Dynamic Density Functional theory for steady currents: Application to colloidal particles in narrow channels

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We present the theoretical analysis of the steady state currents and density distributions of particles moving with Langevin dynamics, under the effects of an external potential displaced at constant rate. The Dynamic Density Functional (DDF) formalism is used to introduce the effects of the molecular interactions, from the equilibrium Helmholtz free energy density functional. We analyzed the generic form of the DDF for one-dimensional external potentials and the limits of strong and weak potential barriers. The ideal gas case is solved in a closed form for generic potentials and compared with the numerical results for hard-rods, with the exact equilibrium free energy. The results may be of relevance for microfluidic devices, with colloidal particles moving along narrow channels, if external driving forces have to compete with the brownian fluctuations and the interaction forces of the particles.

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I. INTRODUCTION

Microfluidics, or the manipulation of liquids at the pico-liter scale, is an emerging technology with very interesting perspectives [1, 2]. In particular, the construction of devices which might control colloidal fluxes at the level of single particles, even under the effects of strong correlations at high density and in confined geometries would be of great interest for many applications, and it is already within the range of experimental works [3]. A theoretical description, with quantitative prediction power, for these systems would allow the design of devices on a firmer basis, but such theoretical framework is well established only for the properties of systems at thermal equilibrium, mainly thought the applications of the density functional formalism (see e.g. [4]). In this paper we explore the use of a particular extension of the density functional methods to describe some systems out of equilibrium, like fluxes produced by the time-dependent external forces in micro-pumps or turn-pikes which might control single colloidal particles in a flux.

The extension of the density functional formalism (DDF), from systems at thermodynamic equilibrium to the dynamics of systems out of equilibrium has been a very attractive target for workers in classical and quantum fluids during the last two decades. The goal is certainly ambitious and the success has been limited to some particular types of problems and levels of description. Thus, the modern theory of phase transitions dynamics [4] is based on quasi-local thermodynamic descriptions, which may be considered as an empirical extension of the squared gradients density functional approximation to study the dynamics of a 'coarse grained' variable. The generic form for such descriptions, for a conserved 'coarse grained' density $\hat{\rho}(r,t)$ is

$$\frac{\partial \hat{\rho}(r,t)}{\partial t} = \nabla \left[ \Gamma(\hat{\rho}(x,t)) \nabla \left( \frac{\delta \mathcal{F}[\rho]}{\delta \hat{\rho}(x,t)} + V(x) \right) + \xi(x,t) \right],$$  \hspace{1cm} (1)

where $\mathcal{F}[\rho]$ is the intrinsic the Helmholtz free energy functional, approximated by

$$\mathcal{F}[\rho] = \int dx \left( f(\rho(x)) + \frac{b}{2} \nabla \rho(x)^2 \right),$$  \hspace{1cm} (2)

$x$ runs over all the space variables, $f(\rho)$ gives the free energy per unit volume for bulk systems of homogeneous density $\rho$, and the coefficient $b$ (which may be taken as a function of $\rho(x)$ itself) gives a measure of the free energy associated to the inhomogeneity of the density. $V(x)$ represents any external potential acting on the particles.

The density functional approximation [2] has been extensively used to describe equilibrium systems with smooth spatial inhomogeneities, like the liquid-vapor interfaces [4, 5], although it cannot describe systems with stronger modulations of the local density, like the layered structures of fluids near walls [6]. The use of this $\mathcal{F}[\rho]$ for dynamics requires to specify two other empirical elements, the mobility $\Gamma(\hat{\rho})$ which relates the density current to the local gradient of the thermodynamic chemical potential, and the random noise term $\xi(x,t)$ usually taken as a gaussian (uncorrelated) stochastic field which allows the systems go over thermodynamic barriers, e.g. in the process of nucleation of liquid drops from oversaturated vapors. Both the mobility as a function of the coarse grained density,
and the amplitude of the gaussian noise have to be taken as empirical mesoscopic parameters, which control the relaxation process of the coarse grained density, but without a direct connection to the molecular level. Therefore, and although equation (11) has been very useful to analyze different aspects of the phase transition dynamics [2], it cannot be used down to a molecular level of description, nor can it be extended to make use of the very accurate equilibrium density functional approximations [3] which go much beyond the simple functional form [2] in the description of equilibrium systems. Other approaches to define and use a DDF theory have used a more microscopic descriptions of the density distribution [2,10,11] but still keeping some coarse graining and a random noise term to overcome the energetic barriers of the coarse grained free-energy density functional.

A different DDF approach, which a clear connection between the molecular hamiltonian and a dynamic density functional equation may be obtained [12,13] from the hypothesis of purely relaxative Langevin dynamics at molecular level; i.e. if the positions of the particles $r_i(t)$ (for $i = 1, 2, ..., N$) evolve in time according to the equation

$$\frac{dr_i(t)}{dt} = -\Gamma_o \nabla_i \mathcal{U}(r_1, ..., r_N) + \xi_i,$$  (3)

where $\mathcal{U}(r_1, ..., r_N)$ is the potential energy which includes the interactions between the $N$ particles in the system, and also any external potential acting on them. The molecular mobility $\Gamma_o$ gives the (assumed constant) ratio between the mean velocity of the particles under a constant external force. When the theory is applied to colloidal particles moving in a fluid, the constant $\Gamma_o$ may be obtained by Stokes formula in terms of their radius and the viscosity of the fluid matrix. The second term in the bracket in (3), $\xi_i$ represents a random force acting on particle $i$, with may be interpreted as the zero-average stochastic effect of the fluid matrix molecules on the colloidal particles. This is taken as gaussian uncorrelated function for each particle, but contrary to the random noise $\xi(x, t)$ in (1), its amplitude is perfectly defined by Einstein relation, as twice the diffusion constant $D = \Gamma_o k_b T$. The natural reduced units for the problem are $k_b T = 1/\beta$ for the energy, molecular diameter $\sigma$ for distance, $\beta \sigma^2 / \Gamma_o$ for time, and hence $\Gamma_o k_b T / \sigma$ for the velocity.

Using the standard tools of stochastic analysis [14] and the equilibrium density functional formalism is possible to transform (3) into a Dynamic Density Functional (DDF) equation,

$$\frac{\partial \tilde{\rho}(x, t)}{\partial t} = \Gamma_o \nabla \left[ \tilde{\rho}(x, t) \nabla \left( \frac{\delta \mathcal{F}[\rho]}{\delta \tilde{\rho}(x, t)} + V(x, t) \right) \right],$$  (4)

within the following assumptions:

i) The density $\tilde{\rho}(x, t)$, following the dynamics of the DDF equation (4), has to be interpreted as the average of the instantaneous density $\hat{\rho}(x, t) = \sum_{i=1}^{N} \delta(x - r_i(t))$, over an statistical ensemble of realizations for the random noise $\xi(t)$ for the integration of the Langevin equation, from given initial conditions $\hat{\rho}(x, 0) = \rho_{inc}(x)$. The temperature $T$ is assumed constant and fixed by the bath.

ii) The correlations between the colloidal particles in the dynamical system, at any instant $t$, are assumed to be identical to those in the equilibrium systems, which would be obtained by applied the appropriate external field to the system so that its equilibrium density distribution, $\rho_{eq}(x)$ would be given precisely by the instantaneous value of $\hat{\rho}(x, t)$. These equilibrium correlations are those given by the density functional giving the intrinsic equilibrium Helmholtz free energy of the fluid, $\mathcal{F}[\rho]$. This equilibrium free energy functional, for classical fluids, has an explicit dependence from the ideal gas entropy contribution,

$$\mathcal{F}_{id}[\rho] = k_b T \int dx \rho(x) \left( \log(\rho(x)) - 1 \right)$$

and a contribution, $\Delta \mathcal{F}[\rho] = \mathcal{F}[\rho] - \mathcal{F}_{id}[\rho]$, from the particle interactions, which is known exactly only for a few systems; but approximations with increasing accuracy have been developed for others and give excellent results for the equilibrium properties in many cases.

Beside having a perfectly defined mobility factor, as the density $\tilde{\rho}(x, t)$ times the molecular mobility in the Langevin equation, instead of the generic function $\tilde{\Gamma}(\hat{\rho}(x, t))$ in (11); the main difference between that semi-empirical equation and the DDF equation (4) is the lack of any random noise term in later, which becomes a deterministic functional equation instead of the usual stochastic functional equation (11). The averaging over the random force term in the original Langevin equation (3), required to get $\hat{\rho}(x, t)$ with the interpretation $i)$ above, gives the classical ideal gas contribution, $\mathcal{F}_{id}[\rho]$ to $\mathcal{F}[\rho]$ in the functional derivative of (4), with the exact prefactor $k_b T$ from the precise amplitude of the random force $\xi(t)$; and any extra random noise term in (4) would produce the overestimation of the ideal gas entropy. The interactions between the particles, included in the derivative of $\mathcal{U}$ in (3), give the contribution $\Delta \mathcal{F}$, to the intrinsic free energy functional $\mathcal{F}[\rho]$ in (4), while the contribution to the potential energy from external fields appears explicitly as $V(x, t)$. We may expect that the accuracy of the approach to include the effects of the interactions would
II. STATIONARY SOLUTIONS OF THE DDF

The generic DDF equation (4) may be interpreted as the exact continuity equation between the density of particles, \( \rho(x, t) \) and their current \( j(x, t) \),

\[
\frac{\partial \rho(x, t)}{\partial t} = - \nabla j(x, t),
\]

(5)

together with the approximated DDF closure for the current,

\[
j(x, t) = - \Gamma_o \rho(x, t) \nabla \left( \frac{\delta F[\rho]}{\delta \rho(x, t)} + V(x, t) \right),
\]

(6)
in terms of the equilibrium free energy density functional.

In the presence of a shifting external potential \( V(x, t) = V(x - ct) \) we look for stationary solutions of the form \( \rho(x, t) = \rho(x - ct) \), and \( j(x, t) = j(x - ct) \), so that the continuity equation (4) implies that \( c \nabla \rho(x, t) = \nabla j(x, t) \), which for any problem in one dimension (1D) gives

\[
j(x, t) = c \rho(x, t) - \Delta,
\]

(7)

with an arbitrary integration constant \( \Delta \), which gives the difference between the actual current and that which would be produce by the rigid shift of the density profile at the same velocity \( c \) as the potential. This counter-drift term \( \Delta \) cannot be determined from the DDF equation (4), and it would be obtained only through the boundary conditions that we apply to the system.

Using now equations (6) and (7) we may obtain a closed functional equation for the stationary density \( \hat{\rho}(x, t) \equiv \hat{\rho}(\hat{x}) \), where we defined the variable \( \hat{x} = x - ct \), moving with the external potential \( V(x, t) \equiv V(\hat{x}) \);

\[
\hat{\rho}(\hat{x}) \nabla \left( \frac{\delta F[\hat{\rho}]}{\delta \hat{\rho}(\hat{x})} + V(\hat{x}) \right) + \frac{c}{\Gamma_o} \hat{\rho}(\hat{x}) = \frac{\Delta}{\Gamma_o},
\]

(8)

with the use of accurate forms of \( F[\rho] \), which include the non-local functional dependence in a much better way than (2).

In particular, we may think of colloidal particles, interacting as hard-core molecules of diameter \( \sigma \) and confined along a linear channel, as already explored experimentally (3), which may be theoretically described as hard-rods in one dimension, for which the exact equilibrium free energy density functional is known (15). The solution of (4) for hard-rods has already been studied for the relaxative dynamics under several static external potentials (12). An important conclusion of that work was that the use of the exact \( F[\rho] \) made unnecessary the inclusion of the random noise term in the DDF equation, since the exact free energy is always a convex functional, with only one minimum. The existence of activation barriers, between two different minima of the free energy, which should be overcome by the stochastic noise is an artifact of using an approximated form for \( F[\rho] \). Thus, very long relaxation times which in the solution of (4) would be interpreted as typical of systems with a high free energy barrier between two minima, are recovered from the deterministic equation (4) without any free energy barrier, just from the particle correlations described through the exact free energy \( F[\rho] \). In this context, if we take colloidal particles of size \( \sigma \approx 10^{-7}m \), with mobility \( \Gamma_o \) given by Stokes law in water, at room temperature, the natural unit for velocity is \( \Gamma_o k_B T/\sigma \approx 10^{-4}m/s \), in a reasonable range for potential barrier shifts in microfluidic devices.

In this paper we analyze the results of (4) for a different class of problems, hard-rods particles in time-dependent external potentials \( V(x, t) \). In particular we start with systems in which the external potential moves with constant rate \( c \) with respect to the static framework in which equation (3) applies. These problems would apply to colloidal particles moving along narrow channel under the force created by a moving electrical potential or optical twist; which may be used as a starting point for the design of more complex devices, like micropumps or turn-pikes. The plan of the paper is the following, in the next section we analyze the generic structure of the solutions of the DDF equation (4) for the stationary states with density \( \hat{\rho}(x, t) = \hat{\rho}(x - ct) \) moving along the external potential \( V(x, t) = V(x - ct) \). In section 3 we get an explicit solution for the ideal gas case, when the interaction term \( F[\rho] \) may neglected; this solution helps to give a qualitative classification of the possible behaviour, in terms of the barriers of the external potential and the rate of displacement. In section 4 we explore, numerically the solutions of the DDF when the packing effects are important and described by the exact density functional at equilibrium for hard rods. We end with a general discussion on the observed qualitative behaviour and generic trend in the dependence with the physical parameters: the height and shape of the external potential barriers, the shift rate of these barriers with respect to the static framework for the relaxative dynamics and the effects of molecular packing.
In 1D problems this expression may be formally integrated to give

\[
\frac{\delta \mathcal{F}[^{\hat{\rho}}]}{\delta ^{\hat{\rho}}(\hat{x})} + V(\hat{x}) + \frac{c}{\Gamma_o} (\hat{x} - \hat{x}_o) - \frac{\Delta}{\Gamma_o} \int_{\hat{x}_o}^{\hat{x}} \frac{d\hat{x}'}{\rho(\hat{x}')} = \mu, \tag{9}
\]

where \( \mu \) is the integration constant, linked to the arbitrary value of \( \hat{x}_o \) in the lower limit of the integral.

In the case of static external potentials, \( c = 0 \), the stationary density becomes the equilibrium density, and current \( j \) has to vanish everywhere, so that the counter-drift constant \( \Delta \) in (7) vanishes, and (11) becomes the usual Euler-Lagrange equation for the equilibrium density, \( \rho(x) = \bar{\rho}(\hat{x}) \), with the integration constant \( \mu \) as the equilibrium chemical potential. Thus, in the dynamic case \( c \neq 0 \) the integration constant \( \mu \) in (9) will still be used to control the total number of particles in the system, since for a given external potential \( V(\hat{x}) \) and drifting rate \( c \), that functional equation should have different solutions representing dynamic systems with different mean densities. The presence of a second integration constant \( \Delta \) in (9) is characteristics of dynamic systems, as it has to vanish in the limit \( c = 0 \). To determine the value of \( \Delta \) we may consider a further symmetry assuming that the drifting potential \( \hat{V}(\hat{x}) \) and hence the stationary density \( \bar{\rho}(\hat{x}) \) are periodic functions with spacial period \( L \) (which imply a time period \( T = L/c \)). In that case, comparing the values of (9) for \( \hat{x} \) and \( \hat{x} + L \) we get

\[
\frac{c}{\Gamma_o} L = \frac{\Delta}{\Gamma_o} \int_{\hat{x}}^{\hat{x}+L} \frac{d\hat{x}'}{\bar{\rho}(\hat{x}')},
\]

for any value of \( \hat{x} \), which implies

\[
\Delta = \frac{c}{(\bar{\rho}^{-1})},
\]

and the stationary current is

\[
j(\hat{x}) = c \left( \bar{\rho}(\hat{x}) - \frac{1}{(\bar{\rho}^{-1})} \right), \tag{12}
\]

where the brackets represent the spacial average over a full period of the inverse local density. The last expression makes clear that for static periodic potential, \( c = 0 \), the only stationary solution of (11) is the equilibrium state, with the current vanishing everywhere.

The stationary density distributions and currents created by any periodic external potentials moving with a constant rate \( c \) may now be obtained from the solutions of (9) and (11), with the remaining integration constant \( \mu \) playing the same role as in the Euler-Lagrange equation, to control the mean density of the system. Before including an explicit form for the interaction between the particles, i.e. for the term \( \Delta \mathcal{F}[\rho] \) in free energy density functional, we may still get some generic analysis for particular limits. The case of a shifting external potential limited to a finite region of infinite barriers where \( \rho(x) = 0 \) (as explored in section 2a below) we get \( \Delta = c \rho_o \), determined by the density \( \rho_o(\mu) \) of the uniform system at chemical potential \( \mu \), and equation (9) may be written as:

\[
\frac{\delta \mathcal{F}[\rho]}{\delta \rho(\hat{x})} + V(\hat{x}) + \frac{c}{\Gamma_o} \int_{-\infty}^{\hat{x}} d\hat{x}' \left( 1 - \frac{\rho_o}{\bar{\rho}(\hat{x}')} \right) = \mu. \tag{13}
\]

The current vanishes away from the region crossed by the external potential, and the integrated flow along the system becomes

\[
\int_{-\infty}^{\infty} d\hat{x} j(\hat{x}) = c \int_{-\infty}^{\infty} d\hat{x} (\bar{\rho}(\hat{x}) - \rho_o) = c(N - N_o), \tag{14}
\]

i.e. \( c \) times the excess of particles generated by the shifting external potential, from the solution of (13). This expression is just an integrated form of the continuity equation since the total transport of molecules is precisely the steady shift of the stationary density perturbation \( \bar{\rho}(\hat{x}) - \rho_o \).

A. Complete drift limit

Let us consider a moving external potential which includes a periodic series of infinite barriers, where the density \( \bar{\rho}(\hat{x}) \) which solves (9) has to become zero. Then the average of the inverse density becomes infinite, whatever values
\(\hat{\rho}(\hat{x})\) takes outside the barrier. The counter-drift term \(\Delta\) vanishes and the current becomes equal to the density times the velocity of the external potential \(c\). This is a regime of complete drift, where all the fluid particles trapped between two consecutive barriers of the external potential have to follow the movement of these barriers, so that \(j(\hat{x}) = c \, \hat{\rho}(\hat{x})\). Moreover, the functional equation (11) for the density distribution in that regime becomes equivalent to the equilibrium Euler-Lagrange equation

\[
\frac{\delta F[\rho]}{\delta \hat{\rho}(\hat{x})} + V_k(\hat{x}) = \mu,
\]

with a 'kinetic' external potential \(V_k(\hat{x}) = V(\hat{x}) + c/\Gamma_0 \, \hat{x}\), i.e. with the true external potential plus a linear term proportional to \(c\). In order to simplify the notation, we use a reduced drift rate with inverse length units, as \(\hat{c} = \beta c/\Gamma_0\).

The stationary density profile follows a variational principle equivalent to that of the equilibrium density functional formalism; i.e. \(\hat{\rho}(x, t)\), described in terms of the drifted variable \(\hat{x} = x - ct\), is such that it minimizes the total 'kinetic' grand potential energy of the system

\[
\Omega[\rho] = F[\rho] + \int dx \rho(x)(V_k(x) - \mu).
\]

The constant slope \(c/\Gamma_0\) of the kinetic contribution to \(V_k(x)\) has high (but not infinite) barriers, we may expect that the stationary profiles \(\bar{\rho}(\hat{x})\) would still be very close to the solutions of the equivalent equilibrium equation (13), since everywhere outside the barriers \(\bar{\rho}(\hat{x}) \gg (\bar{\rho}^{-1})^{-1}\) and the contribution from the integral in (10) would be nearly constant (and hence transferable to \(\mu\)). However, the contribution of that integral over a full period has to exactly cancel the contribution of the linear term \(\hat{c} \, \hat{x}\), to get a periodic equation, which is achieved by the integral giving a descending staircase shape, with smoothed steps at the barriers, and nearly planar plateau between them. Thus, with the appropriate choices of \(c\) in each case, the solutions of (14) over a single period, would be similar to those of the DDF equation (9) everywhere except in the low density region at the high potential barriers, where the true stationary profile has to recover the periodicity. Only in the strict limit of infinite barriers the equivalent equation (15) may be regarded as exact, when used for the interval between point at consecutive barriers where \(\hat{\rho}(\hat{x}) = 0\), as the role the integral is only to provide a constant shift of the chemical potential between each period.

Moreover, even if the potential barriers of \(V(\hat{x})\) are apparently very high (on the \(k_B T\) scale) the quasi-complete drift regime described above may be frustrated when the drift rate \(c\) becomes too high, since the energy difference between the maximum and the minimum of \(V_k(\hat{x})\) diminishes with \(c\), the effective barriers of the kinetic potential may become comparable with \(k_B T\), and the counter-drift current grow. Thus, we expect a low velocity regime, in which the velocity of the particles \(v = j(\hat{x})/\bar{\rho}(\hat{x})\) is exactly \(c\), and a saturation range in which further increase of \(c\) does not produce the increase of \(v\).

**B. Weak external potentials**

We consider now the opposite limit when the external potential \(V(\hat{x})\) is very weak everywhere, so that it may be treated as a small perturbation over an otherwise uniform fluid. We may then expand the density around its mean value, \(\bar{\rho}(\hat{x}) = \rho_o + \delta \bar{\rho}(\hat{x})\), with \(\rho_o = \langle \bar{\rho}(\hat{x}) \rangle\), so that \(\langle 1/\bar{\rho}(\hat{x}) \rangle = \rho_o^{-1} + \langle \delta \bar{\rho}(\hat{x})^2 \rangle/\rho_o^2 + \ldots\); the current becomes now

\[
j(\hat{x}) = c \left( \delta \bar{\rho}(\hat{x}) + \frac{\langle \delta \bar{\rho}(\hat{x})^2 \rangle}{\rho_o} + \mathcal{O}^3(\delta \bar{\rho}) \right),
\]

and its average is \(\langle j \rangle = c \langle \delta \bar{\rho}(\hat{x})^2 \rangle/\rho_o + \mathcal{O}^3(\delta \bar{\rho})\). Thus, a shifting weak external potential \(V(x - ct) = V(\hat{x})\) cannot produce the drift of the bulk fluid, the local current is proportional to \(c\) times the perturbation over the homogeneous fluid, with regions of positive and negative sign, and its average goes only as the density perturbation squared; i.e. the propagating waves in the density, \(\hat{\rho}(x - ct) = \hat{\rho}(\hat{x})\), produce a very small mean propagation of particles.

So far in this subsection, we have only used the continuity equation (11) and the requirement of having a periodic stationary density (10) of the DDF equation, to get the current in terms of the density perturbation. To get a relationship between the weak external potential, \(V(\hat{x})\), and the density perturbation \(\delta \hat{\rho}(\hat{x})\) we may use the expansion of the DDF equation (9) around \(\hat{\rho}(\hat{x}) = \rho_o\), as a generalization of the equilibrium linear response theory (1) to the
dynamic case. In terms of the Fourier transform of the density perturbation $\delta \tilde{\rho}(q)$ and the external potential $V(q)$, the linear term of (4) gives,

$$\delta \tilde{\rho}(q) = -\rho_0 \frac{\beta V(q)}{[S(q, \rho_0)]^{-1} + i \tilde{c}/q},$$

where $S(q, \rho_0)$ is the equilibrium structure factor of the homogeneous system, which is proportional to the response function of the system to external field, as given by the second functional derivative of $F[\rho]$, by the standard DF analysis\[^1\][^2]. In the long wavelength limit it is given by the isothermal compressibility, $S(0, \rho_0) = kT \rho_0 \chi(T, \rho_0)$ while $S(q, \rho_0) = 1$ in the short wave limit, $q \to \infty$. The second term in the denominator of (4) comes from the drift and counter-drift terms in (4), which give and imaginary part to the kinetic response function.

If we consider a weak external potential with the form of an harmonic propagating wave, $V(x - c t) = V_q \cos(q \hat{x})$, the density would be $\tilde{\rho}(x - c t) = \rho_0 - \rho_0 \cos(q \hat{x} - \theta)$, with amplitude and phase shift,

$$\rho_q = -\rho_0 \frac{\beta V_q}{[S(q, \rho_0)]^{-2} + (\tilde{c}/q)^2}^{1/2} \quad \text{and} \quad \theta = \tan^{-1} \left( \frac{\tilde{c} S(q, \rho_0)}{q} \right).$$

For low drift rates the density profile will be similar to that created by a static external potential, with the maximum density at the minima of $V(\hat{x})$ and vice versa. When the external potential moves fast enough the effect of the imaginary part in the denominator of (16) puts the density perturbation out of phase with the external potential, and the maximum of $\tilde{\rho}(\hat{x})$ moves toward the region with maximum external force, with $\theta \to \pi/2$, but the amplitude decreases as $\rho_q \sim 1/c$ for large $c$.

The mean velocity of the particles, in same reduced units as $\tilde{c}$, for any weak periodic potential may be written as a Fourier sum with the quadratic contributions of each Fourier component of the potential:

$$\bar{v} = \frac{\beta \langle j \rangle}{\Gamma_0 \rho_0} = \tilde{c} \sum_q \frac{[\beta V(q)]^2}{[S(q, \rho_0)]^{-2} + (\tilde{c}/q)^2}.$$  

The contribution of the short wavelength components, with $\tilde{c} S(q, \rho_0) \ll q$, is similar to the quasi-static limit ($\theta \approx 0$), with $\bar{v}$ linear in $c$ and quadratic with the static response $S(q, \rho_0) V(q)$; in the opposite limit, $\tilde{c} S(q, \rho_0) \gg q$, the kinetic contribution dominates ($\theta \approx \pi/2$) and the contribution to $\bar{v}$ is proportional to $(V(q)q)^2/c$, i.e. decays with $c$, is independent of static structure factor and goes proportional to the mean squared force $\langle V'(x) \rangle^2$, rather than to the mean squared potential. For each Fourier component of $V(x)$, the threshold between the linear growth, $\tilde{v} \sim \tilde{c}$, for low $\tilde{c}$ and the decay, $\tilde{v} \sim 1/\tilde{c}$, for large $\tilde{c}$, would give the optimum shift rate $\tilde{c}_{\text{max}} \sim q/S(q, \rho_0)$ to get the maximum mean velocity. In the ideal gas limit, $S(q, \rho_0) = 1$, this optimum value is $\tilde{c} = q$, becoming very small in the long wavelength limit. For correlated systems, there would be a non monotonic dependence of the maximum $\tilde{v}$ with $c$, depending on $q$ due to the static structure factor.

### III. SOLUTION OF THE DDF EQUATION FOR THE IDEAL GAS

In the previous section we have obtained some generic limiting behaviour for the solutions of the DDF equation. We turn now to explore the general solution of (4), first in absence of particle interactions, and in the following section including the effects of molecular packing as one dimensional hard rods.

The ideal gas case corresponds to take $\Delta F[\rho] = 0$ and it should be the exact low density limit of any fluid system. Moreover, the assumptions to get (4) from (3) become irrelevant, and the DDF equation may be consider as an exact Fokker-Planck equation for the density distribution. The equation (4) becomes

$$\nabla \tilde{\rho}(\hat{x}) + \tilde{\rho}(\hat{x}) (\beta \nabla V(\hat{x}) + \tilde{c}) = \frac{\beta \Delta}{V_0}.$$  

When $\Delta$ is zero (i.e. in the static limit, $c = 0$, or in the complete drift limit described above), the homogeneous linear differential equation is directly solved to give $\tilde{\rho}(\hat{x}) = A \exp(-\beta V_k(\hat{x}))$ in terms of the Boltzmann factor of the kinetic potential $\beta V_k(\hat{x}) = \beta V(\hat{x}) + \tilde{c} \hat{x}$. The arbitrary constant $A$ is the activity, playing the same role as the chemical potential $\mu$ in (4) to control the total number of particles.

The general solution of the inhomogeneous equation with $\Delta \neq 0$ is obtained, by the usual Green function method. For periodic external potentials, with period $L$, it has the generic form,

$$\tilde{\rho}(\hat{x}) = A \exp(-\beta V_k(\hat{x})) \left( 1 + \frac{e^{\beta L} - 1}{L} \int_0^L dy e^{\beta V_k(y)} \right),$$  

For periodic external potentials, with period $L$, it has the generic form,

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(19)
which may be evaluated in terms of single integrals of the inverse Boltzmann factor of $V_\alpha(x)$. The counter-drift term $\Delta$, is $\Gamma_\alpha A/\beta$ times the prefactor of the integral, inside the bracket.

The average velocity of the particles, defined as the ratio between the mean current $\langle j(\hat{x}) \rangle$ and the mean density $\langle \rho(\hat{x}) \rangle$, and in the same reduced units as $\bar{v}$ is

$$\bar{v} \equiv \frac{\beta \langle j(\hat{x}) \rangle}{\Gamma_\alpha \langle \rho(\hat{x}) \rangle} = \bar{c} \frac{\xi(\bar{c})}{1 + \xi(\bar{c})},$$

with the dimensionless auxiliary function

$$\xi(\bar{c}) = \frac{\bar{c}}{L} \int_0^L dx e^{-\bar{c}x} \int_0^x dy \left( e^{\beta(V(y) - V(x))} - 1 \right) e^{\bar{c}y}$$

$$+ \frac{c}{L} e^{-\bar{c}L} \left( \int_0^L dx e^{-\beta V(x) - \bar{c}x} \right) \left( \int_0^L dy e^{\beta V(y) + \bar{c}y} \right) - \frac{1 - e^{-\bar{c}L}}{\bar{c}}.$$  \hspace{1cm} (21)

It is instructive to analyze the structure of this equation for potential barrier $V(x)$ which is zero outside an interval, taken as $0 \leq x \leq a$, much shorter than the periodic length of the system $L$. When the maximum height of the potential barrier, $\beta V(x)$, is well above the maximum kinetic term $\bar{c}L$, the results of (19,20) is always within the quasi-complete drift regime described above, with $\Delta \ll c/\rho$ and $\bar{v} \approx \bar{c}$. For larger drifting rates, when $\bar{c}L$ becomes much larger than the maximum of $\beta V(x)$, the main contribution to $\xi(\bar{c})$ comes always from the first term in the right hand side of (21), with a delicate balance between the fast growing exponentials in the integrals.

The simplest case of a square barrier with $V(x) = V_o$ in an interval of width $a$ and $V(x) = 0$ outside, may be solved analytically to give $\xi(\bar{c})$ and $\bar{v}$. For large drifting rates, $\bar{c} \min[a, (L - a)] \gg 1$, we get

$$\bar{v} \approx \bar{c} \frac{e^{\beta V_o} - 1}{\bar{c}L + e^{\beta V_o} - 1}.$$  \hspace{1cm} (22)

Therefore, a square potential barrier of height $V_o$ would be enough to produce the complete shift of the ideal particles up to (reduced) drifting rates $\bar{c}$ well below $(e^{\beta V_o} - 1)/L$. For $\bar{c}$ beyond this limit the mean velocity would saturate to a constant value $\bar{v} \approx e^{\beta V_o}/L$ for $V_o \gg 1$ and $\bar{v} \approx \beta V_o/L$ for $V_o \ll 1$. In Figure 1 we compare the values of $\bar{v}$ for square barriers, parabolic barriers, $V(\hat{x}) = V_o(1 - (2\hat{x}/w)^2)$ for $-w/2 \leq \hat{x} \leq w/2$, and gaussian barriers $V(\hat{x}) = V_o \exp[-\hat{x}^2/(2\alpha^2)]$. At low $\bar{c}$ the three barriers give similar results, with $\bar{v}$ proportional to $\bar{c}$ both for high barriers (Fig. 1(a)) and low barriers (Fig. 1(b)). The fortes case corresponds to the complete drift regime $\bar{v} = \bar{c}$, predicted in section 2(a) for large enough values of $\beta V_o$; while the second corresponds to the linear response result $\bar{v} \sim \bar{c} (\beta V_o)^2/L$ predicted in section 2(b) for low $\bar{c}$. At higher values of the shifting rate $\bar{c}$, the results of the square barrier differ qualitatively from those of the parabolic and gaussian barriers. The two later reach a maximum value of the mean velocity, $\bar{v}_{\text{max}} = \bar{c} (\bar{v}_{\text{max}})^2/L$, and then decay as $\bar{v} \sim 1/\bar{c}$, while the square barrier produce a monotonous increase of $\bar{v}$ up to a constant value for large $\bar{c}$. The comparison of the results with different barrier shapes and parameters shows that the most relevant aspect of $V(\hat{x})$ is the maximum slope, rather than the barrier width or the barrier height. Thus, reducing the width of a parabolic barrier, while keeping unchanged its maximum value $V_o$, increases rather than decreases the maximum value of the mean velocity, since it increases the maximum force acting on the particles. In this sense the square barrier model should be consider unphysical, since the infinite force acting at the barrier borders creates the saturation of $\bar{v}$ at large $\bar{c}$. Choosing the parameters of the parabolic and gaussian barriers to have similar maximum slopes, produces very similar results for $\bar{v}(\bar{c})$, as shown in Figure 1 for the empirical choice of $w = 5.5a$ and the same barriers height, $V_o$. This robustness of the results to the particular form of $V(\hat{x})$, as far as it does nor include unrealistic discontinuities, might help to eventual comparisons of the theory with experimental results.

The weak potential limit, integrated over the Fourier components of the different barriers $V(\hat{x})$, may be compared with the exact results obtained from (17,21). The qualitative difference between the sharp square barrier and the gaussian or parabolic models is a consequence of the slow, $V(q) \sim 1/q$, decay of the external potential Fourier components for the discontinuous square barrier; while the first derivative discontinuity (i.e. $V(q) \sim 1/q^2$) for the parabolic barrier is already weak enough not to change the qualitative dependence of $\bar{v}(\bar{c})$ with respect to the smooth gaussian barrier. For the later, and assuming that the distance $L$ between barriers is large compared with the barrier width $\alpha$, we may perform the sum over Fourier components in (17) as an integral to get an analytic form for the mean velocity within the linear response approximation:

$$\bar{v}(\bar{c}) = \frac{(\beta V_o)^2}{L} \alpha \bar{c} (\sqrt{\pi} - \pi \alpha \bar{c} e^{\alpha \bar{c}} \text{Erf}c[\alpha \bar{c}]).$$
in terms of the complementary error function which leads to 

\[ \bar{v}(c) = \frac{\sqrt{\pi} (\beta V_o)^2}{L} \left( \frac{1}{2\alpha c} - \frac{3}{4(\alpha c)^2} + \ldots \right), \]

for large \( c \) and

\[ \bar{v}(c) = \frac{\sqrt{\pi} (\beta V_o)^2}{L} \left( \alpha c - \sqrt{\pi}(\alpha c)^2 + 3(\alpha c)^3 + \ldots \right), \]

low \( c \); with a maximum \( \bar{v}_{\text{max}} = 0.4346(\beta V_o)^2/L \) at \( c_{\text{max}} = 0.82132/\alpha \).

The results in the inset of Figure 1(b), shown that for \( \beta V_o = 1 \) the linear response approximation for \( \bar{v}(c) \) is very similar to the exact result. In general, we may expect such good agreement for gaussian barriers up to barrier height \( \beta V_o \approx (\alpha/L)^{-1/2} \), beyond this limit the linear response for low drifting rates would predict unphysical values of \( \bar{v}(c) > \bar{c} \), beyond the complete drift limit; which would indicate the breakdown of such linear response analysis since would predict negative densities at the potential barrier. However, for large drifting rates, when \( \bar{v} \sim 1/\bar{c} \), the predictions of the linear response approximation are quite good even for very large values of \( \beta V_o \), as shown in the inset of Figure 1(a). The optimum value \( \bar{c} = \bar{c}_{\text{max}} \) to get the maximum \( \bar{v} \) would be independent of \( \beta V_o \) in the linear response approach, while the exact result gives \( \bar{c}_{\text{max}} \) growing roughly linearly with \( \beta V_o \), as the indicated by the crossover between the regimes \( \bar{v} \approx \bar{c} \) and \( \bar{v} \sim (\beta V_o)^2/(L\alpha \bar{c}) \), for low and high values of \( \bar{c} \), respectively. However, the maximum value of \( \bar{v} \) from the exact result remains rather close to the predicted by the linear response, even at barriers as high as \( \beta V_o = 20 \), despite the different predictions for the value \( \bar{c}_{\text{max}} \) at which that \( \bar{v}_{\text{max}} \) is achieved. This behaviour is clearly shown in Figure 2, with logarithmic scales for both \( \beta V_o, \bar{v}_{\text{max}}, \bar{c}_{\text{max}} \) and the slope of \( \bar{v}(\bar{c}) \) at \( \bar{c} = 0 \), and it may be explained as the results of cancellations of two different effects: a tendency of the exact \( \bar{v}(c) \) to grow faster with \( \beta V_o \) than the prediction of the linear response, for low barriers, and the tendency of \( \bar{c}_{\text{max}} \) to grow linearly with \( \beta V_o \) at high barriers, leading to \( \bar{v}_{\text{max}} \sim \bar{c}_{\text{max}} \sim \beta V_o/\sqrt{\alpha L} \) for very large \( \beta V_o \). Similar results, with different analytic forms for \( \bar{v}(c) \) may be obtained for the parabolic barriers or other parametric forms of the external potential.

In Figure 3 we present the density profiles and the steady currents for a smooth gaussian barrier of width \( \alpha = 0.707\sigma \), space period \( L = 30\sigma \), and two set of the barrier heights and the shifting rates. For \( \beta V_o = 1 \) the results of the linear response theory gives a reasonably accurate description of the exact density profiles for the slowest shifting rate, \( \bar{c} = 1\sigma^{-1} \) in Fig. 3(a) and a very accurate results at \( \bar{c} = 10\sigma^{-1} \) in Fig. 3(b). The shape of \( \bar{\rho}(\bar{x}) \), relative to the potential barrier (shown by the dot-filled gaussians) reflects the difference between the quasi-static behavior for \( \bar{c} = 1\sigma^{-1} \), and the strong effects of the kinetic effective potential \( V_k(\bar{x}) = V(\bar{x}) + \bar{c}\bar{x} \) at \( \bar{c} = 10\sigma^{-1} \), which pushes the maximum of \( \bar{\rho}(\bar{x}) \) toward the maximum of \( V(\bar{x}) \). The current, which may be represented by the same line with the appropriate changes in the vertical axis to get \( \bar{j} \) has a positive contribution in front of the barrier partially cancel by the negative contribution across the barrier.

For higher barriers, \( \beta V_o = 5 \), and low drift rate Figures 3(c), the system becomes close to the complete drift regime (\( \Delta \to 0 \)), with a strong accumulation of particles in front of the advancing barrier, which decays exponentially \( \bar{\rho}(\bar{x}) \sim \exp(-\bar{c}\bar{x}) \), so that for long distances \( L \) between the periodic barriers the density at the receding side is extremely low compared with the density at the advancing side. The linear response results are quite out of the mark, predicting unphysical negative density at the barrier. At higher values of \( \bar{c} \) Figures 3(d) the accumulation of particles at the barrier front is so large that the barrier becomes ineffective to keep the complete drift regime, the local chemical potential, \( \mu(\bar{\rho}) = \beta^{-1}\log(\bar{\rho}) \) becomes comparable to \( V_o \) and the particles jump over the barrier. The final effect is that the counter-drift \( \Delta \) grows and the total effective potential in \( \bar{\bar{\rho}} \) becomes much weaker that the external potential \( V(\bar{x}) \). In this way, the current decreases and it becomes closer to the linear response result, with the limit of no density perturbation or steady current for very rapid displacements of the barrier (i.e. \( \bar{c} \to \infty \)), for any smooth shape of the barrier.

IV. STEADY STATE FOR HARD-ROD PARTICLES

In the solution of the DDF equations for the ideal gas case the mean density of the system is irrelevant for the mean velocity \( \bar{v} \), as both the density \( \rho(\bar{x}) \) and the current \( j(\bar{x}) \) have the common factor \( A \) to include the constrain of fixed number of particles. In this section we explore the effects of molecular packing and correlations on the stationary currents created by the shifting external potentials \( V(x - ct) = V(\bar{x}) \). For particles moving along a linear channel, the choice of hard-rods (with length \( \alpha \)) to model the interactions allows the use of the exact DF for the equilibrium free energy \( \bar{\delta} \). The functional derivative of the equilibrium free energy in \( \bar{\delta} \) is

\[
\frac{\delta \beta \mathcal{F}[\bar{\rho}]}{\delta \bar{\rho}(x)} = \log \left( \frac{\rho(x)}{1 - \eta(x)} \right) + \int_{x-\sigma}^x dx' \frac{\rho(x')}{1 - \eta(x')},
\]
with the local packing fraction \( \eta(x) \) defined as
\[
\eta(x) = \int_x^{x+\sigma} d x' \rho(x').
\]  

The equation for the stationary density becomes now an integral equation, to be solved with periodic boundary conditions and the self-consistency requirement. The total number of particles in a period \( N = L(\rho(\hat{x})) \), should be controlled by the chemical potential \( \mu \), with non-trivial dependence of \( \rho(\hat{x}) \), \( \Delta \) and \( j(\hat{x}) \). Alternatively, we may solve dynamic equation \( \frac{\partial \rho(x,t)}{\partial t} = j(x,t) \), from a reasonable guess for the initial density distribution at \( t = 0 \), and integrate in time until the stationary limit \( \rho(x,t) = \rho(x - c \cdot t) \) is achieved. In that case, the number of particles is set with the initial guess (since equation (4) keeps constant \( N \)). We have checked that both procedures lead to the same stationary results, and the relative computational efficiency would depend on the characteristics of the external potential, and the choice of the initial profile.

For weak perturbations (weak external potentials or very large drifting rates) the linear response analysis, has to be applied with the hard-rods structure factor,
\[
S(x, \rho) = \left[ 1 + 2 \frac{\eta}{1-\eta} \frac{\sin(q\sigma)}{q\sigma} + 2 \left( \frac{\eta}{1-\eta} \right)^2 \frac{1-\cos(q\sigma)}{(q\sigma)^2} \right]^{-1},
\]
with the packing fraction \( \eta = \sigma \rho \). Near the complete packing limit \( \eta \to 1 \), the effect of a shifting oscillatory external potential \( V(x,t) = V_0 \cos(q(x - c \cdot t)) \), would depend strongly on the wave vector \( q\sigma \); as shown in Figure 4(a) for constant value of \( V_0 \). The system is close to the complete drift limit, with very low density at the potential barrier. On both sides of the barrier here are strong oscillatory structures, around a nearly constant density. The amplitude of the oscillations is larger at the advancing side than at the receding side of the potential, but this may be understood in terms of the equilibrium density profiles for the effective kinetic potential \( V_k(\hat{x}) = V(\hat{x}) + \beta^{-1} \tilde{c} \hat{x} \), which makes sharper the effective wall at one side and smoother at the opposite side.

Increasing \( \tilde{c} \), in Figures 5(b-c), produces an apparently weak effect on the density at the outside the barrier. For comparison we include the ideal gas results, for the same mean density and barrier \( \beta V_0 = \tilde{c} \), chosen to be equivalent to the effective barrier in the hard rod, with the recipe describe below,which have high peak densities at the advancing front with maximum values of \( \hat{\rho}_{\text{max}} = 3.3 \sigma^{-1} \) for \( \tilde{c} = 1 \sigma^{-1} \) and \( \hat{\rho}_{\text{max}} = 7.5 \sigma^{-1} \) for \( \tilde{c} = 1.7 \sigma^{-1} \), with exponential decays toward a much lower on the receding edge of the next barrier. The low compressibility of the dense hard-rod fluid strongly reduces such accumulation of particles in front of the barrier and their sensibility to the value of \( \tilde{c} \); the main change between the results for hard-rod in Figures 5(a) and 5(b) is in the increase of the minimum density, near the barrier maximum, which indicates that the local chemical potential may get easy over \( V_0 \) with very weak changes in the local density, as the compressibility of the system \( (\beta \rho)^{-1} d\rho/d\mu = (1-\eta)^2 \) produces strong changes in \( \mu \) with small changes in \( \eta \), and the particles start jumping over the barrier without building up the high local densities of the ideal gas. Only for the largest value of the shifting rate, \( \tilde{c} = 10 \sigma^{-1} \) in Fig. 5(d), we start to see a clear accumulation of particles at the advancing front, but still being a small fraction of the total number of particles in the system. The oscillatory structures become damped, with respect to their shapes for lower \( \tilde{c} \) and this effect is stronger on the advancing than on the receding front, as a signature that the effect of term proportional to \( \Delta \) in the effective potential of the Euler-Lagrange equation is getting over linear kinetic contribution \( \tilde{c} \hat{x} \). The linear response results, presented as the dotted lines in Figures 5, are quite different from the full DDF calculations, as could be expected for such a high barrier, except for the largest value of \( \tilde{c} = 10 \sigma^{-1} \). However, even in that case the linear response fails to reproduce the layering structure.

Finally, we present in Figure 6, the mean velocities produced by gaussian barriers, as functions of the shifting rate, in system of different mean density. The results for the ideal gas with a barrier height of \( \beta V_0 = \tilde{c} \) are compared
with those for mean densities of \( \rho_o = N/L = 0.2, 0.4, 0.6 \) and \( 0.8\sigma^{-1} \), with barrier heights adjusted to give the same effective barrier, \( V_o - \Delta \mu(\rho_o) \), in terms of the excess chemical potential over the ideal gas, at each mean density. This semi-empirical recipe is effective to give similar values of \( \bar{v} \) for different \( \rho_o \), while keeping the same absolute barrier height produces a rapid decrease of \( \bar{v} \) with the mean density. In all the cases the qualitative shape of \( \bar{v}(\bar{c}) \) is similar to that of the ideal gas, with a linear growth, \( \bar{v} \approx \bar{c} \) in the quasi-complete drift regime, followed by a maximum mean velocity and a decrease \( \bar{v} \sim 1/\bar{c} \) at large shifting rates. The particular values of \( \bar{v}_{\text{max}} \) are tied to our empirical choice of the values of \( \beta V_o \) at each mean density, but the optimal rate \( \bar{c}_{\text{max}} \) at which it is achieved, and the generic shape of the curve are roughly independent of the barrier height. In this respect, the main effect of the hard-core interactions seems to be the broadening of the maxima which becomes much less sensitive to the value of \( \bar{c} \) than for ideal gas systems. For very large shifting rates the linear response analysis becomes valid again, as for ideal gas systems, and it becomes independent of \( S(q, \rho) \) and hence equal to that for the ideal gas. This may be interpreted, in physical terms, as the result of a very rapid series of of pushing and pulling forces, acting on the particles as the potential barriers go over them, with a time period much shorter than the typical collision time between particles; so that the later become irrelevant.

V. CONCLUSIONS

We have applied the dynamic density functional (DDF) theory to study the relaxative dynamic of particles moving along one-dimensional channels, under the action of external potential shifting at constant rate. Our results could be of interest for systems of colloidal particles, with typical sizes of \( \sigma \sim 10^{-7}m \), following brownian motion on water at room temperature. In that case the relevant values of the shifting rates of the external potential would be around \( 10^{-4}m/s \), which could be achieved by the the dielectric force created on the colloidal particles by a moving laser beam or the force created on surface charged colloidal particles by a moving electric potential. Although strongly simplified with respect to the complexities of real micro-fluidic devices, we may hope that the model and its theoretical treatment contains the essential features of real systems. In principle the model could be studied directly from the stochastic equation for the brownian motion of the particles, without relaying on the equilibrium density functional formalism and its approximate application to the description of systems out of equilibrium. For the ideal gas case the results should be identical, but the DDF theory allows a direct extension to interacting systems, which we have considered here as pure repulsive interactions treating the colloidal particles in a narrow channel as hard rods particles in one dimension.

Under the effects of a periodic external potential shifted at constant rate \( c \), the systems would achieve a steady state, with density distributions and local currents following the shift of the external potential. These are the only problems analyzed in this paper, leaving for future works the analysis of the transient evolutions to achieve such steady state from arbitrary initial conditions. The steady states are particularly appropriate to be studied within the DDF, since the structure of the relevant equations becomes similar to that of the usual density functional formalism for the equilibrium properties. Thus, the generic equation \( \Theta \) is equivalent to an Euler-Lagrange equation for the equilibrium density distribution but including two extra terms as external potentials. The first one, which we have called the kinetic contribution, is just a linear potential, proportional to the shifting rate \( c \) which breaks the symmetry between the advancing and the receding front of a shifting potential barrier. The second contribution to the effective external potential is a self-consistent term which depends on the integral of the inverse density distribution over the system, and it is proportional to the second integration constant, \( \Delta \), which (together with the chemical potential \( \mu \)) is required to get the general solution of the integro-differential Euler-Lagrange equation for the problem. For external potentials made of periodic barriers, we have given an intuitive interpretation to \( \Delta \) as the counter-drift current, associated to those particles which jump over the barriers and so reduce the mean current in the system, with respect to the complete-drift regime in which the full density is shifted at the same rate as the barriers, and the density distribution may be obtained as the equilibrium profiles for the fluid in presence of the external plus kinetic potentials. This regime would appear, and hence the integration constant \( \Delta \) would vanish, whenever the potential barriers are large enough, compared with the kinetic effective potential. In the opposite limit, for very weak shifting external potentials, we have extended to the DDF the usual linear response analysis of the equilibrium density functional formalism. The range of application for such analysis is in fact enlarged with respect to the equilibrium case, since strong external potentials moving at very large rate would produce much weaker effect than the same external potentials at rest. In that limit, opposite to the complete-drift, the self-consistent contribution to the effective potentials cancels out most of the linear kinetic term and a good part of the external potential, so that the density distribution is much smoother as a function of the position that the static equilibrium density profile. Only for discontinuous external potentials, like square barriers, there would be a remnant effect of the shifting external potential in the limit of \( c \to \infty \), and it should be considered as an artifact of the infinite forces acting on the particles at the jumps of \( V(x) \).

Although we have used periodic potential barriers in our analytical and numerical solution of DDF problems, we
have also considered the case of single potential barriers as the $L \to \infty$ limit of the periodic potentials. In that case, the integration constant $\Delta$ goes to the shifting rate $c$ times the bulk density of the fluid, $\rho_o$ far away from the moving external potential. This is the requirement to get null current away from the external perturbation as the only possible solution for the stationary density distribution in an infinite one-dimensional system with a shifting potential acting on a finite region. Any solution of the Euler-Lagrange equation with $\Delta \neq c\rho_o$ would imply the accumulation of particles at the advancing front of the potential barrier and the depletion of the density behind it, so that the system would not be at any stationary state. In any realistic problem, like possible devices to control the flow of colloidal particles along channels, the finite length of the channels would probably produce typical density distributions and currents closer to those analyzed here for periodic systems than to those predicted for infinite long channels.

For the periodic systems studied here, we have found that the mean velocity of the particles may be maximized by the appropriate choice of the shifting rate. The hard core interactions among the particles reduces the optimal value of $\bar{v}_{\text{max}}$, but makes this mean velocity a broader function of the shifting rate. At high packing fractions, $\bar{v}_{\text{max}}$ has a strong and non-monotonic dependence on the period of the external potential, as a results of the correlations between particles. Such effect could be used to design more effective micro-pumps or turn-pikes, in which the flow of colloidal particles would be controlled by the oscillatory external potential. The particular models studied here, ideal gas and hard-rods, under the action of gaussian potential barriers or harmonic periodic potentials, have been chosen to explore the main regimes and generic properties of stationary flows in one-dimension. There are obviously many open questions to answer and different models to be explored. The application of the density functional techniques to these systems is still at its beginnings, and it would take time to ascertain its full capabilities. However, the generic theoretical requirements: the absence of hydrodynamic effects and the similarity between the particle correlations in the dynamic and in the equivalent equilibrium systems, seem likely to be reasonable assumptions in systems of colloidal particles moving at rates of the order of microns per second, under the effects of controlled external potentials. The application of the DDF techniques to systems in higher dimensions and to non-stationary problems would hopefully benefit from what we have learned with our simpler models and problems. The design of practical micro-fluiditic devices could also be supported by the generic principles developed with these simple models, and the experimental realization of these systems appears to be within the range of the present technologies.

VI. ACKNOWLEDGMENTS

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FIG. 1: Mean velocity of the particles as a function of the barrier drift rate, for square barrier (solid line) of width $a = 2\sigma$; parabolic barrier (dotted line) of width $w = 5.5\sigma$ and gaussian barrier (dashed) of width $\alpha = 1\sigma$. The barrier heights are $\beta V_o = 7$ in figure (a) and $\beta V_o = 1$ in figure (b). The insets compare, for the gaussian barriers, the exact results (solid lines) with the linear response theory (dashed lines).

FIG. 2: Maximum mean velocity value $\bar{v}_{max}$, drift rate, $\bar{c}_{max}$, at which this maximum mean velocity value is achieved, and the derivative of mean velocity at zero drift rate, $\bar{v}'(\bar{c} = 0)$, for a gaussian barrier as functions of the barrier height. The solid lines give the exact values and the dashed lines give linear response approximation, which are similar to the exact for low barriers.

FIG. 4: Mean velocity of the particles under a shifting oscillatory external potential as a function of its wave-number $q$, for constant value of the barrier amplitude, $\beta V_q = 1$, in (a), and constant force amplitude $q\sigma\beta V_q = 1$ in (b). The full line gives the result for hard-rods at $\rho_o = 0.8\sigma^{-1}$ with $\bar{c} = 2\sigma^{-1}$, and the dashed lines the same for $\bar{c} = 10\sigma^{-1}$. The dotted lines gives the ideal gas (i.e. $\rho_o\sigma = 0$) under the same drifting potentials for $\bar{c} = 2\sigma^{-1}$ and the dash-dotted line for $\bar{c} = 10\sigma^{-1}$. All the results are calculated with the linear response theory.

FIG. 5: Density distributions (solid lines referred to the left axis) and currents (the same lines but referred to the right axis), for hard rods of mean density $\rho_o = 0.8\sigma^{-1}$ under the influence of an external gaussian potential of height $\beta V_o = 10.6$ and width $\alpha = 0.707\sigma$. The density distribution predicted by the linear response theory (dotted lines) and the ideal gas for an external gaussian potential of height $\beta V_o = 5$ and width $\alpha = 0.707\sigma$ (dashed lines) are also presented for comparison. The drift rates are $\bar{c} = 0.2\sigma^{-1}$ in (a), $\bar{c} = 1.0\sigma^{-1}$ in (b), $\bar{c} = 1.7\sigma^{-1}$ in (c), and $\bar{c} = 10\sigma^{-1}$ in (d).

FIG. 6: Mean velocity of hard-rod particles, as function of the drift rate, $\bar{c}$, produced by a gaussian barrier of high $\beta V_o = 5$ in an ideal gas system, and a gaussian barriers of height $\beta V_o = 5.47, 6.18, 7.41$, and $10.6$ for systems with mean density $\rho_o\sigma = 0.2, 0.4, 0.6, 0.8$ respectively. The width of all gaussian is $\alpha = 0.707\sigma$. 

FIG. 3: Exact density distributions for an ideal gas system (solid lines referred to the left axis) and currents (the same lines but referred to the right axis), for gaussian barriers of width $\alpha = 0.707\sigma$ and heights $\beta V_o = 1(a)$ and (b) and $\beta V_o = 7(c)$ and (d). The drift rates are $\bar{c} = 0.5\sigma^{-1}$ for (a) and (c), and $\bar{c} = 10\sigma^{-1}$ for (b) and (d). The dot-filled lines represent the external potential barrier (not at scale) just to show the relative position of the density structures to the barrier. The dashed lines (referred to the left axis) give the density distributions predicted by the linear response theory.