

\( \rho^{(2)}(r, R_1, R_2; v) \) that depends on the locations \( R_i \) of the colloids, \( (i = 1, 2) \), and parametrically on the velocity \( v \). In this case, the numerical solution of the Smoluchowski equation is more difficult such that a direct particle-resolved computer simulations is more appropriate. However, let us motivate a simple superposition approximation. As the bath particles are noninteracting, in the case of thermodynamic equilibrium, \( v = 0 \), \( \rho^{(2)}(r, R_1, R_2; 0) \) can be exactly factorized as the product of the density fields \( \rho^{(1)}(r - R_i; 0) \) divided by \( \rho_0 \). In what follows, we employ the same factorization ansatz also for the non-equilibrium situation, \( v \neq 0 \). Thereby, we introduce the dynamical analog of the superposition approximation that was first introduced by Attard \( ^{25} \) for equilibrium problems dealing with interacting particles, in order to calculate static depletion forces. Hence, in this dynamical superposition approximation (DSA), we write:

\[
\rho^{(2)}(r, R_1, R_2; v) \approx \rho^{(1)}(r - R_1; v)\rho^{(1)}(r - R_2; v) / \rho_0. \tag{1}
\]

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 non-equilibrium 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 \( ^{6} \). Generalizing to a steady-state average in non-equilibrium, the effective force reads as \( ^{26} \):

\[
F_i = - \int d^3r \rho^{(2)}(r, R_1, R_2; v) \hat{V}_r \cdot \nabla \rho^{(1)}(r - R_i; v). \tag{2}
\]

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 \( F_{\text{depl}, i} \) acting on the \( i \)-th particle can be obtained. The latter is defined as the force \( F_{\text{depl}, i} = F_i - F_d \), relative to the constant the drift force \( F_d \) acting on a single big particle \( \beta F_d \sigma = 2.96 \) for \( v^* = 1 \) and \( \beta F_d \sigma = 11.76 \) for \( v^* = 5 \). We accompanied the DSA with standard Brownian Dynamic simulations \( ^{27} \), in which the Langevin equations for each bath particle are solved iteratively. Here, the bath particles are driven by an external force \( \nu / \Gamma \) for a prescribed flow velocity \( \nu \). 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 \( R_2 \) away from another colloid at the origin \( (R_1 = 0) \), are depicted in Fig. 2. A comparison between Figs. 2c) and 2d), (DSA vs. BD-simulation), shows that the former captures the features of the non-equilibrium depletion force quantitatively, even for drifting speeds as large as \( v^* = 5 \). Whereas for the case of equilibrium, Fig. 2a), 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 non-conservative force. Indeed, if a putative depletion potential \( V_{\text{depl}} \) existed in the dynamical case at hand, translational invariance of space (which is not broken by the steady flow) would imply \( V_{\text{depl}} = V_{\text{depl}}(R_1 - R_2) \). As \( F_{\text{depl}, i} = -\hat{V}_r \cdot \nabla \rho^{(1)}(R_1 - R_2; v) \), \( i = 1, 2 \), this would have the consequence \( F_{\text{depl}, 1} = -F_{\text{depl}, 2} \). 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 non-equilibrium, 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 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 should expect also for the case of completely overlapping colloids \( ^{26} \), \( -2.0 \lesssim X / \sigma \lesssim 2.0 \) and \( -2.0 \lesssim Z / \sigma \lesssim 2.0 \). For \( R_1 = R_2 \), the depletion force on both colloids is ob-
viously the same, \( F_{\text{dep},1} = F_{\text{dep},2} \) but, in contrast to the equilibrium case, it does not vanish. 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 \( v^* = 1 \), but for large drifting speeds as high as \( v^* = 5 \) deviations near the maxima and minima are getting more pronounced.

In conclusion, we have generalized the depletion concept to a simple non-equilibrium 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 modelling 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 (DDFT) 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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