

Diffusion of interacting Brownian particles: Jamming and anomalous diffusionSergey Savel'ev,^{1,2} Fabio Marchesoni,^{1,3} Alessandro Taloni,^{1,4} and Franco Nori^{1,5}¹*Frontier Research System, The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama, 351-0198, Japan*²*Department of Physics, Loughborough University, Loughborough LE11 3TU, United Kingdom*³*Dipartimento di Fisica, Università di Camerino, I-62032 Camerino, Italy*⁴*Dipartimento di Fisica, Università di Perugia, I-06123 Perugia, Italy*⁵*Center for Theoretical Physics, Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1040, USA*

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The free self-diffusion of an assembly of interacting particles confined on a quasi-one-dimensional ring is investigated both numerically and analytically. The interparticle pairwise interaction can be either attractive or repulsive and the energy barrier opposing thermal hopping of two particles one past the other is finite. Thus, for sufficiently long times, self-diffusion becomes normal or conventional diffusion. However, depending on the particle density, subdiffusive transients with exponent 1/2 and suppression of normal diffusion are observed. Above a certain density threshold, a sudden drop to zero of the diffusion coefficient for attractive particles signals the transition to a jammed phase. Furthermore, a Gaussian cluster of attractive particles condenses, by shrinking in size, for densities larger than such density threshold; lower density clusters spread out, regardless of the interaction sign, through a diffusion mechanism that is anomalous at short times, and normal for sufficiently long times. These effects could be observed in systems with colloidal particles, vortices, electrons, among other interacting particle systems.

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I. INTRODUCTION

We recently studied [1,2] the transport of interacting particles, including binary mixtures, moving on a quasi-one-dimensional substrate and driven by external forces (either constant [2] or oscillating [1–3]). By focusing on the first moment of the particle distribution (i.e., on the net particle current), we singled out interesting rectification mechanisms where the particle pair interactions play a central role. Finally, we showed that under appropriate temperature and/or density conditions, attracting particles can jam [1,4,5].

In this paper we take a different approach. We now look at the diffusion mechanisms associated with particle transport in order to better understand the statistical properties of an assembly of interacting Brownian particles. The literature on the diffusion of interacting particles is vast and touches upon hydrodynamics and transport theory [6]. Almost all studies, however, incorporate temperature effects through the canonical ensemble formalism of equilibrium statistical mechanics. Here we assume that all particles are subject to spatially uncorrelated thermal fluctuations at a given temperature so that they can be treated as independent Brownian particles. On doing this we neglect the mutual influence they exert on one another owing to the spatio-temporal memory effects of the heat bath (hydrodynamic interactions), which is correct if the relaxation time of the surrounding “liquid” is short enough with respect to time scales of the moving particles. The latter topic has been the focus of extensive investigations in the 1970’s [6,7].

The diffusion of an assembly of N Brownian particles is intrinsically an $N \times N$ process: the diffusion and the friction coefficients from the standard Brownian motion theory must be replaced by the tensor matrices \mathbf{D}_{ij} and ζ_{ij} , respectively, with the indices i, j labeling the individual particles [7]. However, the self-diffusion coefficient, i.e., the diffusion co-

efficient of a single particle, defined in three dimensions as

$$\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 6D(t)t, \quad (1)$$

is a quantity of prime interest in the description of the dynamics of interacting Brownian particles. When $D(t)$ scales asymptotically as $t^{\alpha-1}$ with $\alpha \neq 1$, the diffusion mechanism is termed anomalous [8]. A typical example is diffusion in constrained geometries [9]. Sometimes, like in light-scattering experiments, $D(t)$ simply interpolates two constant values D_s and D_l for short and long times, respectively, with $D_l < D_s$ [10]. In both limits self-diffusion is a normal diffusion process of the Einstein-type with exponent $\alpha = 1$.

In this paper we restrict ourselves to the study of (quasi)-one-dimensional systems, where independent pointlike Brownian particles can diffuse across one another by overcoming the action of an attractive or repulsive pair potential. To avoid unwanted geometric constraints such as single filing (a subdiffusive process with $\alpha = 1/2$ [9]), we exclude the case of hardcore interactions between particles. Indeed, solid spheres moving in a narrow channel can always pass one another by deforming either the channel walls, or their shape, or both. Such quasi-one-dimensional geometries are of wide application to the modeling of a variety of processes and devices in biological physics and nanotechnology [11].

To this regard we remind that the efficiency of noise-assisted transport on a periodic substrate is controlled by both the first and the second moment of the velocity distribution of the diffusing particles, especially in the absence of external ac drives [12]. The relevant net current should not become swamped with the unavoidable fluctuations caused by the environment. There occurs a competition between two mechanisms [13]: an enhancement of the diffusion [14] and an optimization of the net transport velocity [15]. A first option aims at controlling the magnitude of the effective dif-

fusion independently of the temperature. It thus carries a rich potential for technologically useful separation devices. A second option attempts to achieve a maximal ‘‘coherence,’’ that is mobility, for transport. Such a coherence is of relevance for the modeling of biophysical molecular motors [11]. Of course, accounting for interparticle interactions makes our task much more demanding than in the presence of only particle-substrate interactions [12].

In extremely small systems, Brownian motion is often described to a good approximation in the overdamped limit; namely, by assuming that the diffusing particles are massless. This is the case, for instance, of most biological processes at both the cell level (for instance, transport in ion channels [9,16]) and the body level (muscle operations [17]). The same assumption inspires the design of devices to guide tiny particles on nanoscales and microscales. Some of these devices have already been realized experimentally to control the motion of vortices in superconductors [18], particles in asymmetric silicon pores [19], arrays of optical tweezers [20], and colloidal particles in one-dimensional geometries [21], among others.

Our analysis makes use of two key ingredients: the Langevin equation (LE), mostly for the numerical simulation, and the Fokker-Planck equation (FPE) to gain theoretical insight on the collective properties of the system. In Sec. II we numerically simulate large one-dimensional assemblies of either repelling or attractive free Brownian particles, that is in the absence of a substrate. Depending on the density of interacting particles, subdiffusive transients with exponent $\alpha=1/2$ (ascribed to temporary single filing) and normal diffusion suppression (due to dense particle packing) are observed. In the case of attractive particles, a sudden drop to zero of the diffusion coefficient above a definite density threshold, signals the onset of a jamming, or condensation phenomenon. Such a phenomenon was predicted in Refs. [2,5] to explain certain anomalies in the density dependence of interacting particle rectification. In Sec. III these properties are interpreted in the framework of the nonlinear FPE formalism of Refs. [1,4] by means of simple phenomenological arguments. In particular, a Gaussian cluster of attractive particles is proven to collapse for densities larger than the jamming density threshold. At lower densities, clusters dissolve, irrespective of the interaction sign, anomalously ($\alpha \neq 1$) at short times, and then normally ($\alpha=1$) for long enough times. In Sec. IV, the jamming of an assembly of attracting particles is analyzed in some detail by studying the stationary solution of the relevant nonlinear FPE.

II. SIMULATION RESULTS

Our starting point is the set of Langevin equations

$$\dot{x}_i = - \sum_{j \neq i} \frac{\partial}{\partial x_i} W(x_i - x_j) + \sqrt{2kT} \xi^{(i)}(t) \quad (2)$$

for an assembly of N interacting particles moving along the x axis subject to thermal fluctuations only (no substrate, no external drives are considered here). The Gaussian white noises $\xi^{(i)}(t)$ with zero average $\langle \xi^{(i)}(t) \rangle = 0$ satisfy the

fluctuation-dissipation relation $\langle \xi^{(i)}(t) \xi^{(j)}(0) \rangle = \delta_{ij} \delta(t)$; T is the resulting system temperature, k is the Boltzmann constant. The potential $W(x_i - x_j)$ denotes the symmetric interaction between the particle pair (i, j) ; the particle indices i and j run from 1 to N . Equation (2) represents an overdamped diffusive dynamics in Smoluchowski approximation with viscous coefficient equal to 1.

We integrated the equation set (2) over a finite length l by means of a standard numerical routine [5]; periodic boundary conditions were imposed with no prejudice of the overall diffusive dynamics (as long as the pair interaction length λ is taken much smaller than l). In our simulations, the pair interaction has been modeled by means of the symmetric, piecewise linear potential

$$W(x) = \frac{g}{\lambda} \left(1 - \frac{|x|}{\lambda} \right) \quad (3)$$

for $|x| \leq \lambda$, and $W(x)=0$, otherwise. Here, a negative coupling, $g < 0$, denotes an attractive pair potential, while $g > 0$ corresponds to repulsive interactions. Note that g/λ is the hopping energy ΔW (respectively, a trapping well or a repulsive barrier) that two particles must overcome to pass one another. The diffusion properties investigated in the present work are rather robust independent of the actual form for $W(x)$.

The particle self-diffusion in the assembly is measured by

$$\langle \delta x^2(t) \rangle = \frac{1}{N-1} \sum_{i=1}^N [x_i(t) - x_i(0)]^2, \quad (4)$$

where $\{x_i(0)\}$ are the particle positions at time $t=0$. In Fig. 1(a) we plotted $\langle \delta x^2(t) \rangle$ vs t for $N=10^3$ repulsive particles.

A. Subdiffusion to normal-diffusion crossover

Two different diffusive behaviors are clearly resolved: (a) a subdiffusive regime for $10 < t < 10^3$, when self-diffusion (4) grows proportional to \sqrt{t} ; (b) a normal diffusive regime for $t > 5 \times 10^3$, with $\langle \delta x^2(t) \rangle$ linear in t . Normal diffusion sets in only for times much longer than the escape time $\tau_K \approx 5 \times 10^3$, which characterizes the thermal hopping of one particle past another (or pair exchange); of course, $\tau_K \approx t_d e^{\Delta W/kT}$, where t_d is the mean free-diffusion time of a particle between two subsequent collisions, i.e., $t_d = (2kT\eta)^{-1}$.

The subdiffusive behavior at short times $t \ll \tau_K$ is an effect of the repulsive pair barriers ΔW , that force the particles to retain their initial, randomly assigned order (single file constraint [22]). Indeed, single-file diffusion is known [23] to be of the subdiffusive type with exponent 1/2, as in the present case. Normal diffusion in a one dimensional gas of interacting particles is restored either when thermal hopping eventually allows the particles to pass one another [24], as in our model, or when the non-passing Brownian particles are set free to expand (open-end file [25]). The latter case will be considered in Sec. III.

Separating these two diffusive regimes required extensive and time-consuming molecular dynamics simulations, as the

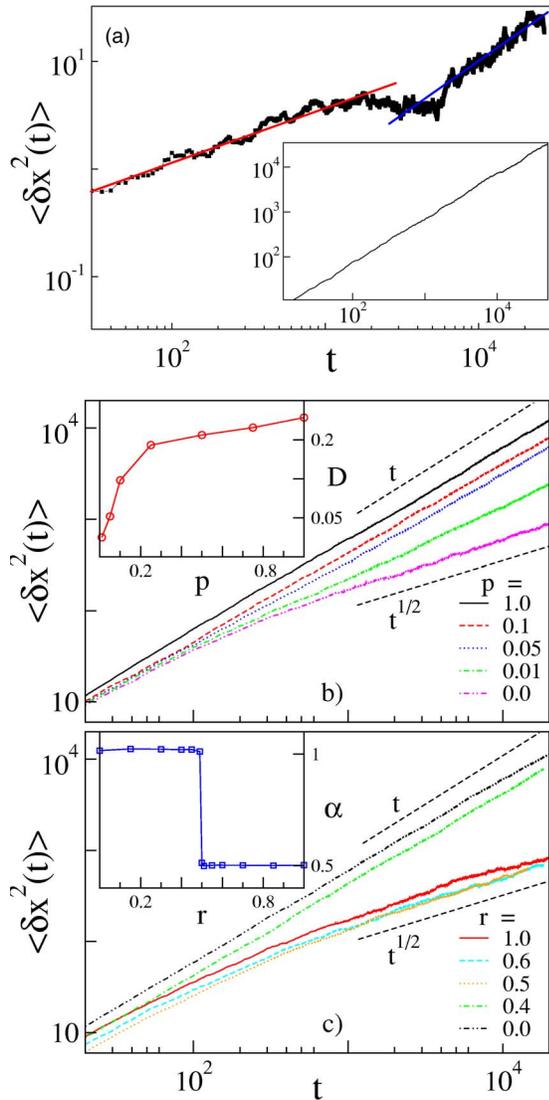


FIG. 1. (Color online) Mean square displacement $\langle \delta x^2(t) \rangle$, defined in Eq. (4), versus t for an assembly of N particles on a ring of length l interacting via the pair potential (3). (a) Molecular dynamics simulations for $N=10^3$, $l=400$, $kT=0.07$, $\lambda=0.05$, and $g=0.1$. Inset: as in the main panel but for $N=2 \times 10^3$ and $g=0.06$. (b) Monte Carlo simulations (model 1) for $N=3.5 \times 10^3$, $l=3.5 \times 10^4$, $kT=0.2$, and different values of p . Inset: the corresponding fitting diffusion constant D versus p . (c) Simulations of model 2 for the same assembly parameters as in (b) and different values of r . Inset: the diffusion exponent α versus r .

crossover becomes detectable only for relatively low particle densities $n \equiv N/l$, that is $n\lambda \ll 1$, and high hopping barriers $\Delta W \gg kT$ [see panel (a) of Fig. 1]. To speed up our simulation analysis and gain a better understanding of the microscopic mechanisms at work, we also modeled the pair interactions in a more schematic way. Let us denote by v_i and v_j the velocities of any pair of particles (i, j) undergoing a collision, and by v'_i and v'_j their velocities immediately after the interaction process is completed; we replaced the underlying molecular dynamics by the simpler kinematic prescription

$$v'_i = (1-r)v_i + rv'_j,$$

$$v'_j = (1-r)v_j + rv'_i. \quad (5)$$

We simulated two distinct implementations of the kinetics described by Eq. (5). (i) Model 1: the parameter r can be either 0 with probability p , or 1 with probability $q=1-p$. Here, p models the probability of thermal hopping, which, by construction, incorporates information about the pair potential W and the thermal energy kT , but is independent of the particle density (as it should for $n\lambda \ll 1$). (ii) Model 2: the parameter r is set constant within the closed interval $[0, 1]$. As a consequence, particles i and j pass one another only for $0 \leq r < 1/2$, whereas for $1/2 < r \leq 1$ pair exchanges are ruled out; $r=1/2$ indicates a completely inelastic collision. Here, collisions are elastic only for $r=0$ and $r=1$; setting $0 < r < 1$ allows for the dissipation of particle kinetic energy into the environment (possibly including hidden internal degrees of freedom of the scatterers).

In Figs. 1(b) and 1(c) we show $\langle \delta x^2(t) \rangle$ versus t for models 1 and 2, respectively. The assembly parameters are the same in both panels. Model 1 in panel (b) shows the expected crossover from single-file to normal diffusion at a characteristic p -dependent time $t_c \sim t_d/p$. Note that in this reduced Monte Carlo scheme the diffusion crossover is not as closely localized as in the molecular dynamics simulation [see panel (a)].

Model 2 in panel (c) exhibits totally different diffusion properties. For $0 \leq r < 1/2$ the particles pass each other and, therefore, their self-diffusion is of the Langevin type at all times, i.e., normal—the relevant diffusion constant $D(r)$ is a decreasing function of r (not shown); for $1/2 < r \leq 1$ particles bounce off their neighbors (though inelastically) and are thus subject to the single file constraint; correspondingly, their motion is subdiffusive with exponent $1/2$ (normal diffusion can be observed for $t \ll t_d$). The transition between these two asymptotic diffusive regimes occurs at $r=1/2$ and sharply depends on the control parameter r .

The crossover from single file to normal self-diffusion for an assembly of finite-size disks (with diameter a) moving in a narrow two dimensional channel (with cross-section d) and repelling one another through a Lennard-Jones potential, has been investigated numerically by a number of authors [24]; their primary purpose was to explain certain intriguing experimental observations concerning the transport of adsorbants in zeolites [9]. At variance with their picture, where two molecules can squeeze their way past one another for $d \geq 2a$, only marginally overlapping, in the molecular dynamics simulation of panel (a) the system is strictly one-dimensional and the diffusing particles are pointlike; finite trapping or barrier energies ΔW control the effective pair hopping probability, represented by $p \propto e^{-\Delta W/kT}$ in model 1. The abrupt transition between subdiffusion and normal-diffusion observed in the simulations of Ref. [24], for d very close to $2a$, is well captured by model 1 with $p > 0$.

B. Self-diffusion versus particle density

We now go back to the initial problem of a one-dimensional assembly of N particles diffusing according to the LE (2) on a ring of length l ; asymptotically, each particle

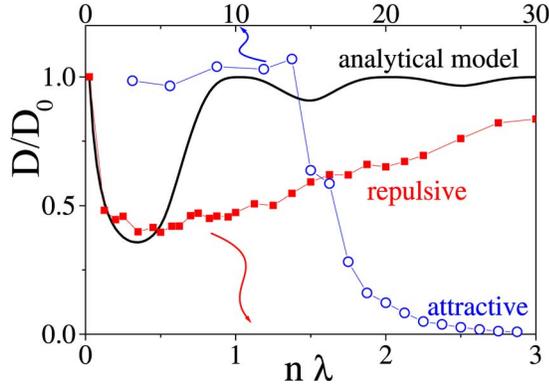


FIG. 2. (Color online) Self-diffusion constant D versus density n for an assembly of attractive (open blue circles, $g=-0.02$, $\lambda=0.5$) and repulsive particles (solid red squares, $g=0.08$, $\lambda=0.05$). The constant D is given in units of $D_0=kT$ and the density in units of λ^{-1} (see text). The pair interaction potential is defined in Eq. (3). Other simulation parameters $l=2$ and $kT=0.5$. The solid line represents our “one-particle” approximation (6) for the repulsive case.

is subject to normal self-diffusion, i.e., $\langle \delta x^2(t) \rangle \approx 2Dt$ for $t \gg \tau_K$. In Fig. 2 we plotted the normal diffusion constant D versus the particle density $n=N/l$, both for an attractive and a repulsive choice of the pair potential (3). The dependence of the diffusion process on the sign of g is apparent. For $g < 0$, corresponding to attractive particles, D drops sharply to zero above a critical density value, n_c , which can be regarded as a jamming, or condensation threshold. In Sec. III B we derive an analytical estimate for n_c ; molecular dynamics simulations suggest that λn_c is proportional to $kT/\Delta W$ (not shown).

In the case of a repulsive pair interaction, $g > 0$, the curve $D(n)$ in Fig. 2 first plunges below $D_0/2$, where $D_0 \equiv kT$ is the free-diffusion constant for $W \equiv 0$, and then drifts upwards back towards D_0 . To explain the nonmonotonic behavior of $D(n)$ we assumed that the computed self-diffusion coincides with the diffusion constant of a single “test” particle moving on the substrate formed by the remaining $N-1$ particles arranged in a fixed chain lattice with spacing constant $a_n = l/(N-1)$. In such a “one-particle” approximation, the resulting substrate potential experienced by the test particle would be

$$V_n(x) = \sum_{i=1}^{N-1} W(x - ia_n).$$

Note that V_n is periodic by construction, i.e., $V_n(x+l) = V_n(x)$, and the origin of the x axis can be set arbitrarily. In view of the shape of the simulated pair potential $W(x)$, Eq. (3), it turns out that $V_n(x)$ describes a sawtooth potential with maximum barrier height for $N-1=l/\lambda$, whereas it becomes a constant for an optimal packing geometry with $N-1=2l/\lambda$ (no substrate). In the former case the corresponding diffusion constant gets suppressed due to barrier hopping [26]; in the latter case the test particle undergoes free diffusion with $D = D_0$. In a crude approximation the curve $D(n)$ can be com-

puted analytically by integrating the well-known formula [27]

$$\frac{D}{D_0} = \left[\frac{1}{l^2} \int_0^l dx \exp[V_n(x)/kT] \int_0^l dy \exp[-V_n(y)/kT] \right]^{-1}, \quad (6)$$

as shown in Fig. 2. The agreement with our simulation data is reasonably good only at low densities, where the *ad hoc* substrate potential $V_n(x)$ is more robust to thermal fluctuations; a more sophisticated approach [1,2,5] is then required to estimate self-diffusion in a dense gas of long-range interacting particles. This is the main goal of the forthcoming sections.

III. PHENOMENOLOGICAL APPROACH

A fully analytical solution of the LE set (2) is impossible. The mechanisms governing the diffusion of interacting Brownian particles can be grasped in the framework of the Fokker-Planck equation (FPE) formalism [27]. The resulting nonlinear FPE can be investigated only by means of phenomenological arguments that help unravel the complexity of the underlying stochastic dynamics.

A. Nonlinear Fokker-Planck equation

Accounting for the particle pair potential W led us to formulate the following approximate nonlinear FPE [1,4,5] for the one-particle distribution function $F_1(t,x)$, i.e.,

$$\begin{aligned} \partial_t F_1(t,x) &= kT \partial_x^2 F_1(t,x) + \partial_x F_1(t,x) \\ &\times \int d\tilde{x} F_1(t,\tilde{x}) G(t,x,\tilde{x}) \partial_x W(x-\tilde{x}), \end{aligned} \quad (7)$$

where $\partial_t \equiv \partial/\partial t$, $\partial_x \equiv \partial/\partial x$, and $F_2(t,x,\tilde{x}) \equiv F_1(t,x)F_1(t,\tilde{x})G(t,x,\tilde{x})$ denotes the binary distribution function. It is apparent that particle-particle correlations decay on a scale of the order of either the interaction length λ for low particle densities $n \ll 1/\lambda$, or the inter-particle distance $1/n$ for high particle densities $n \gg 1/\lambda$. As a consequence, the function G , which describes the particle-particle correlation, differs appreciably from 1 (uncorrelated particle motion) for particle separations $|x-\tilde{x}| \lesssim \min\{n^{-1}, \lambda\}$, only. This has been numerically proved in Ref. [4]. Therefore, if each particle interacts with many neighbors, i.e., $n\lambda \gg 1$, the function G in the integral of Eq. (7) can be safely approximated to 1 over the entire integration domain.

Hereafter, the one-particle distribution function $F_1(t,x)$ is normalized to the total number N of particles in the system, namely,

$$\int_0^l F_1(t,x) dx = N. \quad (8)$$

In order to make the problem more tractable, we further discard nonlocal effects by assuming the relevant spatial scales to be much longer than the interaction length λ . Therefore, inserting the expansion

$$F_1(t, \tilde{x}) = F_1(t, x) + (\tilde{x} - x)\partial_x F_1(t, x) + \frac{1}{2}(\tilde{x} - x)^2 \partial_x^2 F_1(t, x) + \dots \quad (9)$$

in Eq. (7) and keeping the first nonvanishing term, only, lead to

$$\partial_t F_1(t, x) = \partial_x [g F_1(t, x) + kT] \partial_x F_1(t, x) \quad (10)$$

with

$$g \equiv \int dx W(x). \quad (11)$$

For the piecewise linear potential (3) this quantity coincides with the pair coupling constant, also denoted by g . Throughout our investigation we assumed that the pair potential $W(x)$ is symmetric under reflection $W(x) = W(-x)$, and vanishes for distances larger than λ , i.e., $W(|x| \rightarrow \infty) = 0$. Making contact with the simulation potential (3), pair potentials characterized by negative or positive values of the parameter g are defined to be attractive or repulsive, respectively.

In conclusion, Eq. (10) is valid under the restrictions

$$n^{-1} \ll \lambda \ll \sigma, \quad (12)$$

where σ is the characteristic width of the density packet (or particle cluster). Note that the interparticle interaction can still be regarded as a long-range interaction because of the density requirement $\lambda \gg 1/n$. These are the approximations under which we analytically treat Eq. (10) in the following sections and compare our analytical results with data from numerical simulations based on the LE (2).

B. Subdiffusive transients

The time-dependent solution of a nonlinear FPE, no matter how simple, cannot be obtained by means of standard techniques [27]. For this reason we studied our FPE (10) by addressing a less general problem: Suppose that N_1 particles form a cluster centered at $x=0$ with a given shape

$$F_1(t, x) = N_1 f\left(\frac{x}{\sigma}\right) \quad (13)$$

and vanishing tails $f(|x| \rightarrow \infty) = 0$. The normalization

$$\int_{-\infty}^{\infty} f(z) dz = 1$$

sets the number of particles N_1 to be constant in time, whereas the additional condition

$$\int_{-\infty}^{\infty} z^2 f(z) dz = 1$$

defines the cluster width σ as a function of time. Without further loss of generality we assume $f(z)$ to be a Gaussian function.

In view of Eq. (10) the width of $F_1(t, x)$ will vary in time according to a relatively simple ordinary differential equation. Multiplying both sides of Eq. (10) by x^2 and integrating

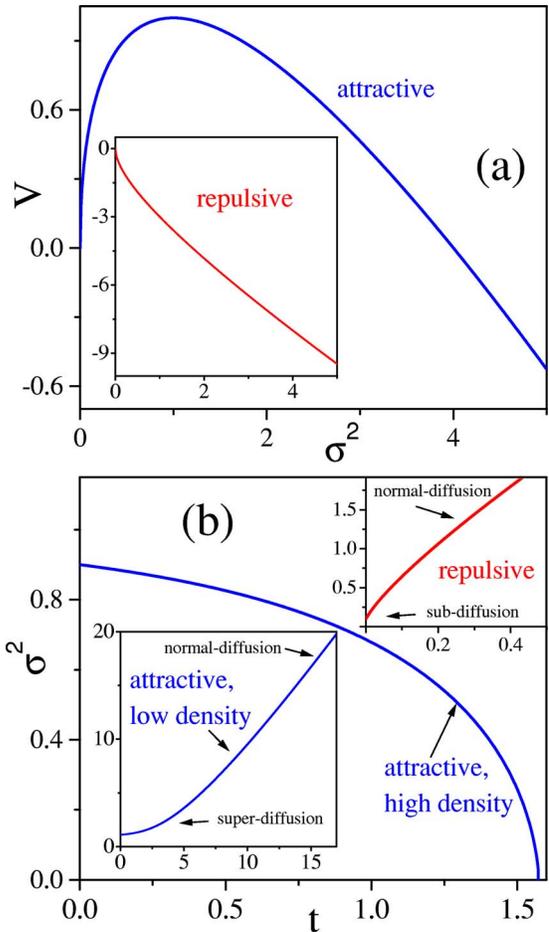


FIG. 3. (Color online) (a) The potential $V(\sigma^2)$ of Eq. (16) in units of $2kT\sigma_c^2$ for attractive (main panel) and repulsive (inset) particles. (b) The corresponding time dependence of $\sigma^2(t)$. Top inset: $g > 0$, $\sigma^2(0)/\sigma_c^2 = 0.1$; main panel: $g < 0$, $\sigma^2(0)/\sigma_c^2 = 0.9$; and bottom inset: $g < 0$, $\sigma^2(0)/\sigma_c^2 = 1.1$. The curves $\sigma^2(t)$ have been obtained by integrating numerically Eq. (15); σ is expressed in units of σ_c and t in units of σ_c^2/kT .

over the entire x domain yield, in shorthand notation,

$$\frac{d}{dt} \langle x^2(t) \rangle = g \int x^2 \partial_x (F_1 \partial_x F_1) dx + kT \int x^2 \partial_x^2 F_1 dx \quad (14)$$

or, after integrating by parts and replacing $\langle x^2(t) \rangle = N_1 \sigma^2(t)$,

$$\frac{d}{dt} \sigma^2 = 2kT + g \frac{\kappa_2 N_1}{\sigma} \quad (15)$$

with $\kappa_2 = \int f^2(z) dz = (2\sqrt{\pi})^{-1}$. Equation (15) can be interpreted as the relaxation process of an overdamped particle of coordinate $\sigma^2(t)$ subjected to the potential

$$V(\sigma^2) = -2kT\sigma^2 - 2g\kappa_2 N_1 \sigma \quad (16)$$

plotted in Fig. 3 for both $g > 0$ [panel (a), inset] and $g < 0$ [panel (a)].

(a) *Repelling particles*: $g > 0$. For $g > 0$ the implicit solution $\sigma(t)$ bridges the two limiting regimes [see Fig. 3(c)]:

$$\sigma^2(t) = 2kTt \quad \text{for } t \rightarrow \infty, \quad (17)$$

$$\sigma^2(t) = \left(\frac{3}{2}g\kappa_2 N_1 t\right)^{2/3} \quad \text{for } t \rightarrow 0. \quad (18)$$

This means that due to repulsion the width of $F_1(t, x)$ increases sub diffusively until it approaches its normal diffusion regime, which is only governed by thermal fluctuations [see Fig. 3(b), top inset].

(b) *Attractive particles:* $g < 0$. The potential (16) for $g < 0$ exhibits a maximum at

$$\sigma_c^2 = \frac{1}{16\pi} \left(\frac{N_1}{n_c}\right)^2, \quad (19)$$

where

$$n_c = \frac{kT}{|g|}. \quad (20)$$

As a result, for $\sigma(0) > \sigma_c$ we recover again, after a transient time of the order of σ_c^2/kT , the asymptotic law (17), i.e., normal diffusion [see Fig. 3(b), bottom inset]. At short times $\sigma(t)$ diverges exponentially,

$$\sigma^2(t) - \sigma_c^2 = [\sigma^2(0) - \sigma_c^2] \exp(kTt/\sigma_c^2),$$

thus suggesting an early superdiffusive decay of the cluster. Conversely, for small aggregates with $\sigma(0) < \sigma_c$, the distribution $F_1(t, x)$ always collapses into a δ -like spike [see Fig. 3(b)].

Our last statement must be taken with caution for at least two reasons. (i) As σ becomes smaller than λ , the condition on the right-hand side of Eq. (12) is no longer obeyed and, as a consequence, our nonlinear FPE approach becomes untenable. (ii) The assumption that the distribution $F_1(t, x)$ retains its shape *and* normalization at any time, Eq. (13), provides an oversimplified description of the diffusion mechanism. Not only the profile of $F_1(t, x)$ evolves with time, but its normalization also evolves in time. For instance, upon collapsing, the particle aggregate can “evaporate” at its boundaries, as an effect of thermal fluctuations, and eventually dissolve in the particle bath. A similar behavior has been observed in dry granular fluids on a vibrating plate [28,29].

Finally, we remind the reader that normal diffusion, in the long time limit, has also been predicted for open-end stochastic single files. For instance, in Ref. [25] an expanding cluster of N Brownian particles with contact repulsion is proven to diffuse normally with a diffusion coefficient inversely proportional to $\ln N$.

The existence of the critical width σ_c defined in Eqs. (19) and (20) has a simple physical interpretation. Going back to Eq. (10) one immediately recognizes that in the case of attracting particles $g < 0$, the stationary condition $\partial_t F_1 = 0$ can be achieved for $F_1 = n_c$, no matter what the average density n of the particles in the system. It has been predicted [4], and numerically checked [1,5], that n_c indeed plays the role of a critical condensation density for an assembly of attracting Brownian particles under diverse dynamical conditions. Therefore, the critical width σ_c identifies clusters of N_1 particles squeezed together above the relevant condensation density. Thus, for $\sigma(0) > \sigma_c$ thermal fluctuations win over the interparticle attraction, while for $\sigma(0) < \sigma_c$ the cluster tends

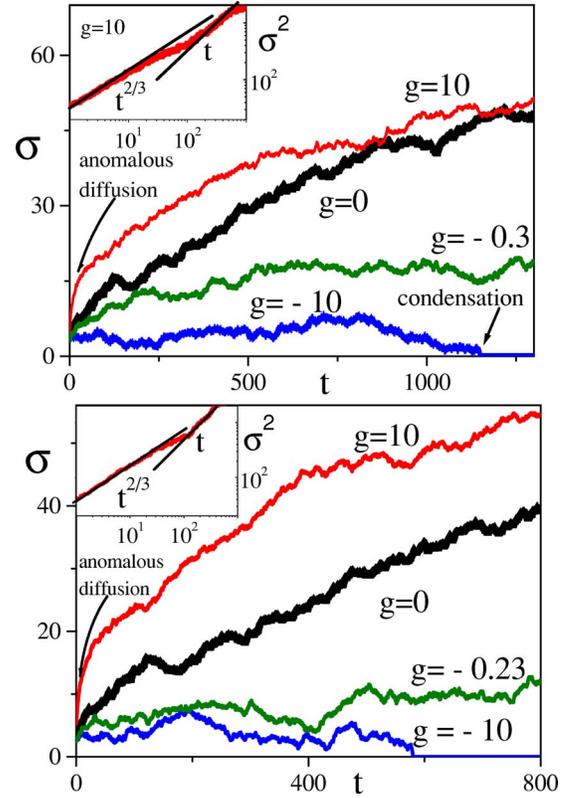


FIG. 4. (Color online) Dispersion $\sigma(t)$ versus time t showing the decay of a Gaussian cluster of interacting particles. This was obtained via molecular dynamics simulations of $N_1=50$ particles, initially forming a Gaussian packet with $\sigma(0)=3.3$ and interacting via the pair potential (3) with $\lambda=1$ and different g . Other simulation parameters are $l=400$ and $kT=1$: (a) cluster surrounded by a uniform particle distribution with $n=0.125$; (b) cluster expanding *in vacuo* with $n=0$. Insets: Logarithmic plot of $\sigma^2(t)$ for $g=10$; the slopes $t^{2/3}$ and t are drawn for the reader's convenience.

to collapse. Note that our estimate (20) for n_c comes close to the density of attracting particles at which the diffusion coefficient D in Fig. 1 drops to zero.

The most significant conclusions of the present section can be summarized as follows.

(1) Interaction affects the time dependence of $\langle x^2(t) \rangle = \sigma^2(t)$; in particular, for relatively short times, the spread of the distribution is clearly a subdiffusive process for repulsive particles. Instead, low density clusters of attractive particles spread out according to an exponential diffusion law, at short time scales, followed by normal diffusion.

(2) Sufficiently dense clusters of attracting particles, under certain conditions, are capable of forming stable spatial aggregates. Such conditions will be investigated in the following section.

Numerical simulations of low-density one-dimensional gasses of interacting particles corroborate our predictions. We adapted the numerical code employed in Sec. II to simulate clusters of pointlike particles diffusing subject to thermal fluctuations. In Fig. 4 we characterize the free expansion of a Gaussian cluster by plotting its width σ versus time t for different values of the coupling g . We simulated the spread of the initial cluster in the presence of a background uniform

particle distribution of density n , Fig. 4(a), and also without background particles (i.e., $n=0$, and all particles were initially lumped together to form the $t=0$ cluster), in Fig. 4(b). To make contact with the phenomenological predictions, Eqs. (17)–(20), in this section, here we focus on the cluster expansion *in vacuo*, panel (b). As expected, for $g>0$ the width $\sigma(t)$ starts to grow very fast, subdiffusively [see both insets in Fig. 4 for $\sigma^2(t)$]; within our numerical accuracy, the cluster diffusion exponent is close to the exponent of Eq. (18). At long times, $\sigma^2(t)$ diverges linearly in t (see insets in Fig. 4) with the free diffusion coefficient kT of Eq. (17). Comparing the curves of $\sigma(t)$ for $g=10$ (repelling particles) and $g=0$ (noninteracting particles), one notices that the particle repulsion helps the cluster expand and normal diffusion set on after all. A cluster of attractive particles $g<0$ decays differently depending on its initial width $\sigma(0)$. The curves in Fig. 4(b) for $g=-0.23$ and $g=-10$ are typical examples of the decay of a broad, $\sigma(0)>\sigma_c$, and a narrow cluster, $\sigma(0)<\sigma_c$, respectively: Only the narrow cluster collapses, as predicted in our phenomenological approach. The growth of cluster size for $g=-0.23$ seems to slow down after an initial expansion; this effect is due to the thermal expansion being compensated by the weak interparticle attraction [1,2,5]; note that under such conditions, as cautioned above, a cluster can dissolve without retaining its shape.

For the sake of comparison, we also simulated the time evolution of clusters of particles diffusing subject to the kinetics (5): As shown in Fig. 5, Gaussian clusters turn out to expand normally, i.e., with $\sigma^2(t) \propto t$, both according to models 1 and 2, regardless of the control parameters p and r , respectively. The reason why here, at variance with Sec. II A, neither model (5) seems to reproduce our simulation results is twofold. (i) The nonlinear FPE (10) in Sec. III A was derived under conditions (12). As both kinetic models assume implicitly zero-range pair potentials, long-range interaction effects with $n\lambda \gg 1$ are not accounted for. (ii) The constrained diffusion of nonpassing (and otherwise noninteracting) particles becomes subdiffusive with $\alpha < 1$ only for stationary (either periodic or confined) single-file geometries; particles of expanding single files diffuse normally as proven by Astangul [25]. On comparing the predictions of model 1, 5(a), and model 2, 5(b), with the simulation data of 4, we conclude that the properties of cluster relaxation reported in this section are indeed an effect of long-range particle interaction.

IV. JAMMING MECHANISM

As shown in Refs. [1,4,5], an assembly of attracting particles tends to jam above a critical density threshold, i.e., for $n > n_c$. Moreover, the phenomenological argument of Sec. III B also suggests that sufficiently dense clusters of attracting particles tend to resist the dispersive action of thermal fluctuations. We want now to investigate in more detail the jamming mechanism predicted by the nonlinear FPE (10).

For an assembly of N attracting particles distributed over a length l , Eq. (10) admits two stationary solutions, namely, $F_1(x)=n$ (normal phase) and $F_1(x)=n_c$ (jammed phase). Particle number (or mass) conservation dictates that only the

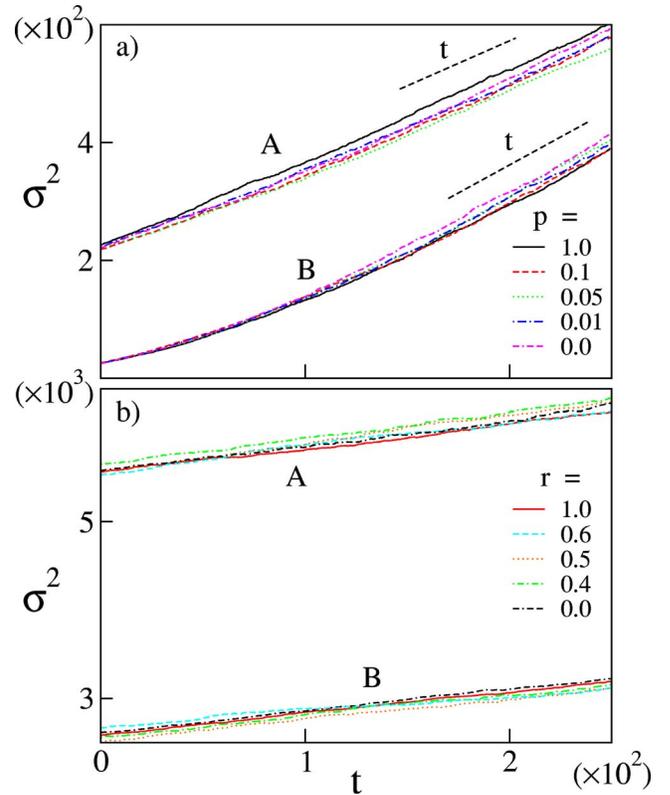


FIG. 5. (Color online) Decay of a Gaussian cluster of interacting particles, $\sigma^2(t)$ vs t . Monte Carlo simulations of a Gaussian cluster of $N_1=600$ particles diffusing against a uniform particle distribution with density $n=0.1$ (curve set A) and *in vacuo* with $n=0$ (curve set B). Particle kinetics of Eq. (5): (a) model 1; (b) and model 2. Other simulation parameters: $l=1.8 \times 10^4$ and $kT=1$; the curves weakly depend on the relevant kinetic parameter p or r .

former distribution is tenable as long as $n < n_c$. However, an interesting question arises when $n > n_c$: As in principle both solutions are physically acceptable, which distribution, and under what circumstances, describes the equilibrium state of the system?

A. Jammed phase

First, we characterize the jammed phase $F_1(x)=n_c$ by generalizing the simple scheme of Sec. III B. Let us add to or subtract from the condensate a cluster of N_1 particles centered at, say, $x=0$. This means that

$$F_1(t,x) = n_c + \psi(t,x), \quad (21)$$

where $\psi(t,x)$ has the preassigned shape (13) and N_1 can be either positive, if the cluster is being added, or negative when the cluster is being removed. On plugging Eq. (21) into Eq. (14) and making use of the definition (20) for n_c , one obtains a simple equation for the time evolution of σ , i.e.,

$$\frac{d}{dt} \sigma^2 = -|g| \frac{\kappa_2 N_1}{\sigma}. \quad (22)$$

For $N_1 < 0$, σ grows in time subdiffusively according to the law (18). This implies that the cluster tends to dissolve and

its N_1 constituents spread out over the entire length l . Eventually, the total average density $n = n_c - N_1/l$ will be subcritical, that is the system falls back into the normal phase.

For $N_1 > 0$, σ vanishes in a finite time interval, irrespective of its initial value $\sigma(0)$, or equivalently,

$$\psi(t, x) \rightarrow N_1 \delta(x). \quad (23)$$

This result answers the question of what happens with the excess particles $(n - n_c)l$ of an assembly of attracting particles undergoing jamming: Excess particles tend to aggregate in distinct clusters of different size with random spatial distribution

$$F_1(x) = n_c + \sum_i N_i \delta(x - x_i) \quad (24)$$

and

$$\frac{1}{l} \sum_i N_i = n - n_c. \quad (25)$$

Note that, as the positions x_i of the δ -like spikes of Eq. (24) form a countable set, the above expression for $F_1(x)$ is indeed a stationary solution of the nonlinear FPE (10) corresponding to the jammed phase with density n_c .

B. Stability of the jammed phase

Finally, we address the question of which stationary solution $F_1(x) = n$ or $F_1(x) = n_c$, of the nonlinear FPE (10) is stable. To this purpose we start with the nonequilibrium distribution

$$F_1(t, x) = n - n_1 + \psi(t, x), \quad (26)$$

with $\psi(t, x)$ defined in Eq. (13) and $n_1 = N_1/l$. At variance with the case of Eq. (21), here the number of the clustered particles N_1 is allowed to vary with time subject to two restrictions. (i) The total number N of particles in the system is conserved. (ii) The width of the cluster $\psi(t, x)$ is also kept constant, σ_0 . Such a constraint models, for instance, the presence of a defect acting as a cluster growth (or condensation) center with characteristic radius σ_0 .

Replacing Eq. (26) into the definition of $\langle x^2(t) \rangle$ yields

$$\frac{d}{dt} \langle x^2(t) \rangle = - \left(\frac{l^2}{12} - \sigma_0^2 \right) \frac{dN_1}{dt} \simeq - \frac{l^2}{12} \frac{dN_1}{dt}. \quad (27)$$

The approximation in Eq. (27) follows the conditions,

$$n_c^{-1} \ll \sigma_0 \ll l, \quad (28)$$

for our ansatz (26) to be consistent with the nonlinear FPE formalism, see Eq. (12). Inserting the approximate expression (27) for the time derivative of $\langle x^2(t) \rangle$ into Eq. (14), we finally obtain

$$\dot{n}_1 = -24 \frac{|g|}{l} [n_c - n + n_1] + \frac{12|g|\kappa_2}{\sigma_0} n_1^2. \quad (29)$$

If, thanks to the first inequality (28), we discard also the right-most term in Eq. (29), then we reach a simple conclu-

sion. For $n > n_c$ the mass of a cluster $\psi(t, x)$ of constant width σ_0 grows until N_1 approaches $(n - n_c)l$; the jammed state represented by the distribution (24) and (25) is thus recovered. On the contrary, for $n < n_c$ the initial cluster diffuses into the particle bath as $N_1(t) \rightarrow 0$. This provides further evidence to the predictions of Refs. [1,4,5], i.e., on increasing n larger than the threshold n_c , the homogeneous distribution $F_1(x) = n$ becomes unstable.

C. Linear stability of the uniform phase

Finally, we perform a linear stability analysis of the uniform state $F_1(t, x) = n$ following the approach of Ref. [30]. We start from the nonlinear FPE (7) in mean field approximation, i.e., with $G(t, x, \bar{x}) = 1$. Setting

$$F_1(t, x) = n + \psi(t, x) \quad (30)$$

and retaining only terms of first order in the perturbation $\psi(t, x)$, yield

$$\partial_t \psi(t, x) = kT \partial_x^2 \psi(t, x) + n \partial_x \psi(t, x) \int d\bar{x} \psi(t, \bar{x}) \partial_x W(x - \bar{x}). \quad (31)$$

On introducing the Fourier transforms

$$\tilde{\psi}(t, q) = \int dx e^{-iqx} \psi(t, x), \quad \tilde{W}(q) = \int dx e^{-iqx} W(x),$$

the eigenvalues of the linear FPE (31) are given by the dispersion relation [27]

$$\omega(q) = [kT + n\tilde{W}(q)]q^2. \quad (32)$$

Clearly, the uniform state $F_1(t, x) = n$ is unstable against deformations with wave vectors q such that $\tilde{W}(q) < -kT/n$, namely, only for attractive potentials. For the short-range potentials considered above, $\tilde{W}(q)$ can be approximated by $\tilde{W}(0) = g$, see Eq. (11), hence the critical uniform state (20), $n_c = kT/|g|$. In the more general case of finite-range potentials, for which $|\tilde{W}(q)|$ is a monotonic decreasing function, the q dependent critical density $n_c = kT/|\tilde{W}(q)|$ suggests that the uniform state is relatively stable against perturbations at the short wavelengths; thus, the problem of cluster stability studied in Sec. III cannot be treated in linear analysis.

V. CONCLUSIONS

We investigated the role of pair interactions in the diffusion of an assembly of Brownian particles in one dimension. Particles are allowed to pass one another, thus mimicking quasi-one-dimensional geometries studied in the earlier literature. In the limit of long observation times self-diffusion is normal. However, for attractive particles the diffusion constant drops to zero for densities larger than a jamming, or condensation threshold n_c ; for repulsive particles the diffusion constant exhibits a minimum in correspondence with an optimal packing geometry. At short times, when the pair interaction suppresses particle hopping (i.e., pair exchanges),

the particles form a chain (single-filing constraint); the ensuing subdiffusive process is apparent in the case of repulsive particles. This picture emerges from extensive numerical simulations based on the Langevin equations describing the Brownian motion of an assembly of particles at thermal equilibrium.

To shed light on the underlying diffusive mechanism, we also studied an approximate nonlinear Fokker-Planck equation derived to incorporate the statistical effects of pair interactions. In particular, we proved that a Gaussian cluster of attractive particles collapses for densities larger than the condensation threshold; this result confirms the stability of the jammed phase above threshold. At lower densities clusters spread out; the relevant dispersion mechanism depends on the interaction sign at short times, whereas normal diffusion

sets on in the asymptotic regime for both attractive and repulsive particles. The discussed effects can be observed in systems with colloidal particles [31,32], vortices [18], electrons [33], among other interacting particles.

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