Velocity correlations and mobility in single-file diffusion

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We study the velocity correlations of a tagged particle in an infinite assembly of interacting particles with a given density in one dimension. The assembly is in contact with a heat bath, and the particles interact via a hard-core repulsion with each other. We evaluate the two-time velocity correlation function exactly as function of time when an ensemble average is taken over initial conditions. This correlation function decays rapidly with time and becomes negative, with the rate of decay increasing with the density. This is followed by a slow decay toward zero through a power-law behavior of the form $-t^{-3/2}$ at large times for all densities. We also consider mobility of the assembly in the presence of a constant force acting on the particles, as well as the mobility of a tagged particle when only the tagged particle is driven by the force. The power spectrum of velocity fluctuations is also presented.

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I. INTRODUCTION

The problem of diffusion of hard-core particles in one dimension or single-file diffusion (SFD) has received sustained interest for the past 50 odd years [1–3]. On the one hand, it models diffusion in narrow crowded channels, which occur in a number of physical situations. Few such examples are: flow of ions and water across channels through cell membranes [4], sliding proteins along DNA [5], transport of adsorbate molecules through pores of Zeolite [2], carrier migration in polymers and superionic conductors [6], diffusion of water molecules through carbon nanotubes [7] etc. On the other hand, the problem is a nice example of an interacting particle problem, which is amenable to exact solution and exhibits nontrivial effects of interaction in a qualitative manner [8].

The first theoretical analysis of the problem was given by Harris [9] in 1965, who showed that the mean-square displacement of a tagged particle grows as $t^{1/2}$. This result excited a lot of interest, and since then a number of authors have revisited the problem and examined its various aspects and extensions [10–24]. Since the most physical situations have several attendant features which do not allow an unequivocal verification of this different diffusion behavior, recently some experiments have been designed to provide one-dimensional channels where this behavior can be examined without corruption from other physical effects [25–27]. Indeed the theoretical prediction is realized pretty closely in these experiments.

The concerns addressed in the existing literature have largely been the following. Several works have presented different derivations of the mean-square displacement of the tagged particle and the probability distribution of its position [10–13,15,16]. In these works one deals with ensemble averages of an infinite assembly of particles with nonzero density. These calculations and arguments have greatly enhanced our physical understanding of the $t^{1/2}$ behavior of the mean-square displacement. References [17,20,21] provide rigorous and exact derivations of these results. The main predictions regarding diffusion have also been tested by numerical computations [11,14]. In Refs. [20,21,24], one finds generalization of solution to the presence of boundaries and potentials. In Refs. [19,23], the authors analyzed the diffusion of a tagged particle by treating other particles as a stochastic bath. It is shown numerically that the bath is non-Markovian with long-range correlations in collision times and free distances between collisions. Some results have also been obtained for a finite number of particle with specified initial conditions [18,22]. Here one does not obtain the $t^{1/2}$ behavior for which the necessary condition seems to be the ensemble average with nonzero density of particles. However, such assemblies show peculiar spatial correlations for positions and velocities [22].

In this paper, our main concern is the velocity correlation function (VCF) of a tagged particle as function of time. There are several motivations for this study. The velocity correlation function is a key theoretical quantity to understand a number of experiments [28]. Experiments such as quasielastic neutron scattering and modulated gradient spin-echo NMR measure VCF directly [29]. In the latter technique the particle carry nuclear spins. We expect that SFD systems would also be investigated by such techniques. There are several other spectroscopic techniques such as quasielastic light scattering, pulsed gradient FT-NMR, Rayleigh-Brillouin scattering, and Raman scattering that measure quantities related to time integrals over VCF [30,31]. These experiments depend on how the coupling of the probe is connected to the motions of the molecule.

On the theoretical side, since the work of Alder and Wainwright which established numerically the existence of long-time tails for the velocity correlation function for a gas of hard disks (spheres) in two (three) dimension [32], there has been much interest in examining the long-time behavior of VCF in other systems. For the gas with hard-core interactions hydrodynamic arguments have been advanced to show that the long-time tails exhibit a power-law behavior of the form $t^{-d/2}$ for a d-dimensional system [33]. To our knowledge, similar long-time tails have also been predicted for three other situations. First situation is for molecular diffusion in confined geometries as the scattering from boundaries apparently leads to non-Markovian effects [34]. Here the velocity correlations become negative and the decay toward zero with a power law whose exponent depends on the geometry of the boundaries. Second case is that of diffusion of a moving particle in a static random medium [35]. In this case also the velocity correlation function becomes negative and has a long-time power-law decay of the form $-t^{-(d+2)/2}$. Finally Spohn [36] argued for a similar behavior for one-dimensional models of stochastic lattice gases. For the SFD, the VCF of the tagged particle has been considered in Refs. [19,23]. They have shown that for the large times, the VCF follows a power law of the form $-t^{-3/2}$, which is required for the consistency with the large time behavior of the mean-square displacement, $\langle \delta x^2(t) \rangle \propto t^{1/2}$. Marchesoni and Taloni [19] also obtained the VCF for all times by numerical simulations.

Here we present an exact calculation of the VCF for all times using Levitt's method [10]. This method has been criticized as being not rigorous, but the recent work of Kalinay and Percus [20] achieves the same result in a rigorous manner, thus greatly clarifying Levitt's approach. Levitt derived results mainly in the long-time limit. So he used the long-time limit of the single-particle diffusion propagator in which the velocity correlations get ignored. Accordingly, for our calculation we use the full position-velocity distribution in a stochastic environment as given by Chandrasekhar [37], which is valid at all times. We present detailed dependence of velocity correlator of the tagged particle with time, density, and temperature. We also relate the velocity correlations to the mobility of the particles when they are subjected to a uniform force. We have calculated the mobility in two situations. The first situation considers the flow of particles when a force acts uniformly on all the particles of the assembly. Here we have obtained the distribution function of position for a tagged particle and find that the distribution is Gaussian with a width which is increasing as $t^{1/2}$ as in the earlier case but with a drift which corresponds to the single-particle mobility of the noninteracting particles. This is to be expected on general grounds, as the two-particle momentum-conserving interactions cannot affect the dc conductivity. The second situation we consider is that of the mobility of a tagged particle in an assembly when the force acts only on the tagged particle. In this case the mobility depends on the density and the interactions do matter. This calculation is relevant to the situation when a small fraction of the particles in the channel are charged and one is interested in their flow under an applied field. Here the mobility is directly obtained from the time integral of the velocity autocorrelation function of the tagged particle.

The paper is organized as follows. In Sec. II, we give a brief account of Levitt's method and then present the calculation of the velocity correlation function. In Sec. III, we first present the calculation of the position distribution function of a tagged particle in the presence of a uniform force in the long-time limit. Next we present the calculation of the mobility of a tagged particle when the force acts on just the tagged particle through the use of Kubo formula. We also include the calculation of the power spectrum of the velocity fluctuations. Finally, we conclude the paper by presenting a summary of our results in Sec IV

II. VELOCITY AUTOCORRELATION FUNCTION

The model system consists of identical interacting particles on an infinite one-dimensional line with a density denoted by ρ. We take the density to be uniform initially. Particles are interacting via hard-sphere interaction, which implies that the particles cannot cross each other and when two particles collide they simply interchange their trajectories. Note that this is true only when the particles are identical. Further this assembly of particles is in equilibrium with a thermal bath at temperature T. The initial velocity distribution of the particles is taken to be the Maxwellian distribution. In the absence of interactions the trajectories of the particles are independent and are given by the distribution $h(x,u,t|x_0,u_0)$, which gives the probability of finding the particle at time t with position x and velocity u, if its initial position and velocity are x_0 and u_0, respectively. For the evaluation of any one-particle correlation function we need the conditional single-particle position-velocity distribution function $f(x-x_0,u,t|u_0)$ in the interacting assembly. The function f gives the probability of finding a tagged particle at position x with velocity u at time t given that it was initially at x_0 with velocity u_0 on ensemble averaging over the initial positions and velocities of all the other particles. An exact expression of $f(x,u,t|u_0)$ was derived by Levitt [10].

In order to be reasonably self-contained, we present a brief account of this result. To understand the following expressions, it is necessary to refer to Fig. 1, which schematically represents the trajectories of a small set of particles around the tagged particle in a space-time plot for a given realization. The bold line shows the trajectory followed by the tagged particle, which is labeled 0 and is initially at $x=0$. To keep track of the position of the particle a straight line is drawn joining the points (x,t) and (0,0), and is called the test trajectory. It is shown as a dotted line in Fig. 1. Since the sequence of particles cannot change, the tagged particle can be at x at time t only under the following conditions. At a time slightly before t it should be: (1) the first left neighbor of the test trajectory; (2) the first right neighbor of the test

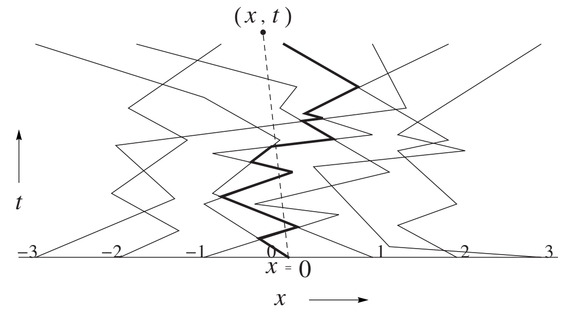

FIG. 1. This diagram shows schematic plots of the trajectories of a few particles around the tagged particle labeled as 0 in a typical realization. When the two identical particles collide, their velocities get exchanged or in other words trajectories simply pass through one another. The bold line shows the trajectory followed by the tagged particle. A dashed line is drawn joining points (x,t) and (0,0) and is called the test trajectory. In order to be at x at time t, a little before t the particle must be either the first neighbor of the test trajectory or be on it. Note that whenever any other particle crosses the test trajectory the neighborhood status of the tagged particle changes by +1 if crossing is from the left and −1 if the crossing is from the right. The kinks in particle trajectories are due to interaction with the stochastic environment of the heat bath.

trajectory; and (3) on the trajectory $h(x,u=x/t,t|0,u_0)$. Each of the first two cases can occur in two ways. The particle can initially start being left or right of the test trajectory. Now the position of the tagged particle as neighbor with respect to test trajectory changes when another particle crosses the test trajectory. Thus it can remain the first neighbor only if the net number of crossings of the test trajectory by all particles is ± 1, where the net number is defined to be: number of crossings from the right−number of crossings from the left. It will be found on the initial trajectory if the number of crossings is zero. Combining all these five possibilities, Levitt [10] obtained

$$f(x,u,t|u_0) = \rho[E_R(A_0P_R + A_1P_L) + E_L(A_{-1}P_R + A_0P_L)] + A_0h(x,u,t|0,u_0). \tag{1}$$

Various terms in the above formula are defined as follows. $E_{R(L)}$ is defined to be the probability that the particle which is initially at $x=0$ with the velocity u_0 is to the right(left) of x at time t. These are given in terms of the single-particle distribution as

$$E_R = \int_x^\infty dx' \int_{-\infty}^\infty du h(x',u,t|0,u_0),$$

$$E_L = \int_{-\infty}^x dx' \int_{-\infty}^\infty du h(x',u,t|0,u_0). \tag{2}$$

$P_{R(L)}(x,u,t)$ denote the probability that a particle initially to the right(left) of the origin is found at x at time t. These are given by

$$P_R(x,u,t) = \int_0^\infty dx' \int_{-\infty}^\infty du_0 h(x,u,t|x',u_0)g(u_0),$$

$$P_L(x,u,t) = \int_{-\infty}^0 dx' \int_{-\infty}^\infty du_0 h(x,u,t|x',u_0)g(u_0), \tag{3}$$

where $g(u_0)$ is the probability distribution of the initial velocities of the particles. $A_\alpha(x,t)$ denotes the probability that the test trajectory is crossed a net α times, and can be written in terms of probabilities Q_R and Q_L as follows:

$$A_\alpha(x,t) = \sum_{n=0}^\infty Q_R(x,n+\alpha,t)Q_L(x,n,t). \tag{4}$$

Here $Q_{R(L)}(x,n,t)$ gives the probability that n trajectories which were started to the right(left) of test trajectory are to left(right) of test trajectory. These are given by

$$Q_R(x,n,t) = \frac{e^{-\bar{B}_R}(\bar{B}_R)^n}{n!},$$

$$Q_L(x,n,t) = \frac{e^{-\bar{B}_L}(\bar{B}_L)^n}{n!}. \tag{5}$$

Thus $A_\alpha(x,t)$ is

$$A_\alpha(x,t) = \exp[-(\bar{B}_R + \bar{B}_L)]\left(\frac{\bar{B}_R}{\bar{B}_L}\right)^{\alpha/2} I_\alpha(2(\bar{B}_R\bar{B}_L)^{1/2}), \tag{6}$$

where $I_\alpha(x)$ denotes the modified Bessel function and $\bar{B}_{R(L)}$ denotes the probability that a particle crosses the test trajectory from right(left) averaged over the initial position. These are given as

$$\bar{B}_R = \rho\int_0^\infty dx_0 \int_{-\infty}^x dx' \int_{-\infty}^\infty du \int_{-\infty}^\infty du_0 h(x',u,t|x_0,u_0)g(u_0),$$

$$\bar{B}_L = \rho\int_{-\infty}^0 dx_0 \int_x^\infty dx' \int_{-\infty}^\infty du \int_{-\infty}^\infty du_0 h(x',u,t|x_0,u_0)g(u_0). \tag{7}$$

We wish to calculate the velocity autocorrelation function for all times starting from zero as the calculation of mobility requires a complete time integral over the VCF. The earlier works by Levitt and others take $h(x,u,t|x_0,u_0)$ to be a diffusion propagator multiplied by a velocity distribution function. Such a propagator is useful only for the long-time limit of the position distribution function and do not yield a nonzero value for the velocity correlator as these correlations decay rather fast with time. Accordingly we take $h(x,u,t|x_0,u_0)$ to be the full position-velocity distribution in a stochastic environment as given by Chandrasekhar [37]. This function is

$$h(x,u,t|x_0,u_0) = \frac{1}{2\pi\sqrt{FG-H^2}}\exp\left[-\frac{1}{2(FG-H^2)} \times (GX^2 - 2HXS + FS^2)\right], \tag{8}$$

where

$$X = x - x_0 - \frac{u_0}{\eta}(1-e^{-\eta t}),$$

$$S = u - u_0e^{-\eta t},$$

$$F = \frac{kT}{m\eta^2}(2\eta t - 3 + 4e^{-\eta t} - e^{-2\eta t}),$$

$$G = \frac{kT}{m}(1-e^{-2\eta t}),$$

$$H = \frac{kT}{m\eta}(1-e^{-\eta t})^2. \tag{9}$$

The heat bath on the particles is characterized by two parameters, temperature T and the velocity relaxation rate η. The relaxation rate η sets the time scale for the problem. Using this value of $h(x,u,t|x_0,u_0)$, we have evaluated the various probabilities involved in the calculation of f. These are given below,

$$E_R = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{x-\nu}{\sqrt{2F}}\right)\right],$$

$$E_L = \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{x-\nu}{\sqrt{2F}}\right)\right], \tag{10}$$

where $\nu = \frac{u_0}{\eta}(1-e^{-\eta t})$.

$$\bar{B}_R = \rho\sqrt{d/2}\left[\frac{1}{\sqrt{\pi}}e^{-\gamma^2} + \gamma(1+\operatorname{erf}(\gamma))\right],$$

$$\bar{B}_L = \rho\sqrt{d/2}\left[\frac{1}{\sqrt{\pi}}e^{-\gamma^2} - \gamma(1-\operatorname{erf}(\gamma))\right], \tag{11}$$

where

$$d = F + \frac{kT}{m}\left(\frac{1-e^{-\eta t}}{\eta}\right)^2,$$

$$\gamma = \frac{x}{\sqrt{2d}}, \tag{12}$$

$$P_R = \frac{1}{2\pi\sqrt{C}}\int_{-\infty}^{x}\exp\left[-\frac{1}{2C}(ay^2 - 2byu + du^2)\right]dy,$$

$$P_L = \frac{1}{2\pi\sqrt{C}}\int_{x}^{\infty}\exp\left[-\frac{1}{2C}(ay^2 - 2byu + du^2)\right]dy. \tag{13}$$

Here

$$C = FG - H^2 + \frac{kT}{m}\left[G\left(\frac{1-e^{-\eta t}}{\eta}\right)^2 - 2He^{-\eta t}\left(\frac{1-e^{-\eta t}}{\eta}\right) + Fe^{-2\eta t}\right],$$

$$a = G + \frac{kT}{m}e^{-2\eta t},$$

$$b = H + \frac{kT}{m}e^{-\eta t}\left(\frac{1-e^{-\eta t}}{\eta}\right). \tag{14}$$

The velocity autocorrelation function is the average of product of velocities of the tagged particle at time t and at initial time over the distribution function $f(x,u,t|0,u_0)$. It takes the form,

$$\langle u(t)u(0)\rangle = \int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}du_0 uu_0[\rho E_R(A_0P_R + A_1P_L) + \rho E_L(A_{-1}P_R + A_0P_L) + A_0 h(x,u,t|0,u_0)]g(u_0). \tag{15}$$

Here we take $g(u_0)$ to be the Maxwell-Boltzmann velocity distribution function at temperature T. Using Eqs. (8), (10), (11), and (13), we get the following result for the VCF:

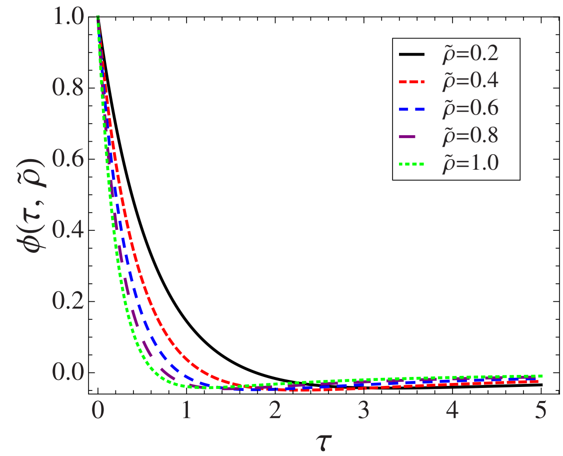

FIG. 2. (Color online) Scaled velocity correlation function $\phi(\tau,\tilde{\rho})$ vs dimensionless time τ for small values of $\tilde{\rho}$.

$$\langle u(t)u(0)\rangle = \rho\left(\frac{kT}{m}\right)\left(\frac{1-e^{-\eta t}}{\eta}\right)\frac{b}{2\pi d} \times \int_{-\infty}^{\infty}dx e^{-x^2/d}(A_1 + A_{-1} - 2A_0) + I_5, \tag{16}$$

where I_5 is the contribution to velocity correlation when tagged particle arrives at x on its initial trajectory. It is given by

$$I_5 = \frac{1}{\sqrt{2\pi}}\frac{kT}{m}\frac{H}{F}\left(\frac{(1-e^{-\eta t})}{\eta d^{3/2}}\right)\int_{-\infty}^{\infty}dx x^2 A_0 e^{-x^2/2d} + \frac{1}{\sqrt{2\pi}}\left(\frac{kT}{m}\right)^2\left(e^{-\eta t} - \frac{H(1-e^{-\eta t})}{\eta F}\right) \times \left(\frac{(1-e^{-\eta t})}{\eta}\right)^2\frac{1}{d^{5/2}}\int_{-\infty}^{\infty}dx x^2 A_0 e^{-x^2/2d} + \frac{1}{\sqrt{2\pi}}\frac{kT}{m}\left(e^{-\eta t} - \frac{H(1-e^{-\eta t})}{\eta F}\right)\frac{F}{d^{3/2}}\int_{-\infty}^{\infty}dx A_0 e^{-x^2/2d}. \tag{17}$$

We have done the numerical integration of Eq. (16). The velocity correlation function has the scale of thermal velocity and can be written as function of two dimensionless variables in the following manner:

$$\langle u(t)u(0)\rangle = \frac{kT}{m}\phi(\tau,\tilde{\rho}), \tag{18}$$

where $\tau = \eta t$ is the dimensionless time and $\tilde{\rho} = \frac{\rho}{\eta}\sqrt{\frac{kT}{m\pi}}$ is the dimensionless measure of density. $\tilde{\rho}$ is also the inverse of the average collision time measured in unit of η^{-1}.

In Figs. 2 and 3, we have plotted the scaled velocity correlation function $\phi(\tau,\tilde{\rho})$ as function of τ for different values of $\tilde{\rho}$. As is clear from the figures $\phi(\tau,\tilde{\rho})$ is not a monotonically decreasing function of τ. Initially it decreases fast with τ and becomes negative. The initial rate of decay increases rather rapidly with the dimensionless density. After the function reaches a negative minimum it rises slowly toward the

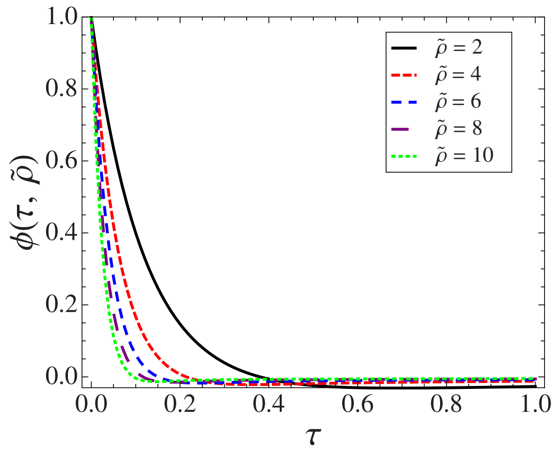

FIG. 3. (Color online) Scaled velocity correlation $\phi(\tau,\tilde{\rho})$ vs dimensionless time τ for large values of $\tilde{\rho}$.

zero value. Note that these plots seem to match well with the numerical simulations of Marchesoni and Taloni [19]. We have investigated the late time behavior of velocity autocorrelation by numerical fitting of the data. We find excellent fits to the power law $-\tau^{-\nu}$ for a rather large range of τ. Figure 4 shows the fits for a range of small $\tilde{\rho}$, while Fig. 5 shows the fits for a range of larger $\tilde{\rho}$. We find $\nu=3/2$ for the entire range of dimensionless densities that we have investigated. It is possible to evaluate the formula for VCF, Eq. (16), in small time and large time limits. These are

$$\langle u(t)u(0)\rangle \approx \frac{kT}{m}\left[1-\eta t\left(1+\frac{4\rho}{\eta}\sqrt{\frac{kT}{m\pi}}\right)\right] \quad \eta t \to 0, \tag{19}$$

and

$$\langle u(t)u(0)\rangle \approx -\sqrt{\frac{kT}{m\pi\eta}}\frac{1}{8\rho t^{3/2}} \quad \eta t \to \infty. \tag{20}$$

The latter result differs from the asymptotic result derived by Taloni and Lomholt [23] by a factor of 1/2. As pointed out in Ref. [19], the long-time behavior of VCF should be consistent with the $t^{1/2}$ behavior of MSD due to the following relation:

$$\langle \delta x^2(t)\rangle = 2\int_0^t (t-\tau)\langle u(\tau)u(0)\rangle, \tag{21}$$

which is satisfied by the $-t^{-3/2}$ behavior. It is interesting to note that this long-time behavior is identical to the behavior of the velocity correlations in the Lorentz model [35] as well as for stochastic lattice gases in one dimension [36]. Further the same behavior is also observed for the diffusion in the confined geometry situation for the case of long narrow tubes [34]. An experiment using modulated gradient spin-echo NMR has measured VCF in water trapped in a porous material which shows at long times the $-t^{-3/2}$ behavior [29]. For these experimental conditions boundary scattering may be more relevant than single-file diffusion.

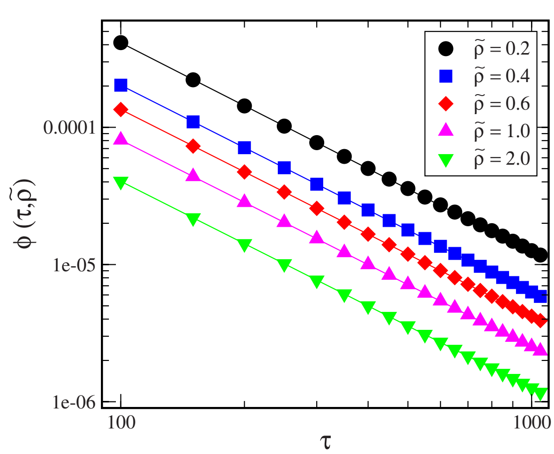

FIG. 4. (Color online) Numerical fit of the scaled velocity autocorrelation function $\phi(\tau,\tilde{\rho})$ for large time τ and for small values of $\tilde{\rho}$. Here various symbols shows the fitted data and continuous lines are plots of the functions which best fit the data.

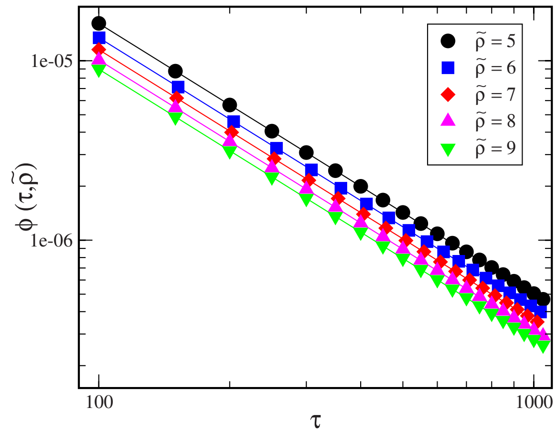

FIG. 5. (Color online) Numerical fit of the scaled velocity autocorrelation function $\phi(\tau,\tilde{\rho})$ for large time τ and for large values of $\tilde{\rho}$. Here again various symbols shows the fitted data and continuous lines are plots of the functions which best fit the data.

III. CALCULATION OF MOBILITY

In this section, we consider the response of the system to a weak uniform force. Our calculations are done in two situations. In the first situation the uniform force pushes all the particles equally, such as subjecting an assembly of charged particles to a uniform electric field. In the second situation, we calculate the mobility of a tagged particle when the force acts only on the tagged particle. This case is relevant to the physical situation in which a small fraction of the particles in the channel are charged and are subjected to an electric field. The present calculation, however, ignores the Coulomb interaction between these particles.

We first present the calculation of the position probability distribution in the presence of a weak force in the long-time limit when the force acts on all the particles equally. We again use the method given by Levitt [10]. For this purpose only the long-time limit of h is needed which in the presence of an external force is given by

$$h(x,u,t|x_0,u_0) = \frac{1}{\sqrt{4\pi Dt}} e^{-(x-x_0-\mu_0 Et)^2/4Dt} g(u), \tag{22}$$

where $g(u)$ is any normalized function of velocity. μ_0 and E are the single-particle mobility and applied force, respectively. Note that the single-particle mobility μ_0 results from the interaction of the particle with the heat bath, and in the present case is given by $1/m\eta$. Levitt [10] has argued that in the long-time limit, the position distribution function is given by $A_0(x,t)$ for the following reason. $A_0(x,t)$ is the spatial probability distribution of the line segment which connects the two neighboring particles which were initially on the opposite side of test trajectory. In long-time limit this distribution (with a different normalization) is the same as position probability $p(x,t)$. We have calculated the $\bar{B}_R$ and $\bar{B}_L$ using Eq. (22). These are given by

$$\bar{B}_R = 2\rho(Dt/\pi)^{1/2}\int_{-\infty}^{\gamma}(\gamma-\beta)e^{-\beta^2}d\beta,$$

$$\bar{B}_L = 2\rho(Dt/\pi)^{1/2}\int_{\gamma}^{\infty}(\beta-\gamma)e^{-\beta^2}d\beta, \tag{23}$$

where $\gamma = \frac{(u-\mu_0 E)t}{\sqrt{4Dt}}$. In order to find the value of A_0 in long-time limit, we have evaluated $\bar{B}_R$ and $\bar{B}_L$ for $t\to\infty$. These are given as

$$B_R = \rho(Dt/\pi)^{1/2}[1+\sqrt{\pi}\gamma],$$

$$B_L = \rho(Dt/\pi)^{1/2}[1-\sqrt{\pi}\gamma].$$

Thus $p(x,t)$ (after normalizing A_0) is given by

$$p(x,t) = \frac{\sqrt{\rho}}{2(\pi Dt)^{1/4}}\exp\left[-\left(\frac{\pi\rho^2}{16Dt}\right)^{1/2}(x-\mu_0 Et)^2\right]. \tag{24}$$

From this result it is clear that the mean-square displacement is again proportional to $t^{1/2}$. But the important point is that there is a nonzero mean displacement, which is equal to $\mu_0 Et$. This implies that the mobility of the tagged particle is same as the free particle mobility μ_0, or in other words mobility is unchanged by the interaction. This provides a check to the general argument that the momentum-conserving two-body interaction does not affect the mobility.

Next we present the result for the second situation in which the force acts on just the tagged particle. In this case the mobility μ_1 can be obtained from the Green-Kubo formula, as given by

$$\mu_1 = \frac{e}{kT}\int_0^\infty \langle u(t)u(0)\rangle dt = \mu_0\int_0^\infty \phi(\tau,\tilde{\rho})d\tau, \tag{25}$$

where the above expression is specialized to the charged particle and e denotes the charge of the particle. This formula shows that μ_1 depends on the density and temperature in a specific way through $\tilde{\rho}$. In Fig. 6 we have shown the variation in $\mu_1(\rho)/\mu_0$ with ρ. This mobility is seen to be a strong function of the dimensionless density $\tilde{\rho}$. The inset of Fig. 6 shows its rapid fall at small values of $\tilde{\rho}$ while the main plot in Fig. 6 shows the variation over the larger range of $\tilde{\rho}$.

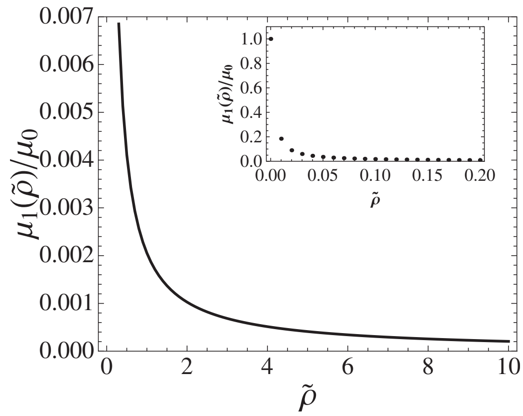

FIG. 6. Charged particle mobility $\mu_1(\rho)/\mu_0$ vs dimensionless density $\tilde{\rho}$. The charged particle mobility decrease very rapidly with $\tilde{\rho}$. The inset shows this sharp variation of μ_1 at small values of $\tilde{\rho}$, while the main plot shows the variation for a larger range of $\tilde{\rho}$.

These results on mobility should be amenable to experimental verification in suitably prepared systems as the theory gives rather specific predictions regarding the dependence of mobility on temperature and particle density.

Since many of the experiments measure the power spectrum of the velocity fluctuations, we have numerically calculated the cosine transform of VCF which gives the power spectrum $S(\omega)$ to be

$$S(\omega) = \int_0^\infty \langle u(t)u(0)\rangle\cos(\omega t)dt. \tag{26}$$

Three plots of $\tilde{S}(\omega/\eta) = (m\eta/kT)S(\omega)$ at typical densities $\tilde{\rho} = 0.2$, 1.0, and 2.0 are shown as function of dimensionless frequency ω/η in Fig. 7. The power spectrum curves become smaller with the increasing particle density, as the motion of the particle gets inhibited with increasing density. The curves rise with frequency and then show a slight decrease at low densities, but seem to saturate at higher frequencies. This is indicative of high-frequency rattling motion of the particles.

IV. CONCLUSION

We conclude the paper with a summary of our results. We have evaluated the velocity autocorrelation function of a

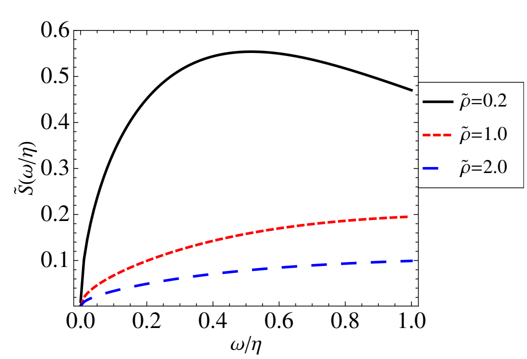

FIG. 7. (Color online) Plots of power spectrum $\tilde{S}(\omega/\eta)$ at three values of $\tilde{\rho}=0.2$, 1.0, and 2.0.

tagged particle in an infinite assembly of interacting particles with a finite density in one dimension. Particles interact via the hard-core interaction. We believe this is the first report of an analytic calculation of the velocity correlation function for all times. We find that the velocity correlation shows an unusual behavior. With time the velocity correlator decreases and becomes negative. After reaching a negative minimum the function decays slowly toward zero obeying the power law $-t^{-3/2}$ over several decades in time. We have verified that when all the particles are subjected to the same uniform force the mobility of a tagged particle remains unchanged from its noninteracting value. On the other hand when the force is applied to just one tagged particle in the system, its mobility decreases rapidly with the density of the particles. The results on this kind of mobility are relevant to the study of electrical transport in channels in which a small fraction of particles are charged. Here we have made specific predictions regarding the dependence of mobility on particle density and temperature which are amenable to experimental verification. For direct comparison to experimental results, we have also presented the numerical results on the power spectrum of the velocity fluctuations.

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