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We discuss two recent models of mesoscopic fluid particles based on a two dimensional Voronoi tessellation. Both models describe a Newtonian fluid at mesoscopic scales where fluctuations are important. From thermodynamic consistency, the equilibrium distribution function is given through the Einstein distribution function. We compute from the Einstein distribution the equilibrium distribution function for a single fluid particle. We observe perfect agreement between the simulation results for the models proposed and the theoretical distribution function.

I. INTRODUCTION

The dynamical regimes of complex fluids like colloidal suspensions or polymeric solutions are strongly affected by the fluctuating character of the solvent. The Brownian diffusive character of small suspended objects can be traced back to the stochastic nature of the surrounding fluid [1]. Mathematically, the equations of fluctuating hydrodynamics (FH) [2] model in the continuum limit the *mesoscopic* regime of a simple Newtonian fluid. This regime corresponds to small length scales where, although the fluid is still well represented by hydrodynamics (a kinetic description is not yet needed), the molecular nature of the fluid is already appreciable and it is modeled through the inclusion of random noise terms in the hydrodynamic equations. The noise appears as the divergence of a random stress tensor and random heat flux, and the structure of these random fluxes is entirely determined from the fluctuation-dissipation theorem [2], [3]. The mesoscopic regime of hydrodynamics is relevant not only in problems involving complex fluids, but also in simple fluids when probed at short length scales, as for example in light scattering experiments.

A simulation of a fluid at mesoscopic scales could be based on a discretization of the fluctuating hydrodynamic equations which however, requires some care [4]. One should introduce the discrete random terms in such a way that they are compatible with the discrete form of the dissipation in the equations, in strict respect of the fluctuation-dissipation theorem even at the discrete level. Only in this way does one expect to have the Einstein distribution for mesoscopic variables as the equilibrium distribution function. Also, one should be careful in select-

ing thermal fluctuations respecting conservation of mass, momentum and energy.

Recently, two models have been devised and implemented in order to simulate fluctuating hydrodynamics [5,6]. Both are based on a dynamical Voronoi Lagrangian grid that follows the flow field. The main differences between both models are the use of the entropy or the energy as independent variable and, more importantly, how the velocity and temperature gradients are discretized. From a methodological point of view, we use different although equivalent and complementary ways of obtaining the stochastic forces in order to fulfill the fluctuation-dissipation theorem. The first one [5,7] consists in writing the equilibrium distribution for the set of variables, guessing the structure of the random noise, computing the Fokker-Planck equation corresponding to the Langevin equations, and deriving the coefficients of the noise by balancing the diffusive and drift parts of the Fokker-Planck on the equilibrium distribution. The second approach is to use the GENERIC formalism [6,8] which encodes in a very simple way the physics behind the First and Second Laws of Thermodynamics *and* the fluctuation-dissipation theorem. It must be emphasized that the GENERIC formalism does not include any new physics, but permits one to rapidly identify whether or not a model is thermodynamically consistent and, if it is not, offers suggestions about how to restore thermodynamic consistency.

In section II we review both models discussing their similarities and differences. We show that the reversible part of the dynamics of the model in Refs. [5] has a tiny production of entropy, but it can be easily modified in order to have a zero production of entropy as corresponds to a purely reversible dynamics. We also show in an appendix that the irreversible part of the dynamics of the model in Refs. [5] can be cast in the GENERIC formalism thus ensuring a positive entropy production. In section III we discuss how one can derive from the N-particle Einstein distribution function the 1-particle distribution function, which is the object measurable in simulations. This allows one to discuss the validity of the models in order to simulate fluctuating hydrodynamics.

The models in Refs. [5] and [6] can be understood as discretized versions of the continuum equations of fluctuating hydrodynamics in terms of fluid particles that move following the flow. The advantage of a Lagrangian description is apparent when one thinks of the highly complex and evolving interstitial domains in a colloidal suspension where the solvent fluid evolves. The fluid particles are defined through the Voronoi tessellation and have, therefore, a definite physical meaning. The Voronoi tessellation is a partition of physical space into a set of non-overlapping regions, or Voronoi cells. Each cell has associated a cell centre, and the cell itself is defined as the region of space closer to the centre of that cell than to any other cell centre. Each cell can be regarded as a thermodynamic subsystem of the whole fluid system and has associated a mass M_i , a momentum \mathbf{P}_i and an internal energy \mathcal{E}_i , which can be defined in microscopic terms from the position and coordinates of the molecules that constitute the fluid [5]. The cells also have a specified volume \mathcal{V}_i which is a geometrical quantity dependent on the coordinates of the cell centres, and an entropy function S_i , which is a prescribed thermodynamic function of the extensive variables $M_i, \mathcal{E}_i, \mathcal{V}_i$. We will refer to the fluid particles defined in terms of the Voronoi cells as *mesoparticles*.

The equations of motion for the mesoscopic variables have been obtained either from molecular considerations [5] plus simple finite differences approximation of velocity gradients or from a finite volume discretization of the Navier-Stokes equations [6]. We present the connection and differences between both models by separating the equations of motion into their reversible and irreversible parts.

A. Reversible part

The evolution equations of an inviscid fluid are completely reversible. By selecting as independent state variables the position, mass, momentum and entropy $\mathbf{R}_i, M_i, \mathbf{P}_i, S_i$, for $i = 1, \dots, N$, the reversible part of the dynamics of a discrete model for an inviscid fluid is given by [6]

$$\begin{aligned} \dot{\mathbf{R}}_i &= \mathbf{v}_i, \\ \dot{\mathbf{P}}_i &= \sum_j A_{ij} \mathbf{e}_{ij} \frac{P_j - P_i}{2} \\ &+ \sum_j \frac{A_{ij}}{R_{ij}} \frac{\rho_i + \rho_j}{2} \frac{\mathbf{v}_i + \mathbf{v}_j}{2} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij} \\ &+ \sum_j \frac{A_{ij}}{R_{ij}} \mathbf{c}_{ij} \left((P_i - P_j) - \frac{\rho_i + \rho_j}{2} (\mu_i - \mu_j) \right) \end{aligned}$$

$$\begin{aligned} &- \frac{s_i + s_j}{2} (T_i - T_j) \Big), \\ \dot{M}_i &= \sum_j \frac{A_{ij}}{R_{ij}} \frac{\rho_i + \rho_j}{2} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij}, \\ \dot{S}_i &= \sum_j \frac{A_{ij}}{R_{ij}} \frac{s_i + s_j}{2} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij}. \end{aligned} \quad (1)$$

Here, $\mathbf{v}_i = \mathbf{P}_i/M_i$ is the velocity ($\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$), $\rho_i = M_i/\mathcal{V}_i$ is the mass density, and $s_i = S_i/\mathcal{V}_i$ is the entropy density. The pressure P_i and the temperature T_i are given through the equilibrium equations of state as functions of the intensive variables ρ_i, s_i . We have also introduced geometric quantities arising from the Voronoi construction: A_{ij} is the area (length in 2D) of the face between cells i, j , $\mathbf{e}_{ij} = (\mathbf{R}_i - \mathbf{R}_j)/R_{ij}$ with $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ is the unit vector normal to the face i, j and, finally, \mathbf{c}_{ij} is a vector parallel to the face i, j pointing from $(\mathbf{R}_i + \mathbf{R}_j)/2$ to the centre of the face i, j .

The following term in the momentum equation in Eqns. (1)

$$\begin{aligned} &\sum_j \frac{A_{ij}}{R_{ij}} \mathbf{c}_{ij} \left((P_i - P_j) - \frac{\rho_i + \rho_j}{2} (\mu_i - \mu_j) \right. \\ &\left. - \frac{s_i + s_j}{2} (T_i - T_j) \right), \end{aligned} \quad (2)$$

is strongly reminiscent of the Gibbs-Duhem relation which, in differential form, is $dP - \rho d\mu - s dT = 0$. For this reason, we expect that this term (2), although not exactly zero, is very small, and this has been checked in actual simulations [6]. It is rather easy to show that total mass $\sum_i M_i$, momentum $\sum_i \mathbf{P}_i$, and energy $\sum_i \mathbf{P}^2/2M_i + \mathcal{E}(M_i, S_i, \mathcal{V}_i)$ are conserved *exactly* and that the total entropy $\sum_i S_i$ does not change in time due to this reversible motion. It can also be shown that the above equations can be understood as a finite volume discretization of the Euler equations for an inviscid fluid [6].

On the other hand, the reversible part of the dynamics in Refs. [5] is given in terms of the energy instead of the entropy. The equations for the position and mass evolution are identical to those in (1), the equation for the momentum evolution differs only in the absence of the Gibbs-Duhem term (2) and the equation for the internal energy evolution is given by [5]

$$\dot{E}_i = \sum_j \frac{A_{ij}}{R_{ij}} \frac{\epsilon_i + \epsilon_j}{2} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij} - \sum_j A_{ij} \frac{p_i + p_j}{2} \mathbf{e}_{ij} \cdot \mathbf{v}_{ij}. \quad (3)$$

It can be shown that if one computes the time derivative of the total entropy with the equations in Ref. [5], one obtains a non-zero production of entropy which involves a discrete version of the Gibbs-Duhem relation, analogous to (2). This term is expected to be very small

and in practical situations is completely negligible when compared with the entropy production due to the irreversible part of the dynamics. Nevertheless, we propose an energy evolution which respects the zero entropy production of the reversible part of the dynamics. From Eqns. (1) and the chain rule applied to $\mathcal{E}(M_i, S_i, \mathcal{V}_i)$ one readily arrives at

$$\begin{aligned}\dot{\mathcal{E}}_i &= -\frac{\partial \mathcal{E}_i}{\partial \mathcal{V}_i} \dot{\mathcal{V}}_i + \frac{\partial \mathcal{E}_i}{\partial M_i} \dot{M}_i + \frac{\partial \mathcal{E}_i}{\partial S_i} \dot{S}_i \\ &= P_i \sum_j \frac{1}{2} A_{ij} \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} - P_i \sum_j \frac{A_{ij}}{R_{ij}} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij} \\ &\quad + \mu_i \sum_j \frac{\rho_i + \rho_j}{2} \frac{A_{ij}}{R_{ij}} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij} \\ &\quad + T_i \sum_j \frac{s_i + s_j}{2} \frac{A_{ij}}{R_{ij}} \mathbf{c}_{ij} \cdot \mathbf{v}_{ij},\end{aligned}\quad (4)$$

where we have used the particular form of the volume in terms of the positions of the Voronoi cells as given in Ref. [6], and the usual thermodynamic definition of the intensive parameters P_i , T_i and μ_i . Here, the entropy $S_i = S(M_i, \mathcal{E}_i, \mathcal{V}_i)$ should be understood as the dependent variable. It is possible to show, following the steps of Ref. [6], that Eqn. (4) can be understood as a finite volume discretization, valid to first order in spatial gradients, of the continuum equation

$$\partial_t \epsilon = -\nabla \cdot (\epsilon \mathbf{v}) - P \nabla \cdot \mathbf{v}. \quad (5)$$

B. Irreversible part

The dissipative part in the Navier-Stokes equations involves the (negative) divergences of the stress tensor and heat flux, given by the usual forms

$$\begin{aligned}\boldsymbol{\Pi} &= \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^T), \\ \mathbf{J}^q &= \kappa \nabla T,\end{aligned}\quad (6)$$

where η is the shear viscosity (we have assumed a zero bulk viscosity for simplicity) and κ is the thermal conductivity.

The main difference in the dissipative part of the equations between the models in Refs. [5] and [6] appears in the form selected by the discrete versions of the stress tensor and the heat flux. The comparison can be made explicit by noting that the divergence of a flux \mathbf{J} in a given cell can be approximated, up to first order in spatial derivatives, through [6]

$$[\nabla \cdot \mathbf{J}]_i = -\frac{1}{\mathcal{V}_i} \sum_j A_{ij} \mathbf{e}_{ij} \cdot [\mathbf{J}]_{ij}, \quad (7)$$

where $[\mathbf{J}]_{ij}$ is the spatial average of the field \mathbf{J} over the face joining cells i, j . The physical meaning of (7) is

apparent when one thinks of $A_{ij} \mathbf{e}_{ij}$ as the surface normal vector of face i, j .

In Refs. [5], the average of the stress tensor and heat flux fields over the face i, j are approximated by the expressions

$$\begin{aligned}[\boldsymbol{\Pi}]_{ij}^{\alpha\beta} &= \eta \frac{1}{R_{ij}} (\mathbf{v}_{ij}^\alpha \mathbf{e}_{ij}^\beta + \mathbf{e}_{ij}^\alpha \mathbf{v}_{ij}^\beta), \\ [\mathbf{J}^q]_{ij} &= \kappa \frac{1}{R_{ij}} (T_i - T_j).\end{aligned}\quad (8)$$

On the other hand, in Refs. [6] the average $[\mathbf{J}]_{ij}$ of the flux over the face i, j in Eqn. (7) is approximated by the arithmetic mean $[\mathbf{J}]_{ij} = ([\mathbf{J}]_i + [\mathbf{J}]_j)/2$ and afterwards, the flux $[\mathbf{J}]_i$ on cell i (similarly for cell j), which are given in terms of the spatial derivatives (6), are approximated again with (7). The resulting discrete stress tensor and heat flux of Ref. [6] are given by

$$\begin{aligned}[\boldsymbol{\Pi}]_i^{\alpha\beta} &= \frac{\eta}{\mathcal{V}_i} \left[\frac{1}{2} \sum_j A_{ij} [\mathbf{e}_{ij}^\alpha \mathbf{v}_j^\beta + \mathbf{e}_{ij}^\beta \mathbf{v}_j^\alpha] \right. \\ &\quad \left. - \frac{1}{D} \delta^{\alpha\beta} \sum_j A_{ij} \mathbf{e}_{ij} \cdot \mathbf{v}_j \right], \\ [\mathbf{J}^q]_i &= \frac{\kappa}{2\mathcal{V}_i} \sum_j A_{ij} \mathbf{e}_{ij} T_j.\end{aligned}\quad (9)$$

The different structure of the discrete stress tensor and heat flux in Eqns. (8) and (9) leads to different dissipative terms in the equations of motion. In the model in Refs. [5], the dissipative interactions appear in the form of pairwise interactions between the Voronoi cells, much in the spirit of the original DPD model [7], [9], whereas in the model in Refs. [6], the interaction is not pairwise, but includes information about neighbours of a given pair. This seems to have significant implications in the numerical simulations. For example, we have shown in Ref. [6] that the measured kinematic viscosity is in very good agreement with the input viscosity when the stress tensor is given by (9), while it is 10% off for the form (8) [5]. This may be due to the fact that Eqns. (8) are too crude an approximation for the stress tensor since we are actually computing the gradient only in the direction along \mathbf{R}_{ij} . In the discrete implementation in Eqn. (9) we capture more information about the stress tensor so producing more satisfactory numerical results.

III. EQUILIBRIUM DISTRIBUTIONS FOR THE STOCHASTIC MODEL

In the previous section we have discussed the deterministic equations for the discrete model of a Newtonian fluid. If the Voronoi cells are mesoscopic in their physical size, they will be subject to thermodynamic fluctuations.

These fluctuations can be easily introduced following the methods of [5], [6] and we show in the Appendix how they can be formulated for the model in [5] by use of the GENERIC formalism as developed in [6]. The resulting stochastic differential equations are mathematically equivalent to a Fokker-Planck equation that governs the probability distribution function $\rho = \rho(x, t)$ that each Voronoi cell has a particular realization of the state variables denoted globally by x . In the GENERIC notation, this Fokker-Planck equation has the form [8]

$$\partial_t \rho = -\frac{\partial}{\partial x} \left[\rho \left[L \frac{\partial E}{\partial x} + M \frac{\partial S}{\partial x} \right] - k_B M \frac{\partial \rho}{\partial x} \right], \quad (10)$$

where k_B is Boltzmann's constant and L and M are the reversible and irreversible matrices, respectively.

The distribution function of the variables of a given system at equilibrium is given by the Einstein distribution function. This assertion can be proved under quite general assumptions on the mixing character of the microscopic dynamics of the system [10]. If the microscopic dynamics ensures the existence of dynamical invariants like the energy $E(x)$ and, perhaps, other invariants $I(x)$, then the Einstein distribution function takes the form [10]

$$\rho^{\text{eq}}(x) = g(E(x), I(x)) \exp\{S(x)/k_B\}, \quad (11)$$

where the function g is completely determined by the arbitrary initial distribution of dynamical invariants. For example, if at an initial time the value of the invariants $E(x), I(x)$ are known with high precision to be E_0, I_0 , then the Einstein distribution function takes the form

$$\rho^{\text{eq}}(x) = \frac{\delta(E(x) - E_0)\delta(I(x) - I_0)}{\Omega(E_0, I_0)} \exp\{k_B^{-1}S(x)\}, \quad (12)$$

where $\Omega(E_0, I_0)$ is the normalization factor. Given the general argument behind the Einstein distribution function [10], it is sensible to demand that the Fokker-Planck equation (10) has as its (unique) equilibrium distribution function the Einstein distribution. This can be achieved, if the following further conditions on the form of the matrices L, M hold [8],

$$\frac{\partial}{\partial x} \left[L \frac{\partial E}{\partial x} \right] = 0, \quad M \frac{\partial I}{\partial x} = 0. \quad (13)$$

The second condition is just the requirement that the dissipative part of the dynamics should conserve the total mass, energy, and momentum of the system. The first condition can be understood as an incompressibility condition on the reversible dynamics of the system in the state space x . We should note that this incompressibility equation is only approximately satisfied by our reversible dynamics. Nevertheless, as we will show in what follows, the Einstein distribution function is still a very good approximation for the equilibrium solution of the Fokker-Planck equation.

A. Equilibrium N -particle distribution function

In this section we discuss the equilibrium distribution function $\rho^{\text{eq}}(x)$ corresponding to the equations of motion of our discrete models [5,6]. Note that the equilibrium distribution function is the same, irrespective of the actual form of the irreversible part of the dynamics. This is because both sets of equations have the GENERIC structure. The GENERIC structure of the equations of motion ensures that the equilibrium distribution function for these variables is given by the Einstein distribution function in the presence of dynamical invariants, Eqn. (11). As the total mass $M(x)$, total energy $E(x)$ and momentum $\mathbf{P}(x)$ are conserved by the dynamics, the Einstein distribution function will be given in our models by

$$\rho^{\text{eq}}(x) = \frac{1}{\Omega} \delta(M(x) - \mathcal{M}_0) \delta(E(x) - E_0) \delta(\mathbf{P}(x) - \mathbf{P}_0) \times \exp\{k_B^{-1}S(x)\}, \quad (14)$$

where we have assumed that we know with absolute precision the values of the total mass \mathcal{M}_0 , energy E_0 and momentum \mathbf{P}_0 at the initial time. This is the situation in a computer simulation. Ω is a factor that ensures the correct normalization of $\rho^{\text{eq}}(x)$. The total energy and entropy in our models have the form $E(x) = \sum_i P_i^2/2M_i + \mathcal{E}_i$ and $S(x) = \sum_i S_i$.

A word is in order about the total volume. We note that *any* configuration of positions \mathbf{R}_i of the Voronoi particles has the property that the total volume is conserved $\sum_i \mathcal{V}_i = \mathcal{V}_0$. Therefore, even though the total volume is conserved, it does not produce a restriction in the form of a delta function in Eqn. (14). Actually, for our models, it is more convenient to consider the probability of a particular realization of the total set of variables $\{\mathcal{V}, \mathbf{P}, M, S\}$ instead of $\{\mathbf{R}, \mathbf{P}, M, S\}$. This is calculated as

$$P(\{\mathcal{V}, \mathbf{P}, M, S\}) = \int \{d\mathbf{R}\} \delta^N(\mathcal{V} - \mathcal{V}(\{\mathbf{R}\})) \rho^{\text{eq}}(x). \quad (15)$$

Because $\rho^{\text{eq}}(x)$ depends on the positions only through the volume variable, we have

$$P(\{\mathcal{V}, \mathbf{P}, M, S\}) = F(V_1, \dots, V_N) \rho^{\text{eq}}(\{\mathcal{V}, \mathbf{P}, M, S\}), \quad (16)$$

where

$$F(V_1, \dots, V_N) = \int d\{\mathbf{R}\} \prod_i^N \delta(V_i - \mathcal{V}_i(\{\mathbf{R}\})). \quad (17)$$

This function F is proportional to the probability density that the particles have the particular distribution of volumes V_1, \dots, V_N provided that the distribution function of the positions is uniform. Note that, because $F(V_1, \dots, V_N)$ does not contain information about the

location of the volumes, we expect that the probability that a given cell has a particular volume is independent of the vast majority of the volumes of the rest of the cells. In this way, we expect that an approximation in which the volumes are statistically independent in a random distribution of cells might be a good one, particularly if the number M of cells is very large. However, there is a global correlation that must be respected, namely that of total volume conservation. Therefore, we expect

$$F(V_1, \dots, V_N) \propto F(V_1) \cdots F(V_N) \delta \left(\sum_i V_i - \mathcal{V}_0 \right), \quad (18)$$

where $F(V)$ is the probability density that, in a random distribution of points, the volume of a Voronoi cell is V , irrespective of the values of the volumes of other cells. The exact analytical calculation of the function $F(V)$ is difficult, but a phenomenological expression has been given in Ref. [11]. As the only scale in a random distribution of points is the average volume of each cell, the volume distribution function should have a scaling form

$$F(V) = \frac{1}{\bar{V}} \phi \left(\frac{V}{\bar{V}} \right), \quad (19)$$

where \bar{V} represents the mean volume value for the cell. The function $\phi(x)$ is the Gamma distribution function [11]

$$\phi(x) = \frac{\nu^\nu}{\Gamma(\nu)} x^{\nu-1} \exp\{-\nu x\}, \quad (20)$$

properly normalized to unity, $\int_0^\infty \phi(x) dx = 1$. Here, ν is a constant parameter.

In Fig. (1) we plot the cell volume distribution of a Voronoi tessellation of an ensemble of uniform random set of points, together with a fitted Gamma distribution with value $\nu = 3.8420$ and $\bar{V} = 0.0025$.

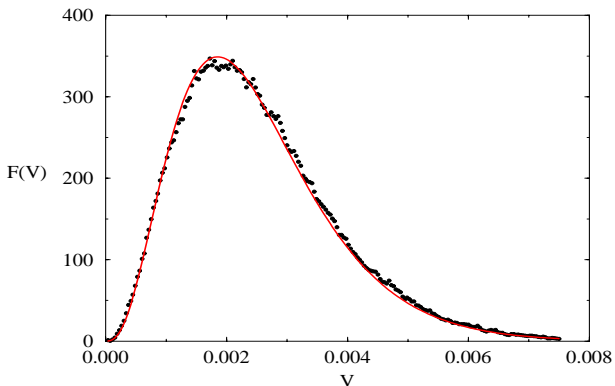


FIG. 1. Distribution function for the Voronoi volume of a random distribution of points for a simulation with $M = 400$ particles in a two dimensional periodic boundary box of length $L = 1$, in dots. Continuous line corresponds to Eqn. (19) with $\nu = 3.8420$ and $\bar{V} = 0.0025$.

B. The most probable state

The most probable state at equilibrium according to Eqn. (14) is the one that maximizes the entropy $S(x)$ subject to the constraints $M(x) = M_0$, $E(x) = E_0$, and $\mathbf{P}(x) = \mathbf{P}_0$. By introducing Lagrange multipliers β , λ and \mathbf{V} , the most probable state is the state that maximizes $k_B^{-1} S(x) - \beta(E(x) - E_0) - \mathbf{V} \cdot (\mathbf{P}(x) - \mathbf{P}_0) - \lambda(M(x) - M_0)$ without constraints. By equating the partial derivatives with respect to every variable to zero, one obtains the following implicit equations for the most probable values $x^* = \{\mathbf{R}_i^*, \mathbf{P}_i^*, M_i^*, S_i^*\}$ where $*$ indicates the most probable state

$$\begin{aligned} \sum_j \frac{\partial \mathcal{V}_j}{\partial \mathbf{R}_i} P_j(x^*) &= 0, \\ \frac{\mathbf{P}_i^*}{M_i^*} &= \mathbf{V}, \\ \mu_i(x^*) &= \lambda + \frac{D}{2} \mathbf{V}^2, \\ T_i(x^*) &= \frac{1}{k_B \beta}. \end{aligned} \quad (21)$$

where D is the number of space dimensions. The second equation in (21) states that in the most probable state all particles move at the same velocity \mathbf{V} which might be set to zero without loss of generality. The last two equations state, then, that the chemical potential per unit mass and the temperature of all the fluid particles are equal at the most probable value of the discrete hydrodynamic variables. This implies that the pressure is also the same for all the fluid particles (in a simple fluid the intensive parameters are not independent [12]). The first equation is, therefore, trivially satisfied (because $\sum_j \mathcal{V}_j = \mathcal{V}_0$, which is independent on \mathbf{R}_i).

C. Equilibrium single-particle distribution function

In order to compare simulation and theoretical results, it is necessary to consider the single-particle distribution function instead of the multidimensional N -particle distribution. For this reason, as a first step, we will integrate out all the momentum variables except that of the first particle. The outcome will be to convert the “microcanonical” distribution (14) into a “canonical” distribution. Afterwards, we will integrate over the volume, mass and entropy of all the particles except the first particle. We denote the state by $x = (y, \{\mathbf{P}\})$ where $y = (\{V\}, \{M\}, \{S\})$ is the set of volumes, masses, and entropies of all particles. Note that the total entropy and internal energy do not depend on momentum variables.

By integrating the distribution function $\rho^{\text{eq}}(x)$ over all momenta except \mathbf{P}_1 we will have the probability $\rho^{\text{eq}}(\mathbf{P}_1, y)$

$$\begin{aligned} \rho^{\text{eq}}(\mathbf{P}_1, y) &= \prod_i \frac{F(V_i)}{\Omega_0} \exp \left\{ \frac{S(y)}{k_B} \right\} \delta \left(\sum_i^N M_i - \mathcal{M}_0 \right) \\ &\times \delta \left(\sum_i^N V_i - \mathcal{V}_0 \right) \prod_{\mu=2}^N (2M_i)^{D/2} \frac{\omega_{D(N-2)}}{2} \\ &\times \left[E_0 - \sum_i \mathcal{E}_i(y) - \frac{\mathbf{P}_1^2}{2M_1} \right]^{\frac{D(N-2)}{2} - 1}, \end{aligned} \quad (22)$$

where we have used the following equation, which is proved in appendix VII of Ref. [13],

$$\begin{aligned} &\int d^{DN} \mathbf{P} \delta \left(\sum_i^N \frac{\mathbf{P}_i^2}{2M_i} - E_0 \right) \delta^D \left(\sum_i^N \mathbf{P}_i - \mathbf{P}_0 \right) \\ &= \frac{1}{2} \omega_{D(N-1)} U_0^{\frac{D(N-1)-2}{2}} \prod_i^N (2M_i)^{D/2}, \end{aligned} \quad (23)$$

where D is the spatial dimensionality, $U_0 = E_0 - P_0^2/2M_0$, and

$$\omega_N = 2 \frac{\pi^{N/2}}{\Gamma(N/2)}. \quad (24)$$

We find now a convenient approximation to Eqn. (22) by noting that this probability is expected to be highly peaked around the most probable state. Therefore, for those values of $\mathcal{E}_i(y)$ for which $\rho^{\text{eq}}(\mathbf{P}_1, y)$ is appreciably different from zero we can approximate it with an exponential

$$\left[E_0 - \sum_i \mathcal{E}_i - \frac{\mathbf{P}_1^2}{2M_1} \right]^P \propto \exp \left\{ -\beta^* \left(\sum_i \mathcal{E}_i + \frac{\mathbf{P}_1^2}{2M_1} \right) \right\}, \quad (25)$$

where $P = D(M-2)/2 - 1 \gg 1$. We have introduced the parameter β^* as

$$\beta^* = \frac{D(M-1)/2 - 1}{E_0 - \sum_j \mathcal{E}_j^*} \approx \frac{DM/2}{E_0 - \sum_j \mathcal{E}_j^*}, \quad (26)$$

where \mathcal{E}_i^* is the most probable value of \mathcal{E}_i . The parameter β^* is proportional to the inverse of the most probable kinetic energy. Finally, we can write Eqn. (22) as

$$\begin{aligned} \rho^{\text{eq}}(\mathbf{P}_1, y) &= \prod_i \frac{F(V_i)}{\Omega_0} \delta \left(\sum_i^N M_i - \mathcal{M}_0 \right) \delta \left(\sum_i^N V_i - \mathcal{V}_0 \right) \\ &\times \exp \left\{ \frac{S(y)}{k_B} - \beta^* \sum_i^N \mathcal{E}_i(y) - \beta^* \frac{\mathbf{P}_1^2}{2M_1} \right\}, \end{aligned} \quad (27)$$

where Ω_0 is a normalization constant. In Eqn. (27) we have neglected a term $\sum_i \log M_i$ since is much less than $\sum_i \mathcal{E}_i(y)$. Note that \mathcal{E}_i is a first order function of its arguments S_i, M_i, V_i and, therefore, it is of order M_i .

We are interested now in the distribution function $P(V_1, \mathbf{P}_1, M_1, S_1)$. It is the probability that a particular mesoparticle takes the values $V_1, \mathbf{P}_1, M_1, S_1$ for its variables, independently from the values of the rest of the variables in the system. We want to integrate (27) over the variables V, M, S of all particles except $V_1, \mathbf{P}_1, M_1, S_1$. We can rewrite

$$\begin{aligned} &P(V_1, \mathbf{P}_1, M_1, S_1) = \\ &= \frac{1}{\Omega_0} F(V_1) \Phi(\mathcal{M}_0 - M_1, \mathcal{V}_0 - V_1) \\ &\times \exp \left\{ \frac{S_1}{k_B} - \beta^* \mathcal{E}_1(M_1, S_1, V_1) - \beta^* \frac{\mathbf{P}_1^2}{2M_1} \right\}, \end{aligned} \quad (28)$$

where we have introduced the function

$$\begin{aligned} \Phi(\mathcal{M}, \mathcal{V}) &= \int d^{(N-1)} \{V\} d^{(N-1)} \{M\} d^{(N-1)} \{S\} \\ &\times \prod_{i=2}^N F(V_i) \delta \left(\sum_{i=2}^N M_i - \mathcal{M} \right) \delta \left(\sum_{i=2}^N V_i - \mathcal{V} \right) \\ &\times \exp \left\{ \sum_{i=2}^N \frac{S_i}{k_B} - \beta^* \mathcal{E}_i(M_i, S_i, V_i) \right\}. \end{aligned} \quad (29)$$

The functional form of $\Phi(\mathcal{M}, \mathcal{V})$ is very well approximated by an exponential, as can be seen by taking derivatives with respect to \mathcal{M} and \mathcal{V} . We expect that when the number of variables M is very large, the integrand becomes highly peaked around this most probable value and then direct computations show

$$\begin{aligned} \frac{\partial}{\partial \mathcal{M}} \Phi(\mathcal{M}, \mathcal{V}) &\approx -\beta^* \lambda^* \Phi(\mathcal{M}, \mathcal{V}) \\ \frac{\partial}{\partial \mathcal{V}} \Phi(\mathcal{M}, \mathcal{V}) &\approx \beta^* \Pi^* \Phi(\mathcal{M}, \mathcal{V}), \end{aligned} \quad (30)$$

where Π^* and λ^* are suitable Lagrange multipliers accounting for the mass and volume conservation. Therefore,

$$\Phi(\mathcal{M}, \mathcal{V}) \approx \exp \{ -\beta^* (\lambda^* \mathcal{M} - \Pi^* \mathcal{V}) \}. \quad (31)$$

Returning back to Eqn. (28) we have the final result for the single-particle distribution function,

$$\begin{aligned} P(V_1, \mathbf{P}_1, M_1, S_1) &= \frac{1}{Z} F(V_1) \exp \left\{ \frac{S_1}{k_B} \right. \\ &\left. - \beta^* \left(\mathcal{E}(M_1, S_1, V_1) + \frac{\mathbf{P}_1^2}{2M_1} - \lambda^* M_1 + \Pi^* V_1 \right) \right\}, \end{aligned} \quad (32)$$

where Z is an appropriate normalization factor. The form of the single-particle distribution function can be interpreted as the probability that a subsystem that can exchange mass, momentum, energy, and volume with a

thermal bath (whose intensive parameters are β^* , λ^* , Π^*) has particular values of these extensive variables. Note that, although the momentum the distribution looks Gaussian, the momentum is not statistically independent of the mass. Concerning the volume, the presence of the factor $F(V)$ inhibits an interpretation of Π^* as giving directly the pressure of the thermal bath.

The most probable values of the single-particle distribution function (32), denoted with a double star, is given by

$$\begin{aligned} P_i^{**} + \frac{F'(V)}{\beta^* F(V)} &= \Pi^* \\ \mathbf{P}_i^{**} &= \mathbf{0} \\ \mu_i^{**} &= \lambda^* \\ T_i^{**} &= \frac{1}{k_B \beta^*}, \end{aligned} \quad (33)$$

which should be compared with Eqns. (21). Here, P_i^{**} is the most probable value of the pressure of particle i . Note the connection between β^* (related to the most probable value of the kinetic energy) and the most probable thermodynamic temperature in Eqn. (33). Note also that the most probable value of the single-particle distribution function x^{**} in Eqn. (33) does not exactly coincide with the most probable value of the N -particle distribution function x^* of Eqns. (21) due to the integrations involved. However, the discrepancies are expected to be very small.

D. Single-variable distribution functions of a mesoparticle

Note that in a simulation, it is difficult to measure the distribution function (32) due to the large number of variables involved (five), which would necessitate binning of frequencies of occurrences in a five-dimensional space. Clearly what we need are the distribution functions over a single variable. In this section, we compute these further marginal distribution functions.

The joint probability distribution function of the volume, mass and entropy of one particle is easily obtained because the momentum variables $\tilde{\mathbf{P}}$ are trivially integrated

$$\begin{aligned} P(V, M, S) &\propto \frac{1}{Z} F(V) \left(\frac{2\pi M}{\beta^*} \right)^{\frac{D}{2}} \exp \left\{ \frac{S}{k_B} \right. \\ &\quad \left. - \beta^* (\mathcal{E}(M, S, V) - \lambda^* M + \Pi^* V) \right\}. \end{aligned} \quad (34)$$

By making use of the analytical expression for $F(V)$ in Eqn. (19), and performing a change of variables from entropy S to internal energy \mathcal{E} , for an ideal gas, we can calculate the mass and volume distribution function. The Jacobian is given by the temperature $T(\mathcal{E})$. The integral

can be performed analytically and the result is (from now on we assume $D = 2$)

$$\begin{aligned} P(V, M) &\propto (V)^{\nu-1} M^2 \left(\frac{cV e^2}{M^2 \beta^*} \right)^{\frac{M}{m_0}} \Gamma \left(\frac{M}{m_0} \right) \\ &\quad \times \exp \left\{ -\nu \frac{V}{V} + \beta^* (\lambda^* M - \Pi^* V) \right\}, \end{aligned} \quad (35)$$

where $\Gamma(x)$ is the Gamma function, $e = \exp(1)$, m_0 is the mass of the molecule of ideal gas we are simulating, and c is a dimensionless constant that depends only on microscopic parameters, being defined as the ratio between λ the typical distance between molecules at chosen temperature T_e and Λ the thermal wavelength

$$c = \left(\frac{\lambda}{\Lambda} \right)^2 = \frac{\lambda^2 2\pi m_0 k_B T_e}{h^2}. \quad (36)$$

We can now integrate over the volume variable in $P(V, M)$ to obtain the mass distribution function. Note that the integration limits are extended to $(0, \infty)$ because the range of variation for one particle's mass is very small compared to the total mass of the system,

$$\begin{aligned} P(M) &\propto \int_0^\infty P(V, M) dV \\ &\propto \Gamma \left(\frac{M}{m_0} \right) \Gamma \left(\nu + \frac{M}{m_0} \right) \left(\frac{M}{m_0} \right)^{2(1 - \frac{M}{m_0})} \\ &\quad \times \left(\frac{c e^2}{k_B^2 \beta^* (\beta^* \Pi^* + \frac{\nu}{V})} \right)^{\frac{M}{m_0}} \exp \{ \beta^* \lambda^* M \}. \end{aligned} \quad (37)$$

Let us calculate the volume distribution function by integrating over the mass in Eqn. (35)

$$P(V) \propto (V)^{\nu-1} \exp \left\{ -\nu \frac{V}{V} - \beta^* \Pi^* V \right\} g(V, \beta^*, \lambda^*), \quad (38)$$

where the function $g(V, \beta^*, \lambda^*)$ is defined as

$$\begin{aligned} g(V, \beta^*, \lambda^*) &= \int_0^\infty M^{2(1 - \frac{M}{m_0})} \left(\frac{cV e^2}{\beta^*} \right)^{\frac{M}{m_0}} \\ &\quad \times \Gamma \left(\frac{M}{m_0} \right) \exp \{ \beta^* \lambda^* M \} dM. \end{aligned} \quad (39)$$

We can extract the density distribution function very easily from Eqn. (35):

$$\begin{aligned} P(\rho) &= \int P(V, M) \delta \left(\rho - \frac{M}{V} \right) dV dM \\ &= \int P(V, \rho V) V dV \\ &\propto \rho^2 h(\rho, \lambda^*, \beta^*, \Pi^*) \end{aligned} \quad (40)$$

where we have introduced the function

$$h(\rho, \lambda^*, \beta^*, \Pi^*) = \int_0^\infty V^{\nu+2} \left(\frac{cV e^2}{(\rho V)^2 \beta^*} \right)^{\frac{\rho V}{m_0}} \Gamma \left(\frac{\rho V}{m_0} \right) \times \exp \left\{ \left(-\frac{\nu}{V} + \beta^* (\lambda^* \rho - \Pi^*) \right) V \right\} dV. \quad (41)$$

Finally, we consider the momentum distribution function. After carrying out the entropy and volume integrations in Eqn. (32) we obtain

$$P(P^x) = \sqrt{\frac{\beta^*}{2\pi}} \int \frac{P(M)}{\sqrt{M}} \exp \left\{ -\beta^* \frac{P^x^2}{2M} \right\} dM. \quad (42)$$

IV. SIMULATION RESULTS

We have already mentioned that the dissipative terms in the model of Ref. [6] produce slightly better results than those of Ref. [5] and for this reason we present the simulation results for this model. The specific details of the simulations are those in Ref. [6]. We simulate $N_{mic} = 40000$ atoms of argon, assumed to be an ideal gas. The system is at temperature $T_e = 273K$ in a periodic boundary box. The typical distance between molecules in an ideal gas at room temperature and pressure in 3 dimensions is about $\lambda = 3 \times 10^{-9}m$. If in two dimensions we want to keep this typical distance, then the linear dimensions of our simulation box should be $L = N_{mic}^{\frac{1}{2}} 3 \times 10^{-9}m = 6.67 \times 10^{-7}m$. In the following, all quantities are expressed in the reduced units defined in Ref. [6]. These simulations are performed using $M = 400$ mesoscopic particles in a 2D box with box length $L = 1$, with constant shear and bulk viscosities and thermal conductivity such that $\eta = \zeta = \kappa = 0.01$. These mesoscopic particles contain typically 100 argon atoms. In reduced units the temperature is initially set to $T = 1$ and the density to $\rho = 1$.

The stochastic equations are integrated with an Euler scheme that conserves total momentum and energy with a time step $dt = 0.000001$ in reduced units. The initial state is set as follows. From a random distribution of particle positions in the box, we obtain the Voronoi volumes. We initialize the mesoparticle masses in such a way that we obtain a constant density for the particles, equal to the global density of the system ($\rho = 1$). Then, the initial entropies and temperatures are calculated using the corresponding functions for the ideal gas. The initial velocities are set to zero, and consequently the total momentum is zero. Note that this initial state, although close to equilibrium, is not a typical equilibrium state. We let the system evolve to the equilibrium state and measure the equilibrium momentum, mass and volume distribution functions.

The equilibrium momentum distribution function measured in the simulations is plotted in Fig. 2. As a first approximation, we can fit it to a Gaussian function (broken line). It is a reasonable fit, but we observe some

significant discrepancies. The origin of this discrepancy arises from the fact that momentum and mass are not statistically independent. Of course, the momentum distribution function is actually given by Eqn. (42). If we use this equation with the distribution function for the mass obtained in the simulations we obtain better agreement. The best fit for the parameter is $\beta^* = 39947.26$, in perfect agreement with the value $\beta^* = \frac{1}{k_b T_e}$ provided by the global temperature of the ideal gas system compatible with the total mass, momentum, and energy of the system.

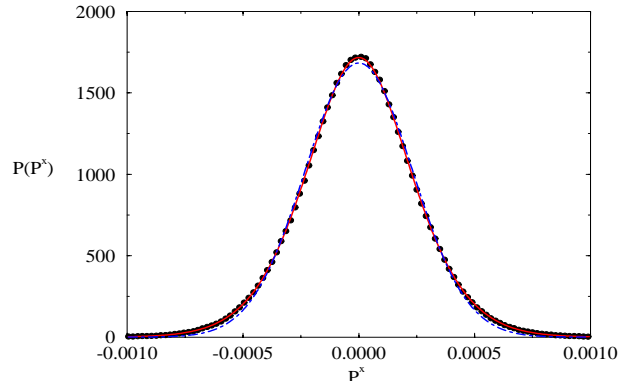


FIG. 2. Equilibrium momentum distribution function. Dotted line corresponds to the simulation results for the $P(P^x)$. The continuous line corresponds to our prediction in Eqn. (42) for the value of $\beta^* = 39947.26$. The broken line corresponds to the best Gaussian fit; note, however, that this should correspond to a system with a fixed mass particles, which is not actually the case in our simulations, as can be seen from the mass distribution function shown in Fig.4.

The identity between the kinetic temperature (given through β^*) and the thermodynamic temperature in Eqn. (33) is validated in the results shown in Fig. 3 where we plot the average kinetic energy per mesoparticle and the mean of all thermodynamic temperatures obtained from the equation of state for each mesoparticle.

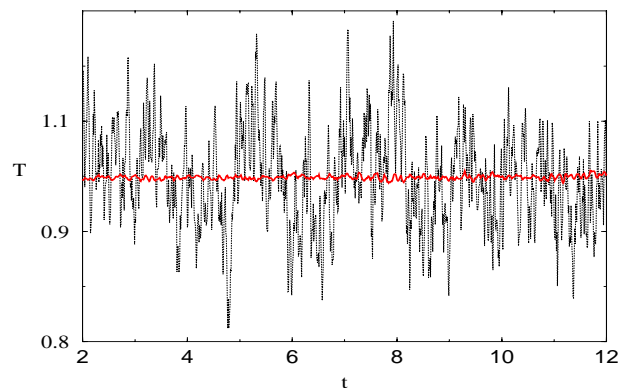


FIG. 3. Time evolution for the kinetic and thermodynamic temperatures (dotted and continuous lines, respectively). The mean values are $T_{thermo} = 1.000 \pm 0.004$ and $T_{kin} = 1.00 \pm 0.08$, in reduced units. The kinetic temperature has bigger fluctuations, associated with the width of the momentum distribution function in Fig. 2.

In Figs. 4, 5 and 6 we show the mass, volume, and density equilibrium distribution function for a single mesoparticle.

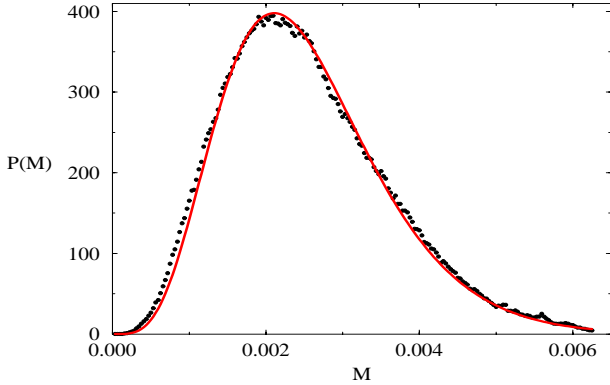


FIG. 4. Mass equilibrium distribution function. Dots correspond to simulation results. The continuous line is the fit to Eqn. (37) for the parameters $\beta^* = 39947.26$, $\Pi^* = 1.009604$, and $\lambda^* = -10.619795$.

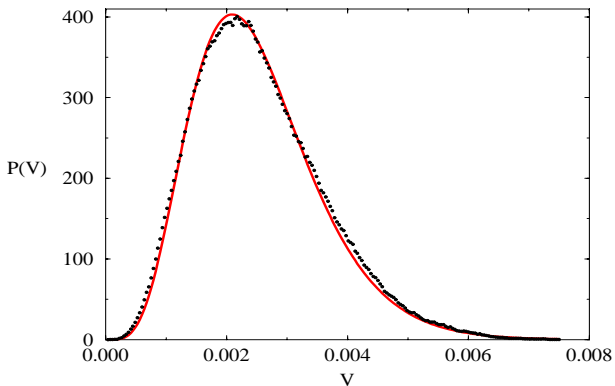


FIG. 5. Volume equilibrium distribution function. Dots correspond to simulation results. The continuous line is the fit to Eqn. (38) for the fitted values $\beta^* = 39947.26$, $\Pi^* = 1.009604$, and $\lambda^* = -10.619795$.

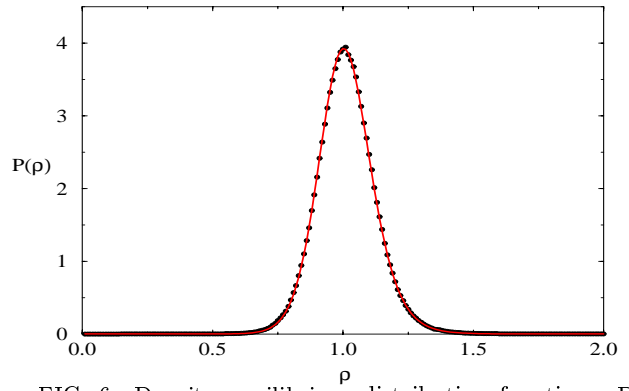


FIG. 6. Density equilibrium distribution function. Dots correspond to simulation results. The continuous line is the fit to Eqn. (40) for the fitted values $\beta^* = 39947.26$, $\Pi^* = 1.009604$, and $\lambda^* = -10.619795$.

In solid lines are shown the best fits of the simulation results to the nonlinear functions dependent on the three parameters (β^* , Π^* , λ^*) given in Eqn. (37), (38), (40). These fits have been obtained through a standard Levenberg-Marquardt nonlinear least-squares routine. The parameter β^* has been fitted from the momentum distribution function. One remarkable fact is that many pairs of values for Π^* , λ^* provide individually reasonable fits for the simulation data $P(M)$, $P(V)$, $P(\rho)$. For this reason, we have minimized *simultaneously* the least squares function for the three distributions. This procedure leads to the optimal values $\beta^* = 39947.26$, $\Pi^* = 1.009604$, and $\lambda^* = -10.619795$. According to Eqns. (33) the Lagrange multipliers are directly connected with the most probable value of the intensive parameters in the simulation. We have measured by direct simulation the marginal equilibrium distributions of the intensive variables and find $T^{**} = 1.00132$, $P^{**} = 0.993759$, $\lambda^{**} = -10.5556$. We obtain perfect agreement with the temperature and reasonable agreement with the pressure and chemical potential.

The size of the fluctuations, that is, the width of the distribution functions, depends on the actual typical size of the Voronoi cells. For a given value of the density, for example, the larger the volume (and the mass) of the cell, the smaller the width of the equilibrium distribution function for the density, in accordance with the usual predictions of equilibrium statistical mechanics. This is illustrated Fig. 7. In a general situation, the size of the cells is dictated by the relevant hydrodynamic length scale that must be resolved. Typically, the “radius” of a cell must be 20 times smaller than the relevant hydrodynamic length scale [6], accounting for why it is necessary to include thermal fluctuations to simulate the hydrodynamic flow around a micron sized colloidal particle but not for simulating the flow around a centimetre sized ping-pong ball.

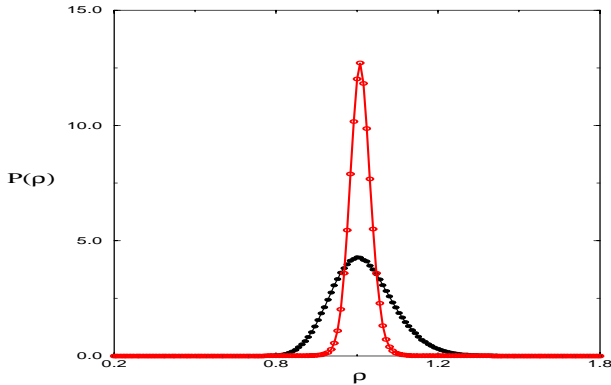


FIG. 7. Density equilibrium distributions for two different typical mean mesoparticle volumes ($\bar{V} = 100$, $\bar{V} = 200$) and the same mean density $\rho = 1$. The plot with smaller width corresponds to the bigger mean volume.

When fluctuations are present, the entropy function $S(x)$ might be a *decreasing* function of time in a general situation. We show an example of this behavior in Fig. 8 in an equilibrium situation. Of course, the fluctuations are small in macroscopic terms.

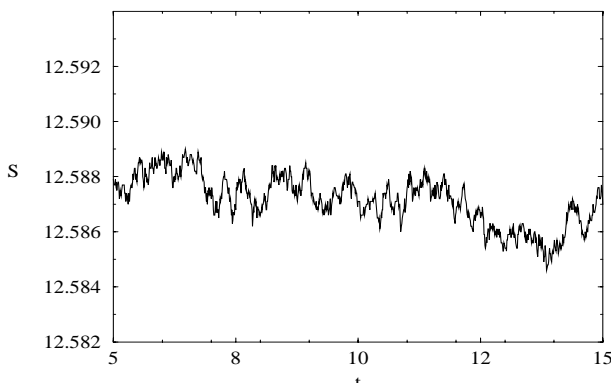


FIG. 8. Time evolution for the total entropy of a system with noise. Simulation details correspond to those of Figs. 4, 5 and 6.

However, if one considers the entropy *functional*

$$\mathcal{S}[\rho_t] = \int S(x)\rho(x, t)dx - k_B \int \rho(x, t) \ln \rho(x, t)dx, \quad (43)$$

it is possible to prove by using the Fokker-Planck equation (10) that $\partial_t \mathcal{S}[\rho_t] \geq 0$ [8]. In other words, the entropy functional plays the role of a Lyapunov function. At equilibrium, the entropy $S(x)$ should be a constant (its maximum value). In a stochastic simulation however, there are fluctuations in the entropy and, as a consequence, it might increase or decrease. Of course, if the mesoparticles are very large (in the thermodynamic limit), the fluctuations are negligible and the entropy function will be a monotonously increasing function of time.

In this paper we have discussed the relationship between two models of mesoscopic Voronoi fluid particles recently introduced [5,6]. Both models can be understood as finite volume discretizations of the Navier-Stokes equations in a Lagrangian description. They include thermal fluctuations that obey the fluctuation-dissipation theorem at the discrete level and, as a consequence, the equilibrium distribution function is given by the Einstein distribution function. The model in Ref. [5] has a reversible part that produces a slight entropy increase which, strictly speaking, should be conserved in a reversible motion. Nevertheless, in practical situations this unphysical reversible entropy production is expected to be negligible in comparison with the entropy production due to the irreversible part of the dynamics. Concerning the latter, both models differ in the actual discrete approximations for the stress tensor and heat flux. It appears that the discretization in Ref. [6] produces better results for numerical values of the transport coefficients due to its non-pairwise form.

We have computed analytically the marginal distribution functions corresponding to a single mesoparticle from the Einstein distribution function, which is defined over all the variables in the system. In practice, these are the only available distributions in a simulation. Excellent agreement is obtained between the theoretical results and the simulations, conferring full confidence in the models.

Several points concerning the actual implementation of the algorithms are worth mentioning. For example, we have used a simple Euler scheme in order to integrate the stochastic equations. This method requires very small time steps in order to reach the desired level of energy conservation. We are currently considering higher order schemes that allow time steps two orders of magnitude larger with the same level of energy conservation; we hope to publish these findings in the future. We should mention that the size of the time step is not only dictated by the physical hydrodynamic time scales in the problem, but also by stability problems in the Voronoi tessellation itself. In the equations of motion, this stability problems can be spotted as originating from the change in the volume of a Voronoi cell due to the rapid twisting of the face between neighbouring cells that occurs when the two centres that define the cells come close to each other (note that the terms with \mathbf{c}_{ij} are proportional to R_{ij}^{-1}). In that situation, a slight motion of the centres produce a large variation of the volume of the cells leading to large pressure differences and unstable forces. This problem can be eliminated if the centre of the cell remains always close to the centre of mass of the cell. This can be achieved, for example, if after every physical time step a fictitious dynamics over the Voronoi centres is applied in such a way that the resulting Voronoi tessellation is centroidal

[14], that is, the centre of the cell coincides with the centre of mass. This method is basically a re-tessellation on a centroidal mesh. We expect that the additional computation involved in the re-tessellation will be compensated by the much larger time steps that can be used.

ACKNOWLEDGMENTS

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VI. APPENDIX: “GENERIC” STRUCTURE OF THE IRREVERSIBLE PART OF THE DYNAMICS

In this appendix we show that the irreversible part of the dynamics of the model in Refs. [5] can be cast in the GENERIC formalism. We follow the notation in Ref. [6].

In order to derive the irreversible part of the dynamics of the DPD model and to get thermodynamically consistent thermal fluctuations, a very useful route is to *first* postulate the thermal noises $d\tilde{x}$ and *then* construct the dissipative matrix M through the fluctuation-dissipation theorem,

$$M = \frac{d\tilde{x}d\tilde{x}^T}{2k_B dt}. \quad (44)$$

In order to have conservation of the energy $E(x)$ and other possible dynamical $I(x)$, like momentum, the following restrictions apply on the noises

$$\begin{aligned} \frac{\partial E}{\partial x} d\tilde{x} &= 0, \\ \frac{\partial I}{\partial x} d\tilde{x} &= 0, \end{aligned} \quad (45)$$

which ensure the usual GENERIC degeneracy requirements

$$\begin{aligned} M \frac{\partial E}{\partial x} &= 0, \\ M \frac{\partial I}{\partial x} &= 0. \end{aligned} \quad (46)$$

We postulate the following form for the thermal noises $d\tilde{x} = \{0, d\tilde{\mathbf{P}}_i, d\tilde{E}_i\}$. Note that we do not assume any fluctuation in the mass, in accordance with the expectation that the mass equation does not contain any irreversibility. The momentum and energy random terms are postulated to be

$$\begin{aligned} d\tilde{\mathbf{P}}_i &= \sum_j A_{ij} d\overline{\mathbf{W}}_{ij} \cdot \mathbf{e}_{ij}, \\ d\tilde{E}_i &= -\frac{1}{2} \sum_j A_{ij} d\overline{\mathbf{W}}_{ij} : \mathbf{e}_{ij} \mathbf{v}_{ij} \\ &\quad + \sum_j C_{ij} dV_{ij}. \end{aligned} \quad (47)$$

Here, i, j label the Voronoi cells, $\mathbf{e}_{ij} = \mathbf{R}_{ij}/|\mathbf{R}_{ij}|$ is the unit vector joining the cell centres, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity between cells i, j . The double dot means double contraction. We have introduced, for each pair i, j of (neighbour) cells, a matrix of independent increments of the Wiener process $d\mathbf{W}_{ij}$. Its traceless symmetric part $d\overline{\mathbf{W}}_{ij}$ is given by

$$d\overline{\mathbf{W}}_{ij}^{\alpha\beta} = \frac{1}{2} \left[d\mathbf{W}_{ij}^{\alpha\beta} + d\mathbf{W}_{ij}^{\beta\alpha} \right], \quad (48)$$

where D is the space dimension. As a convention, superscript refer to tensorial components while subscript label different cells.

In Eqn. (47) we have also introduced an independent increment of the Wiener process for each pair of (neighbour) cells, dV_{ij} . Finally, the functions A_{ij}, B_{ij}, C_{ij} might depend on the state of the system through the mass and internal energy of the particles. We postulate the following symmetry properties

$$\begin{aligned} d\mathbf{W}_{ij} &= d\mathbf{W}_{ji}, \\ dV_{ij} &= -dV_{ji}, \\ A_{ij} &= A_{ji}, \\ B_{ij} &= B_{ji}, \\ C_{ij} &= C_{ji}. \end{aligned} \quad (49)$$

The independent increments of the Wiener processes satisfy the following Itô mnemotechnical rules

$$\begin{aligned} d\mathbf{W}_{ii'}^{\alpha\alpha'} d\mathbf{W}_{jj'}^{\beta\beta'} &= [\delta_{ij}\delta_{i'j'} + \delta_{ij'}\delta_{i'j}]\delta^{\alpha\beta}\delta^{\alpha'\beta'} dt, \\ dV_{ii'} dV_{jj'} &= [\delta_{ij}\delta_{i'j'} - \delta_{ij'}\delta_{i'j}] dt, \\ d\mathbf{W}_{ii'}^{\alpha\alpha'} dV_{jj'} &= 0, \end{aligned} \quad (50)$$

which respect the symmetries (49) under particle interchange. The properties (50) imply the following stochastic properties of the noise in Eqn. (48)

$$\begin{aligned} d\mathbf{W}_{ii'}^{\alpha\alpha'} d\mathbf{W}_{jj'}^{\beta\beta'} &= \frac{1}{2} [\delta_{ij}\delta_{i'j'} + \delta_{ij'}\delta_{i'j}] \\ &\quad \times [\delta^{\alpha\beta}\delta^{\alpha'\beta'} + \delta^{\alpha\beta'}\delta^{\alpha'\beta}] dt. \end{aligned} \quad (51)$$

The dynamical invariants are the total linear momentum and the total energy (no angular momentum conservation is imposed). These total quantities are given by

$$\begin{aligned}
E(x) &= \sum_i \frac{\mathbf{P}_i^2}{2M_i} + \mathcal{E}_i \\
P(x) &= \sum_i \mathbf{P}_i
\end{aligned} \tag{52}$$

Their derivatives with respect to the state variables are

$$\frac{\partial E}{\partial x} \rightarrow \begin{pmatrix} -\frac{\mathbf{v}_j^2}{2} \\ \mathbf{v}_j \\ 1 \end{pmatrix}, \quad \frac{\partial \mathbf{P}}{\partial x} \rightarrow \begin{pmatrix} 0 \\ \mathbf{1} \\ 0 \end{pmatrix}, \tag{53}$$

where $\mathbf{v}_j = \mathbf{P}_j/M_j$ is the velocity of cell i , and $\mathbf{1}$ is the unit tensor. It is a trivial exercise to show that Eqns. (45), which now take the form

$$\begin{aligned}
\sum_i \mathbf{v}_i \cdot d\tilde{\mathbf{P}}_i + d\tilde{E}_i &= 0, \\
\sum_i d\tilde{\mathbf{P}}_i &= 0,
\end{aligned} \tag{54}$$

are exactly satisfied, due to the symmetries (49). In this way, the postulated noises exactly conserve momentum and energy.

A. Deterministic equations

The derivatives of the entropy function are

$$\frac{\partial S}{\partial x} \rightarrow \begin{pmatrix} -\frac{\mu_j}{T_j} \\ 0 \\ \frac{1}{T_j} \end{pmatrix}, \tag{55}$$

where we have defined the chemical potential per unit mass μ_i and temperature T_i according to the usual definitions,

$$\begin{aligned}
\frac{\mu_i}{T_i} &= - \left. \frac{\partial S_i}{\partial M_i} \right|_{\mathcal{E}, \mathcal{V}}, \\
\frac{1}{T_i} &= \left. \frac{\partial S_i}{\partial \mathcal{E}_i} \right|_{M, \mathcal{V}}.
\end{aligned} \tag{56}$$

According to Eqn. (44) theorem, the matrix M is given by

$$M \rightarrow \mathbf{M}_{ij} = \begin{pmatrix} 0 & \mathbf{0}^T & 0 \\ \mathbf{0} & \frac{d\tilde{\mathbf{P}}_i d\tilde{\mathbf{P}}_j^T}{2k_B dt} & \frac{d\tilde{\mathbf{P}}_i d\tilde{E}_j}{2k_B dt} \\ 0 & \frac{d\tilde{E}_i d\tilde{\mathbf{P}}_j^T}{2k_B dt} & \frac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} \end{pmatrix}. \tag{57}$$

The elements of the matrix M are obtained by using the definitions (47) and the property (51). The result is

$$\begin{aligned}
\frac{d\tilde{\mathbf{P}}_i^\alpha d\tilde{\mathbf{P}}_j^\beta}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\delta^{\alpha\beta} + \mathbf{e}_{ik}^\alpha \mathbf{e}_{ik}^\beta \right) \right] \\
&\quad - \frac{A_{ij}^2}{2} \left(\delta^{\alpha\beta} + \mathbf{e}_{ij}^\alpha \mathbf{e}_{ij}^\beta \right), \\
\frac{d\tilde{\mathbf{P}}_i^\alpha d\tilde{E}_j}{dt} &= -\delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\frac{\mathbf{v}_{ik}^\alpha}{2} + \mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \mathbf{e}_{ik}^\alpha \right) \right] \\
&\quad - \frac{A_{ij}^2}{2} \left(\frac{\mathbf{v}_{ij}^\alpha}{2} + \mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \mathbf{e}_{ij}^\alpha \right), \\
\frac{d\tilde{E}_i d\tilde{\mathbf{P}}_j^\alpha}{dt} &= -\delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\frac{\mathbf{v}_{ik}^\alpha}{2} + \mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \mathbf{e}_{ik}^\alpha \right) \right] \\
&\quad + \frac{A_{ij}^2}{2} \left(\frac{\mathbf{v}_{ij}^\alpha}{2} + \mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \mathbf{e}_{ij}^\alpha \right), \\
\frac{d\tilde{E}_i d\tilde{E}_j}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\left(\frac{\mathbf{v}_{ik}}{2} \right)^2 + \left(\mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \right)^2 \right) \right] \\
&\quad + \frac{A_{ij}^2}{2} \left(\left(\frac{\mathbf{v}_{ij}}{2} \right)^2 + \left(\mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \right)^2 \right) \\
&\quad + \delta_{ij} \sum_k C_{ik}^2 - C_{ij}.
\end{aligned} \tag{58}$$

Now we are in position to write the deterministic irreversible part of the dynamics $\dot{x}|_{\text{irr}} = M \frac{\partial S}{\partial x}$, which will be given by

$$\begin{pmatrix} \dot{M}_i \\ \dot{\mathbf{P}}_i \\ \dot{\mathcal{E}}_i \end{pmatrix} \Big|_{\text{irr}} = \sum_j \mathbf{M}_{ij} \begin{pmatrix} -\frac{\mu_j}{T_j} \\ \mathbf{0} \\ \frac{1}{T_j} \end{pmatrix}, \tag{59}$$

The matrix multiplication leads readily to the following equations

$$\begin{aligned}
\dot{M}_i|_{\text{irr}} &= 0, \\
\dot{\mathbf{P}}_i|_{\text{irr}} &= - \sum_j a_{ij} (\mathbf{v}_{ij} + \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \mathbf{e}_{ij}), \\
\dot{\mathcal{E}}_i|_{\text{irr}} &= - \sum_j c_{ij} (T_i - T_j) + \frac{1}{2} \sum_j a_{ij} (\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2),
\end{aligned} \tag{60}$$

where we have introduced the following quantities

$$\begin{aligned}
a_{ij} &= \frac{A_{ij}^2}{8k_B} \left(\frac{1}{T_i} + \frac{1}{T_j} \right), \\
c_{ij} &= \frac{C_{ij}^2}{2k_B T_i T_j}.
\end{aligned} \tag{61}$$

If we make the assumptions

$$\begin{aligned}
a_{ij} &= \eta \frac{A_{ij}}{R_{ij}}, \\
c_{ij} &= \lambda \frac{A_{ij}}{R_{ij}},
\end{aligned} \tag{62}$$

where η is the bulk viscosity, λ the thermal conductivity, and A_{ij} the area of the face i, j , the final deterministic irreversible part of the dynamics (60) becomes

$$\begin{aligned}
\dot{M}_i|_{\text{irr}} &= 0, \\
\dot{\mathbf{P}}_i|_{\text{irr}} &= -\eta \sum_j \frac{A_{ij}}{R_{ij}} (\mathbf{v}_{ij} + \mathbf{v}_{ij} \cdot \mathbf{e}_{ij} \mathbf{e}_{ij}), \\
\dot{\mathcal{E}}_i|_{\text{irr}} &= -\sum_j \lambda \frac{A_{ij}}{R_{ij}} (T_i - T_j) \\
&\quad + \frac{\eta}{2} \sum_j \frac{A_{ij}}{R_{ij}} ((\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 + \mathbf{v}_{ij}^2).
\end{aligned} \tag{63}$$

These equations are *identical* to those obtained in Refs. [5] save for the presence in [5] of a term describing the advection of kinetic energy between cells. This term is very small as it is of third order in \mathbf{v}_{ij} as compared to the second order terms in the rest of the energy equation. In the continuum limit where \mathbf{v}_{ij} is replaced by gradients in velocity such higher order terms are discarded. Note that the second equation in (62) is basically the requirement that the bulk viscosity $\zeta = 2\eta/D$, an assumption made in [5]. Of course, this restriction can be relaxed if desired.

From Eqns. (61) and (62), the functions A_{ij}, C_{ij} are given by

$$\begin{aligned}
A_{ij} &= \left(8k_B \eta \frac{T_i T_j}{T_i + T_j} \frac{A_{ij}}{R_{ij}} \right)^{1/2}, \\
C_{ij} &= \left(2k_B \lambda T_i T_j \frac{A_{ij}}{R_{ij}} \right)^{1/2}.
\end{aligned} \tag{64}$$

B. Stochastic equations

We are still not done, because in order to write the correct Itô stochastic equations $dx|_{\text{irr}} = M \frac{\partial S}{\partial x} + k_B \frac{\partial M}{\partial x} + d\tilde{x}$, we need to compute the term $k_B \frac{\partial M}{\partial x}$. This term can be understood essentially as coming from the stochastic interpretation selected, which is the Itô interpretation.

The derivatives of the matrix M are explicitly written as

$$\sum_j \frac{\partial}{\partial x_j} \mathbf{M}_{ij} = \sum_j \left(\begin{array}{c} 0 \\ \sum_j \frac{\partial}{\partial \mathbf{P}_j} \frac{d\tilde{\mathbf{P}}_i d\tilde{\mathbf{P}}_j}{2k_B dt} + \sum_j \frac{\partial}{\partial E_j} \frac{d\tilde{\mathbf{P}}_i d\tilde{E}_j}{2k_B dt} \\ \sum_j \frac{\partial}{\partial \mathbf{P}_j} \frac{d\tilde{E}_i d\tilde{\mathbf{P}}_j}{2k_B dt} + \sum_j \frac{\partial}{\partial E_j} \frac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} \end{array} \right). \tag{65}$$

By using the results (58) it is easy to compute the above derivatives.

$$\begin{aligned}
k_B \sum_j \frac{\partial}{\partial \mathbf{P}_j} \frac{d\tilde{\mathbf{P}}_i d\tilde{\mathbf{P}}_j}{2k_B dt} &= 0, \\
k_B \sum_j \frac{\partial}{\partial E_j} \frac{d\tilde{\mathbf{P}}_i d\tilde{E}_j}{2k_B dt} &= -\eta \sum_j \frac{A_{ij}}{R_{ij}} d_{ij} (\mathbf{v}_{ij} + \mathbf{v}_{ij} \cdot \mathbf{e}_{ij} \mathbf{e}_{ij}), \\
k_B \sum_j \frac{\partial}{\partial \mathbf{P}_j} \frac{d\tilde{E}_i d\tilde{\mathbf{P}}_j}{2k_B dt} &= (D+1)k_B \sum_j \frac{A_{ij}}{R_{ij}} \left(\frac{T_i T_j}{T_i + T_j} \right) \\
&\quad \times \left(\frac{1}{M_i} + \frac{1}{M_j} \right), \\
k_B \sum_j \frac{\partial}{\partial E_j} \frac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} &= \frac{\eta}{2} \sum_j \frac{A_{ij}}{R_{ij}} d_{ij} ((\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 + \mathbf{v}_{ij}^2) \\
&\quad + \lambda \sum_j \frac{A_{ij}}{R_{ij}} \left[\frac{k_B T_j}{C_i} - \frac{k_B T_i}{C_j} \right],
\end{aligned} \tag{66}$$

where we have introduced

$$d_{ij} = \frac{1}{(T_i + T_j)^2} \left[\frac{T_j^2 k_B}{C_i} + \frac{T_i^2 k_B}{C_j} \right]. \tag{67}$$

Note that d_{ij} is a dimensionless quantity involving the heat capacity at constant volume of mesoparticle i , C_i . For mesoscopic particles, k_B/C_i is a small quantity.

Finally, the irreversible stochastic differential equation $dx|_{\text{irr}} = M \frac{\partial S}{\partial x} dt + k_B \frac{\partial M}{\partial x} dt + d\tilde{x}$ becomes

$$\begin{aligned}
dM_i|_{\text{irr}} &= 0, \\
d\mathbf{P}_i|_{\text{irr}} &= -\eta \sum_j \frac{A_{ij}}{R_{ij}} (1 + d_{ij}) (\mathbf{v}_{ij} + \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \mathbf{e}_{ij}) dt + d\tilde{\mathbf{P}}_i, \\
d\mathcal{E}_i|_{\text{irr}} &= -\sum_j \lambda \frac{A_{ij}}{R_{ij}} (T_i - T_j) dt \\
&\quad + \frac{\eta}{2} \sum_j \frac{A_{ij}}{R_{ij}} (1 + d_{ij}) ((\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 + \mathbf{v}_{ij}^2) dt \\
&\quad - \lambda \sum_j \frac{A_{ij}}{R_{ij}} \left(\frac{k_B T_i}{C_j} - \frac{k_B T_j}{C_i} \right) dt \\
&\quad - (D+1)\eta k_B \sum_j \frac{A_{ij}}{R_{ij}} \frac{T_i T_j}{T_i + T_j} \left[\frac{1}{M_i} + \frac{1}{M_j} \right] dt \\
&\quad + d\tilde{E}_i.
\end{aligned} \tag{68}$$

To leading order in k_B/C_i (which is typically the inverse number of atoms in the cell) these equations coincide with the corresponding equations in Ref. [5]. However, in Ref. [5] the terms proportional to d_{ij} and k_B/C_i are not present, as terms of relative order k_B/C_i are discarded throughout.

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