Supplemental material
Superadiabatic forces in Brownian many-body dynamics

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DENSITY FUNCTIONAL THEORY

The exact density functional of a one dimensional system of hard-particles was developed by Percus [1]. The free energy is

$$F[\rho^{(1)}] = F_{\rm id}[\rho^{(1)}] + F_{\rm ex}[\rho^{(1)}], \tag{1}$$

where $F_{\rm id}$ is the ideal gas contribution and the excess part $F_{\rm ex}$ accounts for the excluded-volume interactions between the particles:

$$\beta F_{\rm id}[\rho^{(1)}] = \int dx \rho^{(1)}(x) \left(\ln(\Lambda \rho^{(1)}(x)) - 1 \right), \tag{2}$$

$$\beta F_{\rm ex}[\rho^{(1)}] = -\frac{1}{2} \int dx \left(\rho^{(1)}(x-\sigma/2) + \rho^{(1)}(x+\sigma/2) \right) \ln(1-\eta(x)).$$

In the above expressions $\beta = 1/k_B T$ with k_B the Boltzmann constant and T the temperature. Λ is the (irrelevant) thermal wavelength, x is the space coordinate, and $\eta(x)$ is the local packing fraction, defined as

$$\eta(x) = \int_{x-\sigma/2}^{x+\sigma/2} dx' \rho^{(1)}(x'), \tag{3}$$

with σ the particle length.

The grand canonical density functional is

$$\beta\Omega[\rho^{(1)}] = F[\rho^{(1)}] + \int dx \rho^{(1)}(x)(V_{\rm ext}(x) - \mu), \tag{4}$$

where μ is the chemical potential and $V_{\rm ext}$ is the external potential.

The equilibrium density profiles are those that minimize the grand potential density functional at constant μ. We use a standard conjugated gradient method to minimize Ω. In order to compare the results with the canonical Brownian dynamics (BD) or Monte Carlo (MC) simulation we find the chemical potential for which the average number of particles is equal to the number of particles in the simulation. Given the reduced number of particles the canonical and the grand canonical ensembles are not equivalent. The grand canonical density profiles are combinations of canonical profiles. We show in Fig. 1 the equilibrium density profiles of a system of $N = 10$ particles confined in a pore with $L_x = 25\sigma$ in the canonical (MC) and grand canonical (DFT) ensembles. The differences are small and do not justify the large discrepancy between the predictions of Dynamic Density Functional Theory (DDFT) and BD.

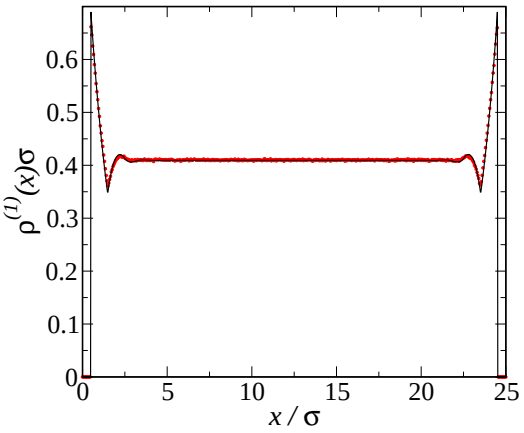

Figure 1. Equilibrium density profiles of a system of hard particles confined between hard walls separated by a distance 25σ. Black-solid line: the grand canonical density profile obtained with DFT at a chemical potential $\beta\mu = 0.3258$ that corresponds to an average number of particles $\langle N \rangle = 10$. Red circles: canonical MC simulation of a system of $N = 10$ particles.

DYNAMIC DENSITY FUNCTIONAL THEORY

In DDFT the time evolution of the density profile is governed by the continuity equation [2, 3]

$$\frac{\partial \rho^{(1)}(\boldsymbol{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}_{\rm ad}(\boldsymbol{r},t), \tag{5}$$

where $\boldsymbol{r}$ is the coordinates vector, t is the time, and $\boldsymbol{J}_{\rm ad}$ is the adiabatic current given by

$$\xi \mathbf{J}_{\rm ad}(\boldsymbol{r},t) = -\rho^{(1)}(\boldsymbol{r},t) \left(\nabla \frac{\delta F[\rho^{(1)}]}{\delta \rho^{(1)}(\boldsymbol{r},t)} + \nabla V_{\rm ext}(\boldsymbol{r},t) \right), \tag{6}$$

where ξ is the friction coefficient and V_{ext} is an external potential.

For the one-dimensional system of particles analysed here, the equation for the time evolution of the density

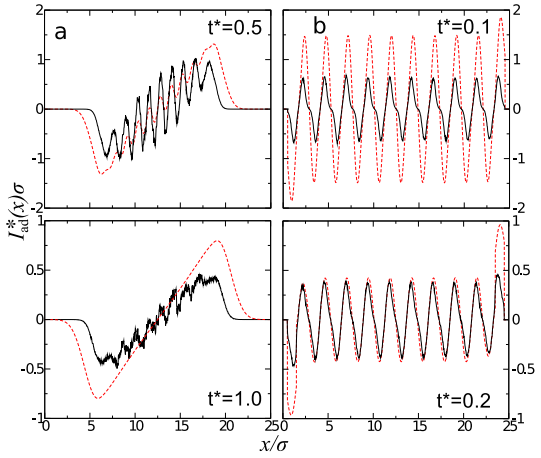

Figure 2. a) Adiabatic force calculated from BD simulations (black-solid line) and DDFT (red-dashed line) at reduced time $t^* = t_s/\tau_B$=0.5 (top), and 1.0 (bottom) for a system initialized in a parabolic trap. b) Adiabatic force calculated from BD simulations (black-solid line) and DDFT (red-dashed line) at reduced time t^*=0.1 (top), and 0.2 (bottom) for a system initialized in a crystal structure.

according to DDFT reads

$$\xi\frac{\partial\rho^{(1)}(x,t)}{\partial t} = \frac{\partial^2\rho^{(1)}(x,t)}{\partial x^2} + \\ + \frac{\partial}{\partial x}\left[\rho^{(1)}(x,t)\left(\frac{\rho^{(1)}(x+\sigma,t)}{1-\eta(x+\sigma/2)} - \frac{\rho^{(1)}(x-\sigma,t)}{1-\eta(x-\sigma/2)}\right)\right] \\ + \frac{\partial}{\partial x}\left(\rho^{(1)}(x,t)\frac{\partial V_{\rm ext}(x,t)}{\partial x}\right). \quad (7)$$

The comparison between simulation and DDFT results for the density are shown in Fig. 1 of the the main article. Figure 2a,b show the same comparison comparison for the computed adiabatic contribution.

MEASUREMENTS OF THE CURRENT IN BROWNIAN DYNAMICS SIMULATIONS

In order to measure the current in Brownian dynamics simulations we solve the one dimensional continuity equation

$$\frac{\partial\rho^{(1)}(x,t)}{\partial t} = -\frac{\partial \mathrm{J}_x(x,t)}{\partial x}. \quad (8)$$

The average

$$\langle\frac{\partial\rho^{(1)}(x,t_s)}{\partial t}\rangle \simeq \langle\frac{\Delta\rho^{(1)}(x,t_s)}{\Delta t}\rangle$$

is computed over 10^6 independent trajectories at a fixed time t_s.

In order to carry out the calculation, we divide the one dimensional simulation box in bins of length x_{bin} and accumulate the histogram of the local density changes

$$\Delta\rho^{(1)}(x,t_s) = \frac{n(x,t_s) - n(x,t_s-\Delta t)}{x_{bin}},$$

where $n(x,t)$ is the number of particles located in the bin at position x and time t. The density histogram is then divide by the sampling time interval Δt.

Once the average is calculated the current is obtained with the following integration

$$\mathrm{J_x}(x,t) = -\int_0^x dx' \langle\frac{\Delta\rho^{(1)}(x',t_s)}{\Delta t}\rangle. \quad (9)$$

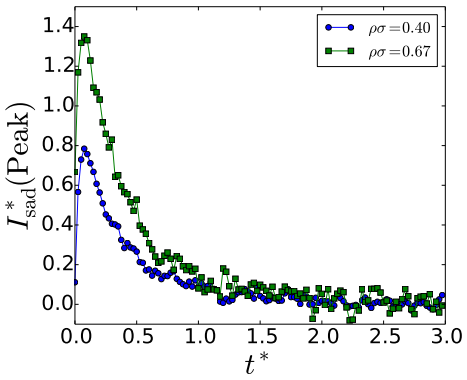

Figure 3. Evolution in time of the superadiabatic force $I^*_{\rm sad}(x_{\rm peak}) = I_{\rm sad}(x_{\rm peak})\sigma^2/k_BT$ at densities $\rho\sigma = 0.4$ (green squares, $L_x = 25\sigma$) and $\rho\sigma = 0.67$ (blue circles, $L_x = 15\sigma$).

SUPERADIABATIC FORCE

The total pair force integral $I(\boldsymbol{r},t) = I_{\rm ad}(\boldsymbol{r},t) + I_{\rm sad}(\boldsymbol{r},t)$ is represented as the sum of an adiabatic term $I_{\rm ad}(\boldsymbol{r},t)$, which contains all contributions that can be described by an equilibrium system, and a superadiabatic term $I_{\rm sad}(\boldsymbol{r},t)$, which contains contributions that can not be reduced to an equilibrium description. Therefore for all equilibrium states the superadiabatic contribution vanishes. Figure 3 shows the evolution in time of the superadiabatic force at the density peak position $x_{\rm peak}$ for the system initialized in a crystal structure. The superadiabatic contribution is zero for the equilibrium configurations at $t^* = 0$ and $t^* \to \infty$. At intermediate times the curve is characterized by a maximum at short times and by an exponential decay of the force at longer times.

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[2] U. M. B. Marconi and P. Tarazona, J. Chem. Phys. **110**, 8032 (1999).
[3] U. M. B. Marconi and P. Tarazona, J. Phys.: Condens. Matter **12**, A413 (2000).