Dynamic density functional study of driven colloidal particles: the effect of the system dimension

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The dynamical properties of classical fluids at pico-liter scale attract experimentally and theoretically much attention in the soft-matter and biophysics communities, due to the appearance of the microfluidics ref.\[3\], also called 'lab-on-a-chip' ref.\[2\], as one of the most relevance 21th century technologies. Theses devices try to put a full chemical laboratory onto your hand thought a sophisticated dispositive that includes particles pump ref.\[3\] and gates, chemical reaction ref.\[4\], etc. In this work we focus our attention on one of the key factors for the design and construction of this type of devices: the system dimension. We consider a generic system formed by a dilute solution of colloidal particles dragged (at a constant rate $c$ in the $\hat{z}$ direction) by a moving potential barrier, modeled by a time dependent external potential ($V_{ext}(\mathbf{r},t) = V_{ext}(\mathbf{r} - ct\hat{z})$) acting on the colloidal particles but with no effect on the solvent. We base our results on a new technique named Dynamic density functional (DDF) theory ref.\[5,\ 6\] which is a generalization of Density functional (DF) theory to out of equilibrium, for systems with relaxative molecule dynamics (those in which hydrodynamic modes are not relevant), under the hypothesis that the dynamic correlations can be approximated by those in a system with the same density distribution at equilibrium; the DDF is a promising way of describe classical fluids dynamics at a microscopic level including our knowledge of the very well developed DF theory for the equilibrium.

The central deterministic DDF equation is,

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = \Gamma_0 \nabla \left[ \rho(\mathbf{r},t) \nabla \left( \frac{\delta F[\rho]}{\delta \rho(\mathbf{r},t)} + V_{ext}(\mathbf{r},t) \right) \right], \tag{1}$$

where $F$ is the Helmholtz free energy in DF theory, usually split onto the ideal gas contribution and the excess due to the interactions ($\Delta F$), and $\Gamma_0$ is the mobility of an isolated colloidal particle in the solvent. In the case of the shifting external potential we are dealing with, $V_{ext}(\mathbf{r} - ct\hat{z}) \equiv V_{ext}(\mathbf{r'})$ (where $\mathbf{r'}$ is the coordinate in the reference framework of the external potential), the most relevant feature comes from the stationary state (achieved after a transient period from any initial state) in which $\rho(\mathbf{r},t) = \rho(\mathbf{r} - ct\hat{z}) \equiv \rho(\mathbf{r'})$ i.e. when the density distribution is shifted at the same rate $c$ as the potential barrier, so that, eq.\[1\] reduces to,

$$\nabla \left[ \rho(\mathbf{r'}) \nabla \left( \frac{\delta F[\rho]}{\delta \rho(\mathbf{r'})} + V_{ext}(\mathbf{r'}) + \frac{cz'}{\Gamma_0} \right) \right] = 0. \tag{2}$$

For non interacting particles, such that $\Delta F = 0$, eq.\[2\] becomes a linear Fokker-Planck equation $\nabla^2 \rho + \nabla(\rho \nabla \beta V_k) = 0$, with a "kinetic potential" given by $\beta V_k(\mathbf{r'}) = V_{ext}(\mathbf{r'}) + cz'$, as a function of the reduced shifting rate $\bar{c} \equiv \beta c / \Gamma_0$, with inverse length units and $\beta = \frac{1}{k_B T}$. In this case, the effective dimension behaviour is completely determined by the difference between the system dimension (container) and the dimensions over which the external potential is homogeneous, so that an effective 1D system got thought a 2D plane barrier dragging particles in a 3D container, is equivalent to a point-like barrier dragging particles in a narrow channel ref.\[7\]; similarly, an effective 2D system may be observed for a cylindrical barrier in a 3D container, or with a point-like barrier in a 2D container. For $\Delta F \neq 0$ (interacting particles) ref.\[8,\ 9,\ 10\] this is not longer true, because the excess free energy depends explicitly on the dimension of the colloidal particles container.

Since the system dynamic behaviour is determined mainly through the particles interaction and the effective system dimension, and we are interested here in the caracteristics induce by this last factor, we consider in this work only non interacting particles which would represent diluted solutions of colloidal particles. We set the notation before we start solving eq.\[2\] for each dimension. In the following, we refer to the front (wake) region as that away from the external potential, well beyond (behind) the $z'$ positions with $V_{ext} \neq 0$; if we assume that this external potential barrier is located around the origin of the shifting reference framework, and restricted to values $|z'| \approx \sigma$ with $\sigma$ the molecular diameter, then the points with $z' \gg \sigma$ are in the front while those with $z' \ll -\sigma$ are in the wake. In both regions $V_{ext} = 0$, eq.\[2\] reduces to $\nabla^2 \rho + \bar{c} \frac{\partial \rho}{\partial z'} = 0$, and the analytic form of $\rho(\mathbf{r'})$ may be obtained as a series with the appropriate asymptotic limit in each dimension. Notice that only for effective 1D systems, the front and the wake are fully separated by the external potential. In higher dimensions, they are connected through those
regions with \(|z'| \leq \sigma\) but \(|r'| \gg \sigma\), for which \(V_{\text{ext}} = 0\). Our result are presented as follow: first we solve analytically eq. (2) (where \(V_{\text{ext}} = 0\)), then we find numerically the full solution, and finally we compare both.

For a shifting repulsive barrier in effective 1D systems ref. [8], the solution of eq. (2) is given by \(\rho(z') = \rho_0 + A \exp(-\bar{c}z')\) at the front, where \(A/\rho_0\) is a constant, fixed by the nature of the barrier and the boundary conditions, and by \(\rho(z') = \rho_0\), without any kind of structure, in the \(\text{wake}\) region. It may be proved by a formal reduction of the stationary DDF equation with \(\Delta F = 0\) in any dimension, that this exponential decay behaviour at the \(\text{front}\), and this absence of excess molecules in the \(\text{wake}\), are generic characteristics of the total excess density distribution, under constant bulk boundary conditions \((\lim |r'| \to -\infty \rho = \rho_0)\), for the integrated excess density distribution across the transverse directions, i.e. \(\frac{\Delta n(z')}{\rho_0} = \frac{1}{\sigma} \int dx (\frac{\rho(r')}{\rho_0} - 1)\) in effective 2D systems, and \(\frac{\Delta N(z')}{\rho_0} = \frac{2\pi}{\sigma^2} \int DrR (\frac{\rho(r')}{\rho_0} - 1)\) in effective 3D systems.

In effective 2D systems, for a shifting cylindric external potential (e.g. the dielectric potential created by a laser beam through a bulk solution), eq. (2), for the region with \(V_{\text{ext}}(r') = 0\), reduces to,

\[
\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z'^2} + \bar{c} \frac{\partial \rho}{\partial z'} = 0.
\]

Through a Fourier transform, the solution is given by,

\[
\rho(x, z') = \rho_0 + \int_0^\infty d\alpha \cos[\alpha x] e^{-\beta z'} g(\alpha);
\]

where,

\[
\beta_{\pm} = \frac{\bar{c}}{2} \pm \sqrt{\left(\frac{\bar{c}}{2}\right)^2 + \alpha^2}.
\]

Far away from the external potential, a fast convergence of the Fourier components \(g(\alpha)\) is observed, and the relevant features come from their behavior for \(\alpha \ll \bar{c}\). Hence we may use \(\beta_+ \approx \bar{c} + \frac{\alpha^2}{2}\) and \(\beta_- \approx -\frac{\alpha^2}{2}\), for the \(\text{front}\) and \(\text{wake}\) regions respectively. The expansion of \(g_\pm(\alpha)\) as an even polynomial function for small \(\alpha\), and the zero \(\text{wake}\) requirement, lead in the \(\text{wake}\) to \(g_-(\alpha) \approx A_1 \alpha^2 + A_2 \alpha^4 + \ldots\), while at the \(\text{front}\) we expect \(g_+(\alpha) \approx B_0 + B_1 \alpha^2 + B_2 \alpha^4 + \ldots\). Thus,

\[
\rho(x, z') \approx \rho_0 + \sqrt{\pi} e^{-\bar{c}z'} e^{-\frac{x^2}{2}} \left[ B_0 \frac{w}{2} + B_1 \frac{w^3}{8} (a^2 - 2) + B_2 \frac{w^5}{32} (a^4 - 12a^2 + 12) + \ldots \right],
\]

for \(z' \gg \sigma\), and

\[
\rho(x, z') \approx \rho_0 + \sqrt{\pi} e^{-\bar{c}z'} \left[ A_1 \frac{w^3}{8} (a^2 - 2) + A_2 \frac{w^5}{32} (a^4 - 12a^2 + 12) + \ldots \right];
\]
Fig. 2: Steady state density profile of colloidal particles under the influence of an external potential $V_{\text{ext}} = V_0 e^{-|z'|/\sigma}$, with $\beta V_0 = 10$, for effective 2D system at drift velocity $\sigma \bar{c} = 10$ (solid line) and $\sigma \bar{c} = 2$ (dotted-dashed line) and for effective 3D system at drift velocity $\sigma \bar{c} = 10$ (dashed line) and $\sigma \bar{c} = 2$ (dotted line). The fixed radial and perpendicular distance to the $z'$axis are a) $R = x = 0$, b) $R = x = 0.75\sigma$, c) $R = x = \sigma$, d) $R = x = 2\sigma$.

for $z' \ll -\sigma$; where $w = \sqrt{|c|/|z'|}$ and $a = wx$.

In effective 3D system, for a shifting spherical external potential (e.g. a driven colloid particle perturbing a bulk solution of others colloids), we use cylindrical coordinates $r' = (R, \phi, z')$, and eq. (2), for the region with $V_{\text{ext}}(r') = 0$, reduces to,

$$\frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \rho(r')}{\partial R} \right) + \frac{\partial^2 \rho(r')}{\partial z'^2} + \bar{c} \frac{\partial \rho(r')}{\partial z'} = 0. \tag{8}$$

Through a Hankel transform, the solution is given by,

$$\rho(R, z') = \rho_0 + \int_0^\infty d\alpha \alpha f(\alpha) J_0[\alpha R] e^{-\bar{c} z'}. \tag{9}$$

where $J_0$ is the zeroth order Bessel function. Proceeding with the Hankel components as in the effective 2D with the Fourier ones, we might take $f_-(\alpha) \approx C_1 \alpha^2 + C_2 \alpha^4 + ...$ in the wake, and at the front $f_+(\alpha) \approx D_0 + D_1 \alpha^2 + D_2 \alpha^4 + ...$. Thus,

$$\rho(R, z') \approx \rho_0 + e^{-\bar{c} z'} e^{-\frac{h^2}{2}} \left[ D_0 \frac{u^2}{2} + D_1 \frac{u^4}{8} (h^2 - 4) + D_2 \frac{u^6}{32} (h^4 - 16h^2 + 32) + ... \right], \tag{10}$$

for $z' \gg \sigma$, and

$$\rho(R, z') \approx \rho_0 + e^{\frac{-h^2}{2}} \left[ C_1 \frac{u^4}{8} (h^2 - 4) + C_2 \frac{u^6}{32} (h^4 - 16h^2 + 32) + ... \right]; \tag{11}$$

for $z' \ll -\sigma$; where $h = wR$.

The coefficients ($A,B,C$ and $D$) are determined by the particular choice of the external potential but, for each dimension, the asymptotic decay forms are generic. In the transverse plane (for fixed $z'$) the excess stationary density
distribution \( \rho(r') - \rho_o \) is given by a gaussian times a polynomial function, and along the direction of the movement \((z' axis)\) for a fixed distance to the origin \((a = \text{const} \text{ in effective 2D systems and } h = \text{const} \text{ in the 3D})\) is given, at the \textit{front}, by an exponential decay \((\exp(-\tilde{c}z'))\) and an inverse power in the \textit{wake}. Over the transverse directions, at the \textit{front}, the maximum density is at the \(z'\) axis, while in the \textit{wake}, this axis is a minimum between two symmetric maxima which produce a cap-like structure with parabolic shape. The distance between the maximum and the \(z'\) axis is \(2 \sqrt{2 |z'| / \tilde{c} \sigma}\) in effective 3D systems and \(\sqrt{6 |z'| / \tilde{c} \sigma}\) in the 2D. In fig.1 we present the numerical solution for the stationary density distribution of colloidal particles under the influence of an external potential \(V_{\text{ext}} = V_o e^{-|r'|/\sigma^6}\), with \(\beta V_o = 10\), shifting at the velocity \(\tilde{c} \sigma = 10\), in \(a)\) an effective 3D and \(b)\) 2D system. The clear cap-like structure, extended further away from the external potential, is clearly observed.

We have mentioned before that only in effective 1D systems the \textit{front} and \textit{wake} are fully separated by the external potential, which implicate that as the solution of eq. (2), the \textit{front} and \textit{wake} should share an unique analytic expression in effective dimensions beyond 1D. This unique expression produces, at the \textit{front} (\textit{wake}), an exponential growth of the \(\beta_+ (\beta_-)\) contribution, which only by the appropriate behaviour of \(g(\alpha) (f(\alpha))\) for large \(\alpha\) be canceled. We have compared our analytical prediction with the numerical solution of eq.(4), the concordance reveal a local asymptotic convergence which makes useful those asymptotic expressions (eqs.(6),(7),(10),(11)), to represent separately (at the \textit{front} and in the \textit{wake} regions) the stationary state. The use of polar (spherical) coordinates, instead of the rectangular (cylindric) ones, would not solve the problem, because the parabolic structure of the \textit{wake} implies the entanglement of the radial and the angular coordinates.

Because this work may be usefully in the construction of particles pumps, we want to point out some effects to be considered in the design of an efficient device to drag particles. For the same radial form of the external potential it is clear that an effective 2D system is more efficient dragging particles than a 3D, because it produces a higher density at the \textit{front} peak. In fig.2 we present the numerical stationary density distribution of an effective 3D (dashed and dotted lines) and 2D system (solid and dotted-dashed lines), for different fixed values of \(x\) and \(R\). The higher \textit{front} density peak in the effective 2D system is clearly observed. For the same reason, an effective 1D system is more efficient than the 2D.

For an effective 1D system we obtained in our previous work ref.8 a non-linear dependence of the total current \(j = \tilde{c} \int (\rho(r') - \rho_o) dr'\) with the drift velocity. If we denoted by \(\tilde{c}_{\text{max}}\), the velocity at which the total current is maximum for a given external potential, the efficiency of a device as a particles pump increases with \(\tilde{c}\) until \(\tilde{c}_{\text{max}}\) is reached, and then diminishes for higher \(\tilde{c}\). As we have mentioned before, the integrated excess of the stationary density distribution across the transverse directions, \(\Delta n\) in effective 2D systems and \(\Delta N\) in the 3D, satisfies the

\[ \text{FIG. 3: Integrated excess of the stationary density distribution over the transverse directions, } a) \text{ for an effective 2D and } b) \text{ 3D system. The external potential } V_{\text{ext}} = V_o e^{-|r'|/\sigma^6}, \text{ \(\beta V_o = 10\) is shifting at the velocities } \sigma \tilde{c} = 10 \text{ (solid lines), } \sigma \tilde{c} = 5 \text{ (dotted lines) and } \sigma \tilde{c} = 2 \text{ (dashed lines).} \]

\[ \begin{align*}
\Delta n/\rho_o &= 5 \\
\Delta N/\rho_o &= 2
\end{align*} \]
same stationary DDF equation as the 1D density distribution, so we may expect for the total current this non-linear behaviour too. To support numerically our analytical result in fig.3 we present the integrated excess of the stationary density distribution, a) in an effective 2D and b) 3D system, the exponential decay behaviour at the front and the absence of structure in the wake as for the 1D stationary density distribution is clearly observed. We have estimated that the maximum total currents are obtain for $\sigma \bar{c}_{\text{max}} \approx 0.5$ in 1D, $\approx 12.41$ in 2D, and $\approx 14.76$ in 3D, which implicate that, apart from the dependence of $\bar{c}_{\text{max}}$ with the external potential shape, it is a function of the effective system dimension. $\bar{c}_{\text{max}}$ determines when for a given external potential the system is saturated by the drift velocity. Increasing the dimension, we increase the paths for the molecules to avoid the external potential so a higher velocity is needed to make the molecules go thought the external potential.

We have considered the geometrical effects of the effective dimension in systems of non-interacting colloidal particles driven by external barriers with constant drift rates. The main difference between the 2D and 3D cases analyzed here and the previously reported 1D case is the appearance of long wake structures behind the moving barrier. In contrast with the common exponential decay $\rho(r') - \rho_o \sim \exp(-\bar{c}z')$ for the structure at barrier front, the structure of the wake decays only as an inverse power, $\rho(r') - \rho_o \sim 1/|z'|^2$ for 3D and $\rho(r') - \rho_o \sim 1/|z'|^{3/2}$ for 2D. However, the transverse integral of the wake, over the directions other than $z'$, gives no excess of particles, with respect to the unperturbed density $\rho_o$ far from the potential barrier. This is in agreement with the complete lack of wake structure behind a 1D barrier, and it implies that the global current induced by the shifting potentials, calculated as the integral of $\bar{c}(\rho(r') - \rho_o)$ comes from the balance between the positive contribution from the density peak at the front, and the void ($\rho(r') < \rho_o$) within the barrier. This total current follows a non-monotonic dependence with the shifting rates, as reported in 1D [3], with an optimum shifting rate $\bar{c}_{\text{max}}$ which increases with the effective dimensions. The colloid-colloid interactions effects, which have being leaved out of this work, may be included within the general framework of the DDF [8, 9, 10] and may help to the design of efficient particle pump devices.

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