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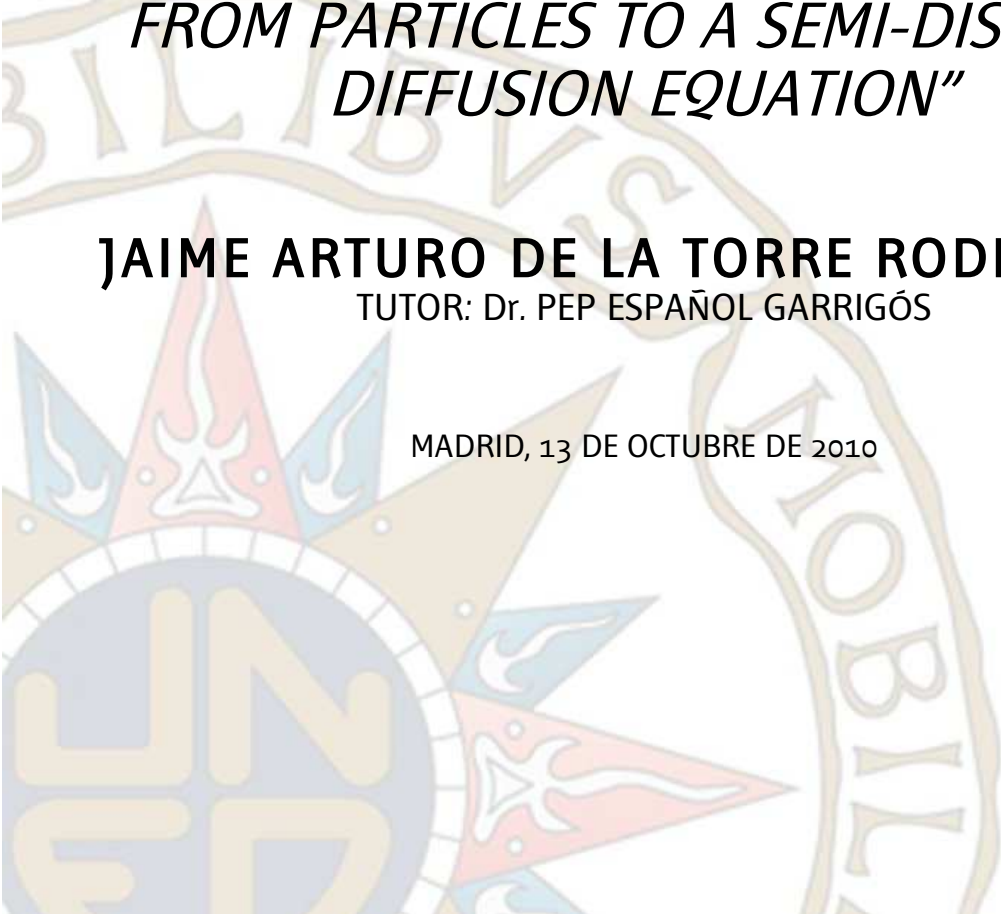
PARA LA OBTENCIÓN DEL TÍTULO

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"COARSE GRAINING BROWNIAN MOTION: FROM PARTICLES TO A SEMI-DISCRETE DIFFUSION EQUATION"

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Coarse-graining Brownian motion: from particles to a discrete diffusion equation

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We consider a recently obtained coarse-grained discrete equation for the diffusion of Brownian particles. The detailed level of description is governed by a Brownian dynamics of non-interacting particles. The coarse-level is described by discrete concentration variables defined in terms of the Delaunay cell. These coarse variables obey a stochastic differential equation that can be understood as a discrete version of a diffusion equation. The diffusion equation contains two basic building blocks which are the entropy function and the friction matrix. The entropy function is shown to be non-additive due to the overlapping of cells in the Delaunay construction. The friction matrix is state dependent in principle, but for near-equilibrium situations it is shown that it may safely evaluated at the equilibrium value of the density field.

I. INTRODUCTION

Coarse-graining is the process by which two levels of description of a given physical system can be related. Usually, it is assumed that the dynamics at a detailed level is known and one is interested in the dynamics at a less detailed, coarser level of description. Perhaps one of the oldest example of such multi-level descriptions is found in simple fluids. At a detailed atomistic level they are reasonably described with force fields between its constituent atoms, with a dynamic given by Newton's laws, while at macroscopic scales they are well described by hydrodynamic fields obeying the Navier-Stokes equations. How to pass from micro to macro descriptions is the issue of coarse-graining or, in other equivalent words, the central problem of non-equilibrium statistical mechanics. For the case of simple fluids, coarse graining has been achieved either by using the one particle distribution in μ-space leading to kinetic theory [1] or by using the hydrodynamic conserved variables [2–4]. In the second case, a crucial assumption is the local equilibrium hypothesis, that states that the system can be regarded as composed of many sub-systems of infinitesimal (compared with macroscopic scales) portions whose properties can be described with equilibrium thermodynamics.

A second, even simpler example of a system to which coarse-graining can be applied is the diffusion of colloidal particles, which at a detailed level are described with the positions of each colloidal particle. The N-particle probability of finding a given configuration of the colloidal particles in space obeys the Smoluchowski equation [5]. Again, two coarse-graining approaches can be followed here, which differ in the selection of the coarse-grained variables [6, 7].

On one hand, one may choose the probability density $n(\mathbf{r}, t)$ of finding a particle at $\mathbf{r}$. The obtention of a dynamic equation for $n(\mathbf{r}, t)$ has been a subject of intense research in the generalization of Density Functional Theory (DFT) to the dynamic realm in recent years [8]. For the case of colloidal systems, this Dynamic Density Functional Theory (DDFT), produces a non-linear generalization of the well-known diffusion equation for $n(\mathbf{r}, t)$, that takes into account the equilibrium microstructure of the system. In that sense, DDFT is a coarse-grained theory of diffusion. We have shown how DDFT can be obtained with the projection operator technique [9]. DDFT gives information at scales on the size of the colloidal particles, and this is, in fact, one of the reasons of the large interest on this technique in recent years [10–15]

On the other hand, we may choose as coarse-grained variable the number of particles per unit volume $c_{\mathbf{r}}$. While in principle, the average concentration $c(\mathbf{r}, t) = \langle c_{\mathbf{r}} \rangle_t$ is expected to be proportional to the probability density $n(\mathbf{r}, t)$, both quantities have a very different meaning and definition. In fact, the concentration field $c_{\mathbf{r}}$ must be defined by recurring to an infinitesimal volume and counting the number of colloidal particles within. Therefore, it makes sense to speak about fluctuations of the number of particles in that volume around the average value. However, it makes no sense to talk about "the fluctuations around the one-particle probability density $n(\mathbf{r}, t)$". As a consequence, the dynamic equation for $c_{\mathbf{r}}$ is a stochastic partial differential equation [16, 17], while the dynamic equation for $n(\mathbf{r}, t)$ is an ordinary differential equation [18]. While one can use a "continuum notation", it should be borne in mind that the concentration field has rooted in its definition the notion of an infinitesimal volume. This means that it cannot vary in length scales smaller than this infinitesimal volume.

In order to acknowledge from the outset the intrinsic presence of an infinitesimal volume, we have followed in Ref. [19] a coarse-graining from the detailed Smoluchowski level to a *discrete concentration* level of description. At the coarse-grained level the system is characterized by a set of discrete concentration variables that are defined through the Delaunay cell associated to a set of nodes seeded through the space. The resulting dynamics for the concentration variables is a stochastic discrete version of the diffusion equation. In Ref. [20] we have discussed that a definition of the discrete concentration in terms of the Voronoi cells of the nodes is problematic while the Delaunay cells provide a well-sounded formulation of the coarse-grained dynamics.

In the present paper, we study in detail how to ob-

tain the two basic objects of the coarse-grained equation, which are the friction matrix and the entropy function. A crucial assumption in hydrodynamic descriptions is the *local equilibrium assumption* in which the entropy function dependent on the hydrodynamic fields is expressed as the integral of the equilibrium entropy density. This means that the entropy is an additive function. While for the case of the discrete variables defined in terms of the non-overlapping Voronoi cell such additive approximation can be justified under certain conditions (see, for example,[21, 22]), the fact that the Delaunay construction has overlapping cells may shed some doubts to the validity of this local equilibrium approximation. On the other hand, the friction matrix was computed in I under an equilibrium approximation that rendered the friction matrix state independent. We explore in this paper whether it is necessary to include the dependence on the state of the friction matrix.

II.   DISCRETE DIFFUSION

The macroscopic description of the dilute colloidal suspension is constructed by seeding the space with M *nodes* located at $\mathbf{r}_\mu$ and associating to each node the number of particles per unit volume in the region surrounding it. If we denote the microscopic state by $z = \{\mathbf{r}_i\}$, i.e. the collection of positions $\mathbf{r}_i$ of the Brownian particles, then the concentration $n_\mu(z)$ of node $\mathbf{r}_\mu$ is defined as

$$n_\mu(z) = \sum_i^N \delta_\mu(\mathbf{r}_i) \tag{1}$$

where we have introduced the discrete delta function through

$$\delta_\mu(\mathbf{r}) = \frac{\Phi_\mu(\mathbf{r})}{\mathcal{V}_\mu} \tag{2}$$

The form for $\Phi_\mu(\mathbf{r})$ is a finite element defined on the Delaunay triangulation, and the explicitly form is given in I. It satisfies the partition of unity property $\sum_\mu^M \Phi_\mu(\mathbf{r}) = 1$, ensuring that no matter the microscopic state z, the sum of the discrete concentration variables gives the correct number of particles in the system, i.e. $\sum_\mu \mathcal{V}_\mu n_\mu(z) = N$. The volume $\mathcal{V}_\mu$ of node μ is defined by

$$\mathcal{V}_\mu = \int d\mathbf{r} \Phi_\mu(\mathbf{r}) \tag{3}$$

We have shown in I that the dynamics of the probability $P(\mathbf{n}, t)$ that the system adopts a particular configuration $\mathbf{n} = n_1, \cdots, n_M$ of concentrations in each node at time t is governed by the following Fokker-Planck equation (FPE)

$$\frac{\partial}{\partial t} P(\mathbf{n}, t) = -\frac{\partial}{\partial n_\mu} \left[M_{\mu\nu}(\mathbf{n}) \frac{\partial}{\partial n_\nu} S(\mathbf{n}) \right] P(\mathbf{n}, t)$$

$$+ k_B \frac{\partial}{\partial n_\mu} M_{\mu\nu}(\mathbf{n}) \frac{\partial}{\partial n_\nu} P(\mathbf{n}, t) \tag{4}$$

where repeated indices are summed over, and k_B is the Boltzmann's constant. In order to have an *explicit* form for the discrete diffusion equation we need to compute in closed form the entropy function $S(\mathbf{n})$ and the friction matrix $M_{\mu\nu}(\mathbf{n})$. As we will see, both quantities are expressed in terms of conditional averages which are difficult to compute explicitly, and we will need to perform some approximations. The purpose of this paper is to assess these approximations. We consider in the following sections each function separately.

III.   THE ENTROPY

In this section, we will evaluate the entropy function of the discrete concentration level of description. The entropy function $S(\mathbf{n})$ is obtained from the equilibrium distribution function

$$P^{\mathrm{eq}}(\mathbf{n}) = \delta\left(\sum_\mu^M \mathcal{V}_\nu n_\mu - N \right) \exp\left\{ \frac{S(\mathbf{n})}{k_B} \right\} \tag{5}$$

which is the stationary solution of the FPE (4). Eq. (5) is the usual expression in Einstein's fluctuation theory [23], suitably modified to include dynamical invariants [24]. While we refer to the logarithm of the probability as the entropy, such a quantity may be better described as a free energy depending on the context. The probability (5) is *microcanonical* in the concentration as it originates from a dynamics that conserves the number of colloidal particles.

The equilibrium distribution function can be computed from the microscopic expression

$$P^{\mathrm{eq}}(\mathbf{n}) = \int dz \rho^{\mathrm{eq}}(z) \prod_\mu^M \delta\left(n_\mu(z) - n_\mu \right) \tag{6}$$

where $\rho^{\mathrm{eq}}(z)$ is the equilibrium distribution of the Brownian particles. Eq. (6) is the way to relate a probability distribution $\rho^{\mathrm{eq}}(z)$ over z with the probability distribution of a function of z, in this case, the concentration variable $n_\mu(z)$. In a periodic box of volume V_T in the absence of external fields, one has an uniform distribution $\rho^{\mathrm{eq}}(z) = V_T^{-N}$. The explicit exact calculation of $P^{\mathrm{eq}}(\mathbf{n})$ is difficult. However, under the assumption that the number of particles per node is sufficiently large, the probability $P(\mathbf{n})$ becomes a Gaussian or in other words, the entropy is $S(\mathbf{n}) \approx S^{\mathrm{Gauss}}(\mathbf{n})$, where

$$S^{\mathrm{Gauss}}(\mathbf{n}) \equiv -\frac{k_B}{2} \frac{6a}{n^*} \sum_{\mu\nu} (n_\mu - n^*) A_{\mu\nu}^{-1} (n_\nu - n^*) \tag{7}$$

is a quadratic function of the concentration (see Appendix VIII). Here a is the volume $\mathcal{V}_\mu$ of the Delaunay cell of the node μ (which is just a length in this one-dimensional case, equal for all nodes). The matrix of correlations is directly related to $A_{\mu\nu}$, this is

$$\langle (n_\mu - n^*)(n_\nu - n^*) \rangle^{\mathrm{eq}} = \frac{n^*}{6a} A_{\mu\nu} \qquad (8)$$

The matrix $A_{\mu\nu}$ and its inverse are given in the Appendix VIII.

Note that this Gaussian form for the probability $P(\mathbf{n})$ does not factorize into products of independent probabilities of each node. This is due to the fact that the Delaunay cells of two neighboring nodes overlap causing non-vanishing correlations of the concentration of neighboring nodes, even for statistically independent Brownian particles. As a consequence, $P(\mathbf{n})$ does not factorize and, therefore, the entropy function is not an additive function in general. Nevertheless, and for the sake of comparison, we will consider the validity of the local equilibrium approximation

$$P^{\mathrm{eq}}(\mathbf{n}) \approx \prod_\mu P(n_\mu) \qquad (9)$$

where $P(n_\mu)$ is the exact probability of finding n_μ particles per unit volume in the node μ. This factorization approximation implies that the entropy is of the form $S(\mathbf{n}) \approx S^{\mathrm{le}}(\mathbf{n})$ where

$$S^{\mathrm{le}}(\mathbf{n}) \equiv \sum_\mu \mathcal{V}_\mu s(n_\mu) \qquad (10)$$

and the total entropy is the sum of the entropies of each cell. The fact that "entropy is additive" as in Eq. (10) is one aspect of the *local equilibrium assumption*. The form of $s(n_\mu)$ is determined by the form of the single node probability $P(n_\mu)$. We compute explicitly in the Appendix VIII this probability of a single node in a one-dimensional setting. The result is given in Eq. (48).

As it is clear from Eq. (4), we will need the derivative of the entropy function with respect to the concentration variable. It is convenient to introduce the chemical potential of the node ν as

$$\mu_\nu \equiv -\frac{T}{\mathcal{V}_\nu} \frac{\partial S}{\partial n_\nu}(\mathbf{n}) \qquad (11)$$

For the different entropy models we have the following models for the chemical potential

$$\mu_\mu^{\mathrm{Gauss}}(\mathbf{n}) = k_B T \frac{6}{n^*} \sum_\nu A_{\mu\nu}^{-1}(n_\nu - n^*)$$

$$\mu_\mu^{\mathrm{le}}(\mathbf{n}) = k_B T \frac{3}{2} \frac{n_\mu - n^*}{n^*} \qquad (12)$$

IV. THE FRICTION MATRIX

In this paper we are considering the process of coarse-graining a colloidal system which is, in fact, described at a detailed level with the Smoluchowski equation. Of course, the Smoluchowski equation itself describes the system at a coarse-grained level, because the only information kept is the position of the colloidal particles and the rest of atomic degrees of freedom in the system is eliminated and its effects modeled with thermal noise. When passing from a stochastic level to a stochastic level as in this case, it is well-known that the friction matrix has two contributions [25], [26]. The first contribution is purely static and reflects the direct transfer of the noise of the detailed level to the coarse-level [27]. The second contribution, which is given in terms of a Green-Kubo expression, accounts for the additional friction that emerges from the elimination of degrees of freedom. If the detailed level is given by Hamilton's equations, only the Green-Kubo contribution exists. On the other hand, in the non-interacting stochastic problem that we consider in the present paper, only the static part of the friction contributes as shown in Ref I. In this case, the friction matrix has the explicit form shown in Ref I

$$M_{\mu\nu}(\mathbf{n}) = \frac{D}{k_B} \left\langle \sum_i \frac{\partial n^\mu}{\partial \mathbf{r}_i} \cdot \frac{\partial n^\nu}{\partial \mathbf{r}_i} \right\rangle^{\mathbf{n}} \qquad (13)$$

By using the definition of the concentration variable in Eq. (1) we obtain

$$M_{\mu\nu}(\mathbf{n}) = \frac{D}{k_B} \sum_i^N \langle \nabla \delta_\mu(\mathbf{r}_i) \cdot \nabla \delta_\nu(\mathbf{r}_i) \rangle^{\mathbf{n}} \qquad (14)$$

The explicit form of the gradient of the discrete delta function is (see Ref. I for the notation)

$$\nabla \delta_\mu(\mathbf{r}) = \frac{1}{\mathcal{V}_\mu} \sum_{e_\mu} \mathbf{b}_{e_\mu} \theta_{e_\mu}(\mathbf{r}) \qquad (15)$$

where $\theta_{e_\mu}(\mathbf{r})$ is the characteristic function of the sub-element e_μ (see Fig. 1 for the 1D situation). The gradient is a discontinuous vector field that takes the constant vector value $\mathbf{b}_{e_\mu}$ within each element e_μ, and zero outside the Delaunay cell. This vector $\mathbf{b}_{e_\mu}$ is directed towards the node μ. Eq. (14) becomes then

$$M_{\mu\nu}(\mathbf{n}) = \frac{D}{k_B} \frac{1}{\mathcal{V}_\mu \mathcal{V}_\nu} \sum_{e_\mu e_\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \left\langle \sum_i^N \theta_{e_\mu}(\mathbf{r}_i) \theta_{e_\nu}(\mathbf{r}_i) \right\rangle^{\mathbf{n}} \qquad (16)$$

Because the sub-elements e_μ, e_ν are non-overlapping, the only surviving terms in the sum over particles in Eq. (16) are those with $e_\mu = e_\nu$. This results in

$$M_{\mu\nu}(\mathbf{n}) = \frac{D}{k_B} \sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu \mathcal{V}_\nu} n_e(\mathbf{n}) \qquad (17)$$
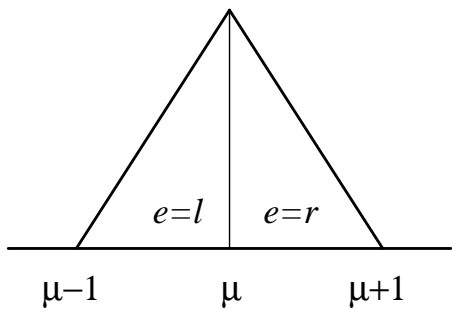
FIG. 1: The finite element $\Phi_\mu(r)$ in a 1D regular lattice. Every node μ has two sub-elements e (left l and right r) which are shared by the neighbors.

Here, e is any of the common elements of the neighbor nodes μ, ν, $\mathbf{b}_{e_\mu}$ is the vector of the element e, directed towards the node μ, $\mathbf{b}_{e_\nu}$ is the vector of the element e, directed towards the node ν, and the concentration n_e of the sub-element e is defined as

$$n_e(\mathbf{n}) \equiv \frac{1}{\mathcal{V}_e} \left\langle \sum_i^N \theta_e(\mathbf{r}_i) \right\rangle^{\mathbf{n}} \tag{18}$$

where $\mathcal{V}_e$ is the volume of the sub-element. In principle, the number density of the element e may depend on the value $\mathbf{n}$ of the density in all the nodes, this is, $n_e = n_e(\mathbf{n})$. However, we expect that n_e will only depend on the values of the nodal points of the element e. We will approximate $n_e(\mathbf{n})$ by the arithmetic mean of the concentration of the $d+1$ nodal values of the sub-element e, this is,

$$n_e(\mathbf{n}) \approx \frac{1}{d+1} \sum_{\nu \in e} n_\nu \tag{19}$$

This local equilibrium assumption in the friction matrix can be checked explicitly by sampling the conditional ensemble with a fictitious dynamics as described in appendix IX. For a one dimensional case, the local equilibrium assumption (19) is simply

$$n_e = \frac{n_\mu + n_{\mu+1}}{2} \tag{20}$$

where $\mu, \mu+1$ are the nodes corresponding to the sub-element e, in this case a line segment.

In Fig. 2 we plot the comparison of the conditional average computed with the sampling method given in Eq. (56) of appendix IX of the concentration of the sub-element n_e defined in Eq. (18), when the the input density profile $\mathbf{n}$ has a sinusoidal shape $n_\mu = 10 + 3\sin(r_\mu/a)$. The agreement is very good and shows indeed that the concentration n_e of the sub-element e is the arithmetic mean of the nodal concentrations, thus confirming Eq. (20). This is better appreciated in Fig. (3) where we plot n_e as a function of $\frac{n_\mu + n_{\mu+1}}{2}$.
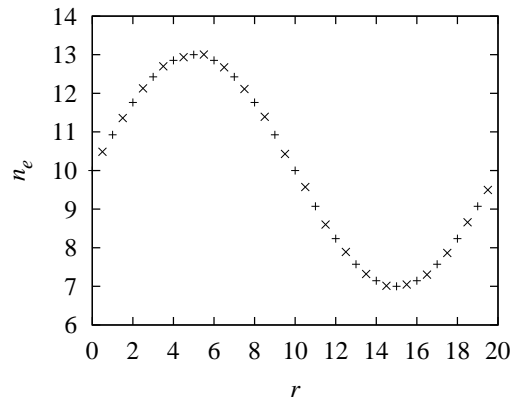

FIG. 2: The conditional average n_e defined in Eq. (18). Crosses $\times$ are the input value $\mathbf{n}$, which in this case is $n_\mu = 10 + 3\sin(r_\mu/a)$. Pluses $+$ are the result of performing the conditional average average in Eq. (18) with the sampling method given in Eq. (56).
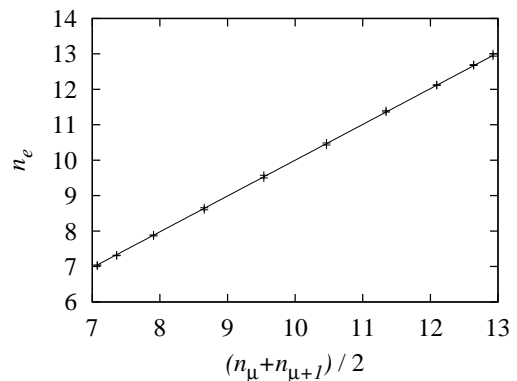

FIG. 3: The conditional average n_e as a function of $\frac{n_\mu + n_{\mu+1}}{2}$. The straight line indicates that these quantities are identical.

While the above results give convincing evidence of the proposal in Eq. (19), they have been obtained for the case of a generically "non-zero smooth discrete field". Care should be taken when a node μ is empty, implying $n_\mu = 0$. It is clear that when a node μ does not contain any Brownian particle, all the sub-elements of this node are also empty and $n_e = 0, \forall e \in \mu$. This is in contrast with the prediction in Eq. (19) that would still give some non-zero value to the sub-element, because the other nodes of the sub-element are not empty.

Eq. (17) is the explicit form of the friction matrix, in terms of geometric quantities and the state variables $\mathbf{n}$. In Ref. [19] we gave the expression of the friction matrix under the further approximation that $M_{\mu\nu}(\mathbf{n}) \approx \langle M_{\mu\nu} \rangle^{\mathrm{eq}}$. In this case we have simply

$$M_{\mu\nu} = \frac{D}{k_B} n^* \Delta_{\mu\nu} \tag{21}$$

where the discrete Laplace operator

$$\Delta_{\mu\nu} \equiv \int d\mathbf{r} \nabla \delta_\nu(\mathbf{r}) \cdot \nabla \delta_\mu(\mathbf{r})$$
$$= \sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu \mathcal{V}_\nu} \qquad (22)$$

is discussed in I.

Now, we have several models for the entropy $S(\mathbf{n})$ and its derivatives in Eq. (12) and an explicit expression for the friction matrix $\mathbf{M}(\mathbf{n})$ given in Eq. (17) with (19) or (21). We are ready to use these explicit forms into numerical simulations. As numerical simulations of stochastic processes are best performed at the level of the stochastic differential equations (SDE) rather than at the level of Fokker-Planck Equations we consider in the next section the SDE which are equivalent to the FPE (4).

V. THE STOCHASTIC DIFFERENTIAL EQUATION

The connection between FPE and SDE is well-known [28]. For the present case of the FPE given in Eq. (4) the corresponding SDE is

$$dn_\mu(t) = M_{\mu\nu}(\mathbf{n}) \partial_\nu S(\mathbf{n}) dt + k_B \partial_\nu M_{\mu\nu}(\mathbf{n}) dt + d\tilde{n}_\mu(t) \qquad (23)$$

where $d\tilde{n}_\mu(t) = B_{\mu i}(\mathbf{n}) dW_i(t)$ is a linear combination of independent increments of the Wiener process, fulfilling the Fluctuation-Dissipation theorem

$$B_{\mu i}(\mathbf{n}) B_{\nu i}(\mathbf{n}) = 2k_B M_{\mu\nu}(\mathbf{n}) \qquad (24)$$

or in a more informal way

$$\frac{d\tilde{n}_\mu d\tilde{n}_\nu}{2k_B dt} = M_{\mu\nu} \qquad (25)$$

The definition of the noise term $d\tilde{n}_\mu(t)$ is not unique because there are many different matrices $B_{\mu i}(\mathbf{n})$ that fulfill Eq. (24). A particular convenient possibility is the following noise term

$$d\tilde{n}_\mu = \frac{1}{\mathcal{V}_\mu} \sum_{e_\mu} \mathbf{b}_{e_\mu} \cdot d\tilde{\mathbf{J}}_{e_\mu} \qquad (26)$$

Here, $d\tilde{\mathbf{J}}_{e_\mu}$ is a vector whose components are proportional to independent Wiener processes. Note that for each sub-element of the Delaunay triangulation (tetrahedralization in 3D) we have a random vector $d\tilde{\mathbf{J}}_{e_\mu}$. The random mass flux has the explicit form, suggested in Ref. [29]

$$d\tilde{\mathbf{J}}_{e_\mu}^\alpha \equiv \sqrt{2Dn_{e_\mu} \mathcal{V}_{e_\mu}} dV_{e_\mu}^\alpha \qquad (27)$$

The independent increments of the Wiener process satisfy the mnemotechnical Ito rule

$$dV_{e_\mu}^\alpha dV_{e_\nu}^{\alpha'} = \delta_{e_\mu e_\nu} \delta^{\alpha\alpha'} dt \qquad (28)$$

Therefore, we have the following variances of the stochastic mass flux defined in Eq. (27)

$$d\tilde{\mathbf{J}}_{e_\mu}^\alpha d\tilde{\mathbf{J}}_{e_\nu}^\beta = \delta_{e_\mu e_\nu} \delta^{\alpha\beta} 2Dn_{e_\mu} \mathcal{V}_{e_\mu} dt \qquad (29)$$

It is straightforward to show, by using (29), that the proposed noise in Eq. (26) fulfills the Fluctuation-Dissipation theorem (25).

In order to write the stochastic differential equations (23), we need to compute the term $k_B \nabla M(x)$

$$k_B \sum_\nu \frac{\partial}{\partial n_\nu} M_{\mu\nu} = D \sum_\nu \frac{1}{\mathcal{V}_\mu \mathcal{V}_\nu} \sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \mathcal{V}_e \frac{\partial n_e}{\partial n_\nu} \qquad (30)$$

For the arithmetic mean approximation in Eq. (19) we have

$$\frac{\partial n_e}{\partial n_\nu} = \frac{1}{d+1} \qquad (31)$$

The final SDE for the discrete concentration variable is

$$dn_\mu(t) = -D \sum_\nu \left(\sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu} n_e \right) \frac{\mu_\nu}{k_B T} dt$$
$$+ D \sum_\nu \left(\sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu \mathcal{V}_\nu} \right) \frac{\partial n_e}{\partial n_\nu} dt$$
$$+ d\tilde{n}_\mu \qquad (32)$$

This SDE is to be interpreted in Ito sense. One nice property of these Eqs. (32) is that the total number of colloidal particles is conserved, this is, $\sum_\mu \mathcal{V}_\mu n_\mu(t) = N$. This is a direct consequence of the definition of the concentration field in terms of the Delaunay cell and the fact that the finite element functions satisfy the partition of unity property. Perhaps the simplest way to see that Eqs. (32) conserve the total number of particles is from the friction matrix expression in Eq. (13) and the fact that the density in Eq. (1) satisfies $\sum_\mu \mathcal{V}_\mu n_\mu(z) = N$, independent of the configuration z.

Note that the noise term $d\tilde{n}_\mu$ in Eqs. (26),(27) scales as the inverse of the square of volume of the cells, while the term (31) scales as the inverse of the volume. This means that by increasing the size of the cells and keeping the average concentration fixed, the effect of the noise terms diminish. Thermal fluctuations are indeed dependent on

the resolution used. This is, of course, consistent with the fact that the probability distribution $P(\mathbf{n})$ becomes more and more peaked as the cell size increases. In the limit of large cells, we may neglect thermal fluctuations in Eq. (32) and we obtain a deterministic evolution equation for the concentration given by

$$\dot{n}_\mu = -D \sum_\nu \left(\sum_{e \in \mu\nu} \mathbf{b}_{e_\mu} \cdot \mathbf{b}_{e_\nu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu} n_e \right) \frac{\mu_\nu}{k_B T} \quad (33)$$

As shown in Appendix X this equation can be understood as a discrete version of the diffusion equation.

VI. NUMERICAL RESULTS

In this section, we present the results of numerical simulations of the fluctuating discrete diffusion equation (32) for the model systems in Eqs. (12) with the friction matrix (17) with (20) and (21). A predictor-corrector Euler method [30] is used for the integration of the SDE. We will compare three different models: the real dynamic using a Brownian dynamic (referred as BD), the Gaussian model in which $\mu_\mu = \mu_\mu^{\text{Gauss}}$ (GA) and the local equilibrium model $\mu_\mu = \mu_\mu^{\text{le}}$ (LE).

We consider the simplest case where the system is 1D, and the nodes are located in a regular lattice separated by a distance a, with periodic boundary conditions (i.e. node $M + 1$ coincides with node 1 and node 0 coincides with node M). We need first to particularize Eq. (32) to this situation. The result, presented in Appendix XI is

$$\begin{aligned} dn_\mu = &-\frac{D}{k_B T} \frac{1}{a^2} \frac{n_\mu + n_{\mu-1}}{2} (\mu_\mu - \mu_{\mu-1}) dt \\ &-\frac{D}{k_B T} \frac{1}{a^2} \frac{n_\mu + n_{\mu+1}}{2} (\mu_\mu - \mu_{\mu+1}) dt \\ &+\frac{\sqrt{Da}}{a^2} (n_\mu + n_{\mu-1})^{1/2} dV_\mu \\ &-\frac{\sqrt{Da}}{a^2} (n_\mu + n_{\mu+1})^{1/2} dV_{\mu+1} \end{aligned} \quad (34)$$

Here dV_μ is an independent increment of the Wiener process associated to the left element of node μ.

The above equations do exactly satisfy the conservation of the number of particles $N = \sum_\mu n_\mu$ but do not necessarily ensure that the concentration of the nodes is always positive. Indeed, due to fluctuations Eqs. (34) may lead, from time to time, to negative values of n_μ. However, an empty cell cannot go emptier. The failure of the discrete diffusion equation to describe this physics must be attributed to the approximation of both the entropy function as a Gaussian and the friction matrix as dependent on the arithmetic mean. Note that if a cell is empty, then the noise terms corresponding to the sub-elements of that cell should vanish, preventing any stochasticity to empty already empty cells. Nevertheless we expect that this occurs very infrequently when the

number of particles per node should is large. Note that the local equilibrium assumption on which the friction matrix expression relies, requires certain "smoothness" of the profiles. Such a smoothness can be achieved only if we have many particles per node.

The probability that a single node has a particular value of the concentration at equilibrium is plotted in Fig. (4). Three models, Brownian Dynamic (BD), simulation Gaussian (GA) and Local Equilibrium (LE) are shown. The relative error between BD and GA is less than 1%. Notice that the overlapping between GA and LE is a direct consequence of the construction of LE. Indeed, we postulated the explicit expression for LE from the probability of the Gaussian model.
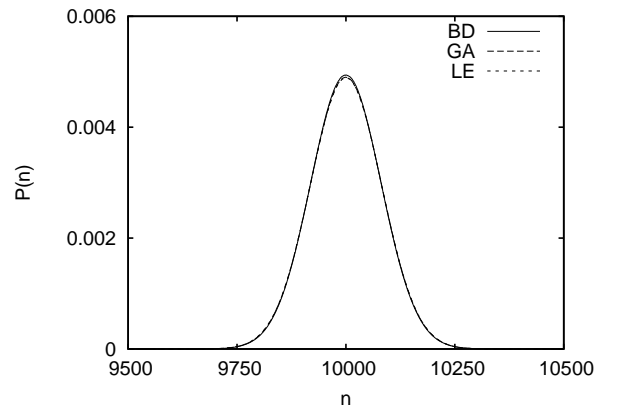

FIG. 4: Probability of finding a particular value of the concentration, n, in a single node using three models. From top to bottom, BD shows a Brownian Dynamic simulation; GA uses the Gaussian approximation and LE the local equilibrium assumption. All three simulations were performed with $n^* = 10000$ particles per node.

While the probability of a single node is essentially the correct one for the two models (GA and LE coinciding with BD), the situation is very different for the joint probability of neighbour nodes. In Fig. (5) we compare the joint probability $P(n_\mu, n_{\mu+1})$ for BD and GA. The results show that very good agreement is obtained between the BD simulation and the Gaussian approximation for the entropy function. In particular, it is apparent that the joint probability has a structure along the diagonal, which is a reflection of the non-vanishing correlation between neighbouring cells.

On the other hand, the LE equilibrium approximation produces a perfectly isotropic distribution, as shown in Fig. (6). The isotropy is a reflection of the product structure of the joint probability in terms of the probability of a single node. Of course, the LE approximation neglects correlations between the concentration of neighbouring cells, leading to large errors when compared with the true BD simulations.

Next we have considered the dynamic behaviour of the different models by computing the autocorrelation function $\langle n_\mu n_\mu(t) \rangle^{\text{eq}}$ of the concentration of each node. This
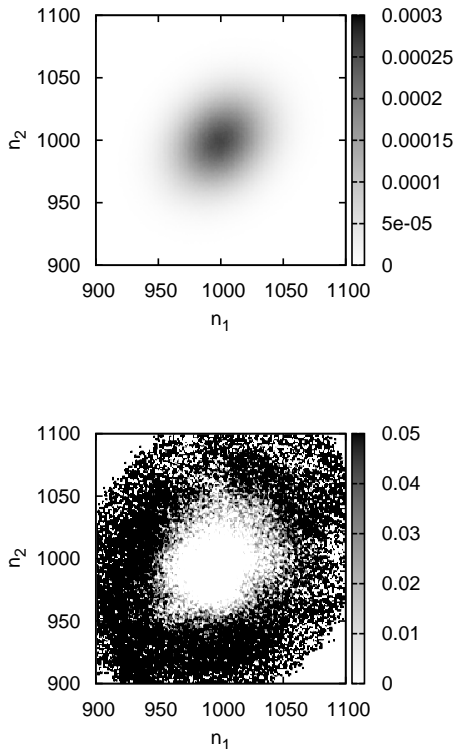
FIG. 5: Probability of finding a node with concentration n_1 and a neighbor node with concentration n_2. On top, the probability of a Brownian Dynamic simulation, shown as a bidimensional map. On the bottom, the relative error between BD and GA. In the region where the probability $P(n_1, n_2)$ is greater than 0.01 %) the relative error is lower than 1 %.

FIG. 6: Probability of finding a node with concentration n_1 and a neighbor node with concentration n_2. On top, the joint probability of neighbour cells in a Local Equilibrium simulation, shown as a bidimensional map. On the bottom, the relative error between BD and LE. The LE model does not allow us to reproduce correctly the joint probability of consecutive nodes because it assumes that neighbor nodes are statistically independent.

correlation function has been computed analytically in Ref. I, thanks to the simplicity of the Brownian dynamics of independent particles. In Fig. (7) we plot the analytical result together with the simulation results of the Gaussian (GA) and Local Equilibrium (LE) models. While the GA model reproduces correctly the theoretical result, the LE model fails to capture the proper autocorrelation function.

The results presented in this section have been conducted with the state-dependent friction matrix given in Eq. (17) with (19) for the 1D case (this is, Eqs. (34) . We have also conducted similar simulations with the state independent friction matrix in Eq. (21). For the near-equilibrium situations analysed in the present paper, we do not find any significant difference between the two models.

VII. CONCLUSION

In the present article we have studied the numerical behaviour of a discrete model for diffusion based on the Delaunay construction that has been proposed in
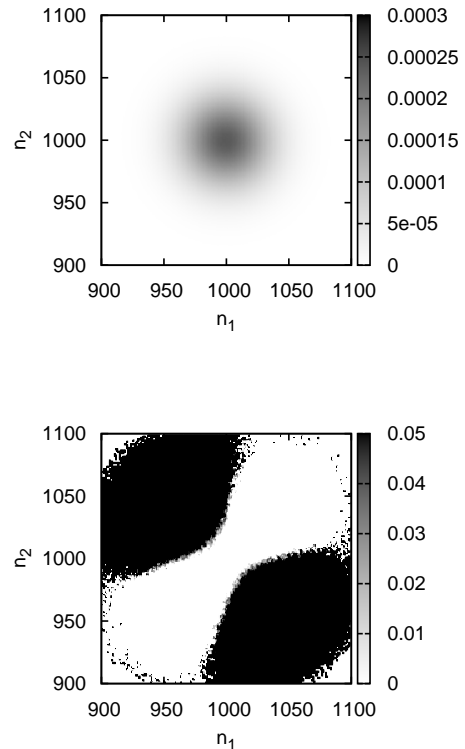
Ref. [19]. The simplicity of the model describing non-interacting Brownian particles allows one to focus on the specific aspects of the Delaunay construction without having to bother about other issues that will necessarily arise when considering more complex systems like interacting colloidal particles and simple fluids. Discrete models based on the Delaunay construction for hydrodynamics are the natural outcome of a coarse-graining process that allows to describe in a thermodynamically consistent way the introduction of thermal fluctuations in finite-element-like discretizations of Navier-Stokes equations [20]. This discrete hydrodynamic Delaunay model shows a great promise for the consistent coupling of atomically described fluids and hydrodynamic descriptions, where the coupling between regions of different detail is done with due account of thermal fluctuations. It is therefore, of utmost importance to understand the behaviour of the models based on the Delaunay construction in simple cases before entering the more challenging and interesting situations. The discrete diffusion equation for non-interacting Brownian particles that we have
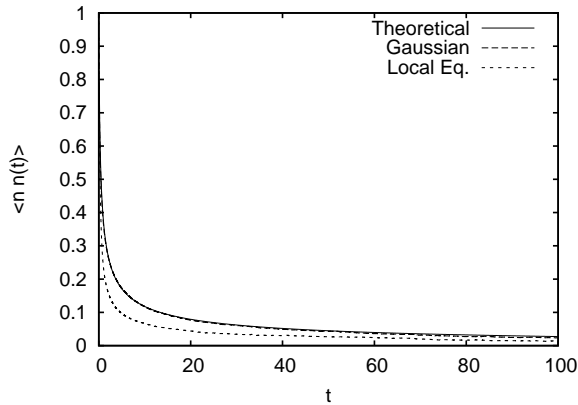
FIG. 7: Autocorrelation function for the different models. BD is the the autocorrelation obtained analytically for the Brownian Dynamics. Slashed curve GA is the simulation result for the Gaussian model. Dotted line LE is the simulation result for the Local Equilibrium model.

considered here is one of these simplest cases.

Two building blocks, the entropy function and the friction matrix, appear in the discrete diffusion equation. Both are functions of the full state of the system, which is the set of concentrations in the M nodes of the system. Although these building blocks are defined in terms of conditional averages, the calculation of this multidimensional functions is not an easy task in general. In particular, a sampling of the conditional averages is subject to the curse of dimensionality. For example, in a system with 100 nodes, a naive histogram for getting the equilibrium distribution function (from which the entropy function can be inferred) in the space 100 dimensional space is absolutely unpractical. It is absolutely necessary to make modeling assumptions on the form of the entropy function. In the present paper we have considered two models, a Gaussian model, which works very well when the typical number of particles for node is large, and a Local Equilibrium model that captures correctly the statistical distribution of particles of a single node, but neglects correlations between neighbouring nodes. The numerical results show that the LE model is not appropriate to model not only the joint statistics of equilibrium fluctuations, but also the dynamics of a single node is poorly recovered. In other words, for the Delaunay construction, the overlapping of neighbour cells needs to be properly accounted for in the entropy function, which then becomes a non-additive function (it cannot be expressed as the sum of single entropies associated to each node). On the other hand, a quadratic expression for the entropy reproduces very well both the static properties and also the dynamic properties of the underlying Brownian dynamics model. Concerning the second building block, which is the friction matrix, we have proposed a state-dependent friction matrix based on a simple arithmetic mean ansatz. We have validated this ansatz from an explicit calculation of the conditional averages involved in the definition of the friction matrix. Nevertheless, it turns out that taking into account the state dependence of the friction matrix does not have a significant impact in the simulation results as compared with an even simpler ansatz for the friction matrix based on a state-independent assumption.

Both, the Gaussian approximation for the entropy and the state-independent assumption for the friction matrix are expected to fail when the number of particles per node is very small. For the entropy, deviations from Gaussian behaviour are expected already at the level of the single node equilibrium distribution function. On the other hand, the friction matrix must reflect the fact that the transport of particles out of an empty cell is forbidden, thus preventing any node from taking negative values of the concentration field. For the practical situations we have in mind (coupling of regions described at different detail but in near-equilibrium situations) such non-trivial behaviour seems to be not necessary, but in highly non-equilibrium situations like shock and rarefaction situations, a proper modelling of the entropy function and the friction matrix is necessary.

VIII.   APPENDIX: THE PROBABILITY $P(\mathbf{n})$

In this appendix we compute the probability distribution $P(\mathbf{n})$ that at equilibrium the discrete concentration "field" takes the values $\mathbf{n}$. We consider a 1D situation where N Brownian particles move in a segment of length L. The configuration of the particles is denoted by $z = \{q_i\}, i = 1, \cdots, N$, where q_i is the position of particle i. We seed the segment with M nodes located at $r_\mu = \mu a, \mu = 1, \cdots, M$, where $a = \frac{L}{M}$ is the lattice spacing, and assume periodic boundary conditions (i.e. we have $r_0 = r_M$). The concentration variable $n_\mu(z)$ in the node μ given in general by Eq. (1) is in the present one dimensional case

$$n_\mu(z) = \frac{1}{a} \sum_{i=1}^{N} \Phi_\mu(q_i) \qquad (35)$$

where the tent function is given in Eq. (57). Note that the volume of the Delaunay cell is a in the present one-dimensional case.

The probability $P(\mathbf{n})$ introduced in Eq. (6) now takes the form

where L^{-N} is the uniform distribution.

$$P(\mathbf{n}) \;=\; \int dz \prod_{\mu}^{M} \delta\left(n_{\mu}(z) - n_{\mu}\right) \frac{1}{L^{N}} \qquad (36)$$

A. Exact first and second moments of $P(\mathbf{n})$

Before computing approximately the probability from Eq. (36) it is instructive to compute exactly the first and second moments of the distribution (36). The first moments are

$$
\begin{aligned}
\langle n_{\mu} \rangle &= \int dn_1 \cdots dn_M P(n_1, \cdots, n_M) n_{\mu} \\
&= \int dn_1 \cdots dn_M n_{\mu} \int dz \frac{1}{L^N} \delta(n_1(z) - n_1) \cdots \delta(n_M(z) - n_M) \\
&= \int dz \frac{1}{L^N} n_{\mu}(z) \\
&= \int dz \frac{1}{L^N} \frac{1}{a} \sum_{i=1}^{N} \Phi_{\mu}(q_i) \\
&= N \int dq \frac{1}{L} \frac{1}{a} \Phi_{\mu}(q) = n^* \qquad (37)
\end{aligned}
$$

The second moments are

$$
\begin{aligned}
\langle n_{\mu} n_{\nu} \rangle &= \int dn_1 \cdots dn_M P(n_1, \cdots, n_M) n_{\mu} n_{\nu} \\
&= \int dz \frac{1}{L^N} n_{\mu}(z) n_{\nu}(z) \\
&= \int dz \frac{1}{L^N} \frac{1}{a^2} \sum_{i=1}^{N} \Phi_{\mu}(q_i) \sum_{j=1}^{N} \Phi_{\nu}(q_j) \\
&= \int dz \frac{1}{L^N} \sum_{i=1}^{N} \frac{1}{a^2} \Phi_{\mu}(q_i)\Phi_{\nu}(q_i) + \sum_{i \neq j=1}^{N} \int dz \frac{1}{L^N} \frac{1}{a^2} \Phi_{\mu}(q_i)\Phi_{\nu}(q_j) \\
&= N \int dq \frac{1}{L} \frac{1}{a^2} \Phi_{\mu}(q)\Phi_{\nu}(q) + N(N-1) \int dq dq' \frac{1}{L^2} \frac{1}{a^2} \Phi_{\mu}(q)\Phi_{\nu}(q') \\
&= N \int dq \frac{1}{L} \frac{1}{a^2} \Phi_{\mu}(q)\Phi_{\nu}(q) + \left(1 - \frac{1}{N}\right) n^{*2} \qquad (38)
\end{aligned}
$$

For sufficiently large N we may neglect the term N^{-1} and we see that there are correlations because for $\nu = \mu$ and $\nu = \mu \pm 1$ the first term does not vanish. In fact we have

$$
\begin{aligned}
\langle n_{\mu} n_{\mu} \rangle &= \frac{2n^*}{3a} + n^{*2} \\
\langle n_{\mu} n_{\nu} \rangle &= \frac{n^*}{6a} + n^{*2} \qquad \text{neighbors} \\
\langle n_{\mu} n_{\nu} \rangle &= n^{*2} \qquad\qquad \text{not neighbors} \qquad (39)
\end{aligned}
$$

In terms of central moments, we have

$$\langle \delta n_{\mu} \delta n_{\mu} \rangle \;=\; \frac{2n^*}{3a}$$

$$\langle \delta n_\mu \delta n_\nu \rangle \;=\; \frac{n^*}{6a} \qquad \text{neighbors}$$

$$\langle \delta n_\mu \delta n_\nu \rangle \;=\; 0 \qquad \text{not neighbors} \tag{40}$$

These are exact results. We see, then, that neighbor cells are correlated, but non-neighbor cells are not. Note that the correlated term has the same size as the variance.

B. Gaussian approximation

Once we know the exact first and second moments of $P(\mathbf{n})$ it is straightforward to calculate the probability under a Gaussian approximation that has precisely these moments. In general we have, for a multivariate system

$$P(\mathbf{n}) \;=\; \frac{1}{Z} \exp\left\{ -\frac{1}{2}(\mathbf{n}-\mathbf{n}^*)\mathbf{A}^{-1}(\mathbf{n}-\mathbf{n}^*) \right\} \tag{41}$$

where Z is a normalization constant, n^* is the mean concentration and $\mathbf{A}^{-1}$ is related to the second moments through

$$A_{\mu\nu} \;=\; \langle n_\mu n_\nu \rangle - \langle n_\mu \rangle^2 \tag{42}$$

From Eqs. (38) and (39) it follows, then

$$n_\mu^* \;=\; n^*$$
$$A_{\mu\nu} \;=\; \frac{n^*}{6a}(4\delta_{\mu\nu} + \delta_{\mu\nu\pm 1}) \tag{43}$$

where $\delta_{\mu\nu}$ is the Kronecker delta. Finally, the explicit form of the probability becomes

$$P(\mathbf{n}) \;=\; \frac{1}{Z} \exp\left\{ -\frac{1}{2}\frac{6a}{n^*}\delta\mathbf{n}^T \mathbf{A}^{-1}\delta\mathbf{n} \right\} \tag{44}$$

where we have introduced the vector $\delta\mathbf{n}$ with components $\delta n_\mu = n_\mu - n^*$.

The entropy that arises in this Gaussian approximation has the following quadratic form

$$S^{\text{Gauss}}(\mathbf{n}) \;=\; -\frac{k_B}{2}\frac{6a}{n^*}\sum_{\mu\nu}(n_\mu - n^*)A_{\mu\nu}^{-1}(n_\nu - n^*) \tag{45}$$

Therefore, in order to have an explicit form, we need to compute the inverse of the matrix $\mathbf{A}$. Fortunately, the inverse of the Toeplitz periodic matrix (43) is known analytically, see Eq. (4.6) of Ref. [31], which needs to be corrected as follows

$$A_{\mu\nu}^{-1} \;=\; \frac{1}{4h_n + 2h_{n-1} + 2}\left\{ \begin{array}{l} h_{n-\nu+1}h_\mu - h_{\mu-1}h_{n-\nu} + h_{\nu-\mu} \ \text{ for } \mu \le \nu \\ h_{n-\mu+1}h_\nu - h_{\nu-1}h_{n-\mu} + h_{\mu-\nu} \ \text{ for } \nu \le \mu \end{array} \right. \tag{46}$$

where

$$h_k \;\equiv\; \frac{\lambda_1^k - \lambda_2^k}{\lambda_1 - \lambda_2}$$
$$\lambda_{1,2} \;\equiv\; -2 \pm \sqrt{3} \tag{47}$$

In order to obtain the probability of the concentration in a single node we may integrate the Gaussian joint probability in Eq. (44) over all except one variable. The result will be a Gaussian and, therefore, we may use the information in Eq. (40) to infer directly the form of this Gaussian, which is

$$P(n) \;=\; \frac{1}{Z} \exp\left\{ -\frac{3(n-n^*)^2}{4n^*} \right\} \tag{48}$$

Once we have this result, it is straightforward to use it under the local equilibrium assumption in Eq. (9) and, hence, we know the explicit expression for the chemical potential in Eq. (12).

By integrating the Gaussian joint probability in Eq. (44) over all except two consecutive nodes, we obtain the joint probability of consecutive nodes, which is

$$P(\overline{n}_\mu, \overline{n}_\nu) = \frac{1}{Z} \exp\left\{-\frac{3(\overline{n}_\mu - n^*)^2}{4n^*}\right\} \exp\left\{-\frac{3\left[(\overline{n}_\nu - n^*) - \frac{1}{4}(\overline{n}_\mu - n^*)\right]^2}{4n^*\left(1 - \left(\frac{1}{4}\right)^2\right)}\right\} \tag{49}$$

IX.   APPENDIX: THE LOCAL EQUILIBRIUM ASSUMPTION FOR THE FRICTION MATRIX

We want to show that the approximation in Eq. (19) is a good one. The calculation of the integral over the conditional ensemble is difficult to perform analytically. For this reason, in this appendix we compute numerically the conditional average in Eq. (18). The method we use is based on the formulation of a fictitious diffusive dynamics that samples an approximate version of the conditional ensemble. However, the approximation can be improved arbitrarily with a corresponding increase in computational cost. This fictitious dynamics is constructed as follows. Consider a system of N Brownian particles that evolve according to the following stochastic differential equation

$$d\mathbf{r}_i = -D\frac{\partial}{\partial \mathbf{r}_i}V(z)dt + (2D)^{1/2}d\mathbf{W}_i \tag{50}$$

Here, $V(z)$ is a dimensionless potential that depends on the microstate $z = \{\mathbf{r}_i\}$ of the system and $d\mathbf{W}_i$ are independent increments of the Wiener process. The Fokker-Planck equation corresponding to (50) is

$$\partial_t P(z) = D\frac{\partial}{\partial \mathbf{r}_i}\left(\frac{\partial}{\partial \mathbf{r}_i}V(z)\right)P(z) + D\frac{\partial}{\partial \mathbf{r}_i}\frac{\partial}{\partial \mathbf{r}_i}P(z) \tag{51}$$

The equilibrium solution of the FPE (51) is

$$P^{\mathrm{eq}}(z) = \frac{1}{Z}\exp\{-V(z)\} \tag{52}$$

Now take as the potential the following function

$$V(z) = \frac{1}{2n_0^2}\sum_\mu (n_\mu(z) - n_\mu)^2 \tag{53}$$

in such a way that the stationary solution of the FPE (51) is

$$P^{\mathrm{eq}}(z) = \frac{1}{Z}\exp\left\{-\frac{1}{2n_0^2}\sum_\mu (n_\mu(z) - n_\mu)^2\right\} \tag{54}$$

In the limit $n_0 \to 0$ this goes to the distribution

$$P^{\mathrm{eq}}(z) = \frac{1}{P^{\mathrm{eq}}(\mathbf{n})}\prod_\mu \delta(n_\mu(z) - n_\mu) \tag{55}$$

where $P^{\mathrm{eq}}(\mathbf{n})$ is the normalization factor. The SDE (50) becomes with the potential (53)

$$d\mathbf{r}_i = -\frac{D}{n_0^2}\sum_\mu (n_\mu(z) - n_\mu)\nabla\delta_\mu(\mathbf{r}_i)dt + (2D)^{1/2}d\mathbf{W}_i \tag{56}$$

Eqs. (56) sample, in the steady state and for sufficiently small n_0, the distribution (55). It is clear that in order to achieve small values of n_0 one needs to reduce correspondingly the time step in the numerical solution of Eq. (56).

We now consider a one-dimensional situation. In a segment of size L we position M nodes at $r_\mu = a\mu$ where $\mu = 0, \cdots, M - 1$ and $a = L/M$ is the lattice spacing. The tent function of node μ is

$$\begin{aligned}\Phi_\mu(r) &= \theta(r - r_\mu)\theta(r_{\mu+1} - r)\left(1 - \frac{r - r_\mu}{a}\right) \\ &+ \theta(r - r_{\mu-1})\theta(r_\mu - r)\left(1 + \frac{r - r_\mu}{a}\right)\end{aligned} \tag{57}$$

Every node has two sub-elements as shown in Fig. 1

The term $\nabla\delta_\mu(\mathbf{r})$ now becomes (neglecting the discontinuities)

$$\begin{aligned}\nabla\delta_\mu(r) &= -\frac{1}{a^2}\theta(r - r_\mu)\theta(r_{\mu+1} - r) \\ &+ \frac{1}{a^2}\theta(r - r_{\mu-1})\theta(r_\mu - r)\end{aligned} \tag{58}$$

In 1D and for a regular lattice, the vectors $\mathbf{b}_{e_\mu}$ in Eq. (15) are simply the numbers $\pm\frac{1}{a}$. The SDE (56) becomes

$$\begin{aligned}dr_i &= \frac{D}{n_0^2 a^2}\sum_\mu (n_\mu(z) - n_\mu)\theta(r_i - r_\mu)\theta(r_{\mu+1} - r_i)dt \\ &- \frac{D}{n_0^2 a^2}\sum_\mu (n_\mu(z) - n_\mu)\theta(r_i - r_{\mu-1})\theta(r_\mu - r_i)dt \\ &+ (2D)^{1/2}dW_i\end{aligned} \tag{59}$$

In order to see how this dynamics works, assume that the i particle is in the element (r_3, r_4). Then,

$$dr_i = \frac{D}{n_0^2 a^2}(n_3(z) - n_3)dt - \frac{D}{n_0^2 a^2}(n_4(z) - n_4)dt$$
$$+ (2D)^{1/2} dW_i \tag{60}$$

Assume further that $n_4(z) = n_4$ and $n_3(z) > n_3$. This means that there is an excess of particles near node 3. In that case, Eqs. (60) tend to move the particle to the right, this is, reducing the density of node 3, as it should.

We present in Sec. IV the results of the conditional average of the sub-element concentration $n_e(\mathbf{n})$ introduced in Eq. (18) for a one dimensional situation.

X. APPENDIX: CONTINUUM THEORY

In this appendix, we show that Eq. (33), which has been obtained under a coarse-graining procedure, can be understood as a particular discrete representation of the diffusion equation

$$\partial_t n(\mathbf{r}, t) = -\boldsymbol{\nabla}\cdot\mathbf{J} \tag{61}$$

where the mass flux vector $\mathbf{J}$ is given by

$$\mathbf{J}(\mathbf{r}) = -\Gamma(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r}) \tag{62}$$

where the mobility $\Gamma(\mathbf{r})$ is a function of the concentration field $\Gamma(\mathbf{r}) = \gamma(n(\mathbf{r}))$ in general. Also, the chemical potential field depends on space because of its dependence on the concentration field, i.e. $\mu(\mathbf{r}) = \mu^{\mathrm{eq}}(n(\mathbf{r}))$, where μ^{eq} is the equilibrium chemical potential. To fix ideas, for a dilute solution we have an ideal gas form for the chemical potential

$$\mu(\mathbf{r}) = k_B T \ln \frac{n(\mathbf{r})}{n^*}$$
$$\Gamma(\mathbf{r}) = \frac{D_0}{k_B T} n(\mathbf{r}) \tag{63}$$

and Eq. (61) becomes the usual diffusion equation

$$\partial_t n(\mathbf{r}, t) = D_0 \nabla^2 n(\mathbf{r}, t) \tag{64}$$

The discretization of Eq. (61) starts by defining the node averaged discrete concentration field

$$\overline{n}_\mu \equiv \int d\mathbf{r}\, \delta_\mu(\mathbf{r}) n(\mathbf{r}, t) \tag{65}$$

Multiply Eq. (61) with $\delta_\mu(\mathbf{r})$ and integrate over all space to obtain an equation for $\overline{n}_\mu$,

$$\partial_t \overline{n}_\mu = -\int d\mathbf{r}\, \boldsymbol{\nabla}\delta_\mu(\mathbf{r})\cdot\Gamma(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r}) \tag{66}$$

where an integration by parts has been performed. Next, introduce the function

$$\overline{\mu}(\mathbf{r}) = \sum_\nu \Phi_\nu(\mathbf{r})\mu^{\mathrm{eq}}(\overline{n}_\nu) \tag{67}$$

which is a piece-wise linear approximations for $\mu(\mathbf{r})$. We expect that if the scale of variation of the concentration field $n(\mathbf{r})$ is large compared with the typical separation between nodes, and for reasonable functional dependencies for $\mu^{\mathrm{eq}}(n)$, that the piece-wise linear function $\overline{\mu}(\mathbf{r})$ will approximate well the chemical potential field $\mu(\mathbf{r})$. By inserting Eq. (67) into (66) we obtain

$$\partial_t \overline{n}_\mu = -\sum_\nu \mathcal{V}_\nu \int d\mathbf{r}\, \boldsymbol{\nabla}\delta_\mu(\mathbf{r})\cdot\Gamma(\mathbf{r})\boldsymbol{\nabla}\delta_\nu(\mathbf{r})\mu^{\mathrm{eq}}(\overline{n}_\nu)$$
$$= -\sum_\nu \frac{1}{\mathcal{V}_\mu} \sum_{e_\mu} \sum_{e_\nu} \mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\mu}$$
$$\times \int d\mathbf{r}\, \theta_{e_\mu}(\mathbf{r})\Gamma(\mathbf{r})\theta_{e_\nu}(\mathbf{r})\mu^{\mathrm{eq}}(\overline{n}_\nu) \tag{68}$$

Again, we approximate $\Gamma(\mathbf{r}) = \gamma(n(\mathbf{r}))$ with the piece-wise linear function

$$\Gamma(\mathbf{r}) \approx \sum_\sigma \Phi_\sigma(\mathbf{r})\gamma(\overline{n}_\sigma) \tag{69}$$

By inserting (69) into the integral in Eq. (68) we obtain

$$\int d\mathbf{r}\, \theta_{e_\mu}(\mathbf{r})\Gamma(\mathbf{r})\theta_{e_\nu}(\mathbf{r}) = \sum_\sigma \gamma(\overline{n}_\sigma)$$
$$\times \int d\mathbf{r}\, \theta_{e_\mu}(\mathbf{r})\theta_{e_\nu}(\mathbf{r})\Phi_\sigma(\mathbf{r}) \tag{70}$$

The integral vanishes unless μ and ν are neighboring nodes. In 2D, for example, we have two sub-elements which are common to the nodes μ, ν that give a non-zero contribution. For each of these sub-elements, σ may be any of the three nodes of the sub-element. For other values of σ the integral in Eq. (70) vanishes. For σ equal to any of the nodes of the element, the integral takes the same value, equal to $\mathcal{V}_e/d$, where $\mathcal{V}_e$ is the volume of the sub-element and d is the space dimension.

Therefore, by defining Γ_e as the arithmetic mean of the nodal values of $\gamma(n_\sigma)$, we have that Eq. (68) becomes

$$\partial_t \overline{n}_\mu = -\sum_\nu \sum_{e\in\mu\nu} \mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\mu} \frac{\mathcal{V}_e}{\mathcal{V}_\mu}\Gamma_e \mu^{\mathrm{eq}}(\overline{n}_\nu) \tag{71}$$

Here, e is any of the common elements of the neighbor nodes μ, ν, $\mathbf{b}_{e_\mu}$ is the vector of the element e, directed towards the node μ, $\mathbf{b}_{e_\nu}$ is the vector of the element e, directed towards the node ν. Eq. (71) coincides with (33) when the mobility is given by Eq. (63), and the chemical potential is that of a local model (as in the last model in Eq. (12)).

In summary, we see that the microscopically derived Eq. (33) can be understood as a discrete version of the continuum equations (61) and (62).

XI. APPENDIX: EXPLICIT FORM OF THE SDE IN 1D

Let us write Eq. (32) in the form

$$dn_\mu(t) = A_\mu dt + B_\mu dt + d\tilde{n}_\mu \qquad (72)$$

Here, A_μ is defined as

$$
\begin{aligned}
A_\mu &\equiv -D\sum_\nu \left(\sum_{e\in\mu\nu} \mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\nu}\frac{\mathcal{V}_e}{\mathcal{V}_\mu}n_e\right)\frac{\mu_\nu}{k_BT} \\
&= \left(\sum_{e\in\mu\mu-1}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_{\mu-1}}n_e\right)\frac{\mu_{\mu-1}}{k_BT} \\
&\quad + \left(\sum_{e\in\mu\mu}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\mu}n_e\right)\frac{\mu_\mu}{k_BT} \\
&\quad + \left(\sum_{e\in\mu\mu+1}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_{\mu+1}}n_e\right)\frac{\mu_{\mu+1}}{k_BT} \qquad (73)
\end{aligned}
$$

where we have used that the volume of the sub-element is $\mathcal{V}_e = a$. As it is clear after Eq. (58) the vectors $\mathbf{b}_{e_\mu}$ in 1D are simply the numbers $\pm\frac{1}{a}$. There is only one sub-element that is shared by the nodes μ and $\mu-1$, or by the nodes μ and $\mu+1$. However, the node μ shares two sub-elements l, r (for left and right) with the node μ itself. This leads to

$$
\begin{aligned}
A_\mu &= -\frac{1}{a^2}n_l\mu_{\mu-1} + \frac{1}{a^2}(n_l+n_r)\mu_\mu - \frac{1}{a^2}n_r\mu_{\mu+1} \\
&= \frac{1}{a^2}n_l(\mu_\mu-\mu_{\mu-1}) + \frac{1}{a^2}n_r(\mu_\mu-\mu_{\mu+1}) \qquad (74)
\end{aligned}
$$

where

$$
\begin{aligned}
n_l &= \frac{n_\mu+n_{\mu-1}}{2} \\
n_r &= \frac{n_\mu+n_{\mu+1}}{2} \qquad (75)
\end{aligned}
$$

The term B_μ in Eq. (72) is given from Eq. (32) by

$$
\begin{aligned}
B_\mu &= \sum_\nu\left(\sum_{e\in\mu\nu}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\nu}\frac{\mathcal{V}_e}{\mathcal{V}_\nu\mathcal{V}_\mu}\right)\frac{1}{d+1} \\
&= \frac{1}{2}\left(\sum_{e\in\mu\mu-1}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_{\mu-1}}\frac{\mathcal{V}_e}{\mathcal{V}_\mu\mathcal{V}_\mu}\right) \\
&\quad + \frac{1}{2}\left(\sum_{e\in\mu\mu-1}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_\mu}\frac{\mathcal{V}_e}{\mathcal{V}_\mu\mathcal{V}_\mu}\right) \\
&\quad + \frac{1}{2}\left(\sum_{e\in\mu\mu+1}\mathbf{b}_{e_\mu}\cdot\mathbf{b}_{e_{\mu+1}}\frac{\mathcal{V}_e}{\mathcal{V}_\mu\mathcal{V}_\mu}\right) \\
&= -\frac{1}{2a^3} + \frac{1}{a^3} - \frac{1}{2a^3} = 0 \qquad (76)
\end{aligned}
$$

Finally, let us consider the thermal fluctuations in Eq. (32). From Eqs. (26) and (27) we have

$$
\begin{aligned}
d\tilde{n}_\mu &= \frac{1}{\mathcal{V}_\mu}\sum_{e_\mu}\mathbf{b}_{e_\mu}\cdot\sqrt{2Dn_{e_\mu}\mathcal{V}_{e_\mu}}dV_{e_\mu} \\
&= \frac{\sqrt{2Da}}{a^2}\left(n_l^{1/2}dV_l - n_r^{1/2}dV_r\right) \qquad (77)
\end{aligned}
$$

We can now collect the results (74), (76), and (77) to write down the final SDE satisfied by the discrete concentration field defined in the 1D lattice

$$
\begin{aligned}
dn_\mu &= \frac{D}{k_BT}\frac{1}{a^2}\frac{n_\mu+n_{\mu-1}}{2}(\mu_\mu-\mu_{\mu-1})dt \\
&\quad + \frac{D}{k_BT}\frac{1}{a^2}\frac{n_\mu+n_{\mu+1}}{2}(\mu_\mu-\mu_{\mu+1})dt \\
&\quad + \frac{\sqrt{2Da}}{a^2}\left((n_\mu+n_{\mu-1})^{1/2}dV_l - (n_\mu+n_{\mu+1})^{1/2}dV_r\right) \qquad (78)
\end{aligned}
$$

In 1D, for periodic boundary conditions, there are as many sub-elements as there are nodes. Therefore, we will rename dV_l and dV_r as dV_μ and $dV_{\mu+1}$, respectively. Eqs. (34), with the different models for the chemical potential in Eqs. (12) are the equations that need to be simulated.

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