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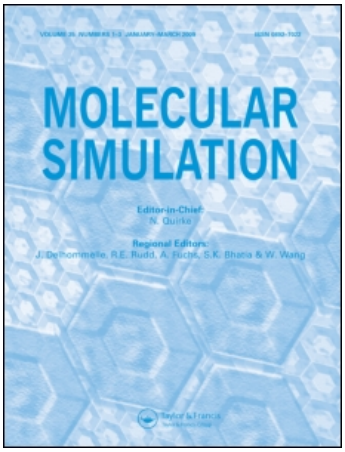

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Quasi One-dimensional Non-passing Self-diffusion

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Quasi One-dimensional Non-passing Self-diffusion

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Anomalous diffusion of fluids in a restricted geometry which forbids passing of one fluid particle by another has been studied for many years. The detailed dependence of the mobility factor of the single-file diffusion on relevant parameters beyond the strictly one-dimensional limit is not well understood. In this paper, we study the mobility factor of single-file diffusion fluids interacting with a hard potential in two-dimensional pores. We present a rationale for a theory of the dynamic mobility in terms of the equilibrium equation of state, and make preliminary comparison with Monte Carlo simulations of hard discs in a channel.

Keywords: Anomalous diffusion; Single-file diffusion; Equilibrium equation; Monte Carlo simulations

PACS: 05.60. + w; 47.55.Mh

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INTRODUCTION

A defining characteristic of present-day many-particle physics lies in our ability to probe smaller and smaller spatial and temporal domains [1–14]. At the spatial side, the matter we thereby deal with has a very large surface to volume ratio, rendering unsuitable many traditional thermodynamics treatments. We will focus here on the fashion in which we can deal at a theoretical level with a particular prototypical system of this kind, that of a (classical) fluid confined to an infinitely long pore, an idealization of situations that occur in practice-channels in zeolites, pores in biological membranes, ... as well as in carefully tuned experiments. We restrict our attention to self-diffusion as the simplest signature of the novel transport associated with such tightly confined systems.

To phrase precise questions, one must make explicit the dynamical regime that is the object of study. Here, we will choose that of massive particles in a Brownian medium, a caricature of a range of mixed fluid dynamics [15–17]. In this caricature, the bathing-medium serves only to supply the distribution of ideally instantaneous jumps that constitute the dynamics of the massive particles. These jumps are certainly modified by prohibitions resulting from substrate walls and other particles, but whatever we say about them, the net effect is that the dynamics of a given particle will be stochastic, parameterized by the probability per unit time of a spatial jump from r' to r,

$$Pr(r|r', \mathrm{d}t) = f(r, r')\,\mathrm{d}t. \tag{1.1}$$

In the absence of external constraints, a single particle in the Brownian medium would then have a probability density satisfying the Master equation,

$$\frac{\partial \rho(r,t)}{\partial t} = \int f(r,r')\rho(r',t)\,\mathrm{d}r' - \int f(r,r')\,\mathrm{d}r'\rho(r,t). \tag{1.2}$$

At long time, the length scale for the variation of $\rho(r,t)$ will become very large, allowing us to expand:

$$\rho(r',t) = \rho(r,t) + (r'-r)\cdot\nabla\rho(r,t) + \frac{1}{2}(r'-r)(r'-r):\nabla\nabla\rho(r,t) + \ldots,$$

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reducing Eq. (1.2) to the driven inhomogeneous diffusion equation

$$\frac{\partial\rho(r,t)}{\partial t}=\int(r'-r)f(r,r')\mathrm{d}r'\bullet\nabla\rho(r,t)$$

$$+\frac{1}{2}\int(r'-r)(r'-r)f(r,r')\mathrm{d}r':\nabla\nabla\rho(r,t)+\ldots \quad (1.3)$$

For a uniform isotropic medium in a space of dimensionality d, $f(r,r')=f(|r-r'|)$, and Eq. (1.3) is further reduced to,

$$\frac{\partial\rho(r,t)}{\partial t}=D\nabla^2\rho(r,t), \quad (1.4)$$

where $D=(1/2d)\int s^2 f(s)\,\mathrm{d}s$.

Equation (1.4) is organized by the diffusion constant D, and can be solved at once for the time development of a density originally concentrated at r_o : if $\rho(r,0)=\delta(r-r_o)$, then,

$$\rho(r,t)=(4\pi Dt)^{\frac{-d}{2}}e^{-(r-r_o)^2/4Dt}. \quad (1.5)$$

An operational definition of the diffusion constant is then that as $t\rightarrow\infty$,

$$\langle|r-r_o|^2\rangle=\int\rho(r,t|r(0)=r_o)|r-r_o|^2\mathrm{d}r$$

$$=2dDt \quad (1.6)$$

or

$$D=\lim_{t\rightarrow\infty}\frac{1}{2dt}\ \langle|r(t)-r(0)|^2\rangle. \quad (1.7)$$

The clean expressions (1.5)–(1.7) are not just modified when the particles are interacting in a quasi-one dimensional enclosure, but will be changed qualitatively as well. It is the nature of these changes that we will attend to by a largely heuristic theoretical analysis, assessed—and in fact motivated—by computer simulations.

ANOMALOUS DIFFUSION: ONE-DIMENSIONAL LIMIT

An extreme version of Brownian dynamics fluid transport in a narrow pore is that of hard cores of diameter a in a hard cylindrical enclosure of radius R, with $R=a/2$. In this case, no transverse motion can take place, and we have strictly longitudinal one-dimensional motion, say $x(t)$. The motion of a particle, in effect a rod of diameter a, is then constrained not only by diffusion, but also by its not being able to pass its neighbors, and Eq. (1.6) no longer holds. Instead, as Levitt [15] showed in 1973 in the case of infinitesimal jumps, one has at long times $\langle|x-x_o|^2\rangle\sim t^{1/2}$, referred to as subdiffusion or anomalous diffusion. Percus [17] solved the general finite jump case in 1974, and gave an explicit expression for the coefficient of $t^{1/2}$. A number of lattice gas models, including the possibility of infrequent particle–particle passing, were investigated in succeeding years [18–23], and the finite jump case was revisited by Hahn and Kärger [24] in 1995. Model numerical simulations appeared frequently, and scaled-up experiments have recently been carried out as well.

We will be examining the strictly non-passing or single-file regime, that in which $R<a$, by analytical and numerical methods, as preparation for an ongoing investigation of the dramatic changes as one goes past the $R\leq a$ restriction.

Although this situation has been considered previously, we will introduce a new approach based on an assertion that the mobility is controlled by a length scale which can be approximated by the equation of state. But let us start by reviewing in cursory fashion the even more restricted one-dimensional case that forms the conceptual basis of the non-passing single-file phenomenology. Exact solutions have relied upon the observation—absolutely valid when the motions are inertial with elastic collisions—that if one is following a given particle, then when it "collides" with another, each particle thereafter continues the motion of the other, but displaced by a distance $\pm a$. In other words, if the distance a is shrunk to zero, equivalent to replacing the specific volume l by $l-a$, or the density n by $n/1-na$, the distinguished particle would not know the difference: we can simply take $a=0$, but $n\rightarrow n/1-na$. The key point is then that if $a=0$, point particles, the *set* of particle positions obtained dynamically is indistinguishable from that of a set of non-interacting particles—they just exchange labels on meeting.

Let us make a brief strictly heuristic analysis of the primitive case of hard point particles of mean linear density n on an infinite line. A labeled particle initially at the origin can have a large excursion, say $\Delta x(t)$ to the right, only when its right neighbor does likewise, and its right neighbor, etc. but of course with displacements predominantly of decreasing amplitude. Meanwhile, particles to the left fill in the gap created, in complementary fashion, some remaining on the left. Thus we can imagine that a cluster of, say, $M(t)$ particles is "significantly" displaced, and $\Delta x(t)$ can be associated with the center of mass Δx_{cm} of the cluster. In this cartoon (see Fig. 1), self-diffusion of the labeled particle is mimicked by the cooperative diffusion of the surrounding cluster, a relationship familiar in the context of the self-diffusion of a polymer in a dense polymer solution (see e.g. [25]). We now estimate the relation between the weakly fluctuating $M(t)$ and the ensemble average $\langle(\Delta x_{cm}(t))^2\rangle$ in two different ways, sufficient to determine both.

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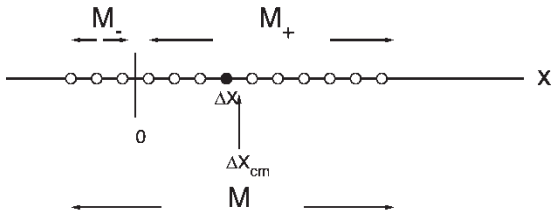

FIGURE 1 A cartoon that is used in the heuristic analysis of single-file diffusion. The filled circle represents a labeled particle initially at the origin that has a large excursion of Δx to the right. This involves a cluster of M particles that has been displaced and $\Delta x_{\rm cm}$ denotes the center of mass of the cluster. M_- and M_+ represent, respectively, the number of particles in the cluster to the left and right of the origin.

First, since exchange of particle labels does not affect the set of particle locations in the cluster, we can regard the particles that happen to be in the cluster as having independently diffused, and conclude that

$$\langle(\Delta x_{\rm cm})^2\rangle = \frac{1}{M}\langle(\Delta x)^2\rangle_{\rm o}, \tag{2.1}$$

where subscript "o" refers to free particle Brownian motion (or any other, for that matter) and all quantities depend upon the time of observation. Next, since the mean particle density of a large cluster fluctuates weakly about the global mean n, the physical size of the cluster is M/n, and $M_\pm = 1/2(M \pm n\Delta x_{\rm cm})$ represent, respectively, the number of $\pm$ particle displacements from the origin. In other words,

$$n\Delta x_{\rm cm} = M_+ - M_- = \sum_{j=1}^{M} {\rm sgn}(x_j), \tag{2.2}$$

where the $[x_j]$ are the labeled particles in the cluster. But again the $[x_j]$ can be regarded as unlabeled and independent. Replacing the cluster by the average cluster, which is symmetric about the origin, then $\langle {\rm sgn}(x_j)\rangle = 0$, of course ${\rm sgn}(x_j)^2 = 1$, and so Eq. (2.2) implies that

$$n^2\langle(\Delta x_{\rm cm})^2\rangle = M. \tag{2.3}$$

We can then combine Eqs. (2.1) and (2.3), identify $\Delta x_{\rm cm}$ with Δx, and conclude that

$$\langle(\Delta x_{\rm cm})^2\rangle = \frac{1}{n}\left[\langle(\Delta x)^2\rangle_{\rm o}\right]^{1/2} \tag{2.4a}$$

$$M = n\left[\langle(\Delta x)^2\rangle_{\rm o}\right]^{1/2}. \tag{2.4b}$$

Equation (2.4a) is qualitatively the same as, and quantitatively quite close to, the exact result

$$\langle(\Delta x)^2\rangle = l\langle|\Delta x|\rangle_{\rm o}, \tag{2.5a}$$

$l = 1/n$, for typical underlying independent particle distributions of Δx, e.g. true diffusion, inertial motion.... The difference between Eqs. (2.4a) and (2.5a,b) appears to be due primarily to the mean field character of the argument: the cluster is in fact symmetric about the origin only as an ensemble average, but not at all for typical realizations. It is not trivial to modify the above argument to account for this aspect.

If the particles have diameter a, and if the dynamics of a "collision" produce a pair of trajectories indistinguishable from that of independent particles except for an offset of $\pm a$, then as we have noted above, the only change is that the "free volume" per particle is $l - a$:

$$\langle(\Delta x)^2\rangle = (l-a)\langle|\Delta x|\rangle_{\rm o}. \tag{2.5b}$$

In the one-dimensional case, the asymptotic Eq. (1.3), and consequent Eqs. (1.4) and (1.5), remain valid, and the move distribution dependence is trivial; the situation in 2 or 3 dimensions is notably non-trivial.

SINGLE-FILE DIFFUSION

Proceeding to the effect of particle–particle interaction, actually exclusion in our case, the situation complicates substantially. But the heuristic argument in the "Anomalous diffusion: one-dimensional limit" section offers an effective leading approximation: what we have learned is that we can focus on the slow motion of a suitable particle cluster. Let us reduce our consideration to the longitudinal component of the motion. It is certainly not true that the x-component trajectories of a colliding pair remain the same to within a spatial offset, but of course this does hold on the average. What we need then is the relevant effective or mean longitudinal center-to-center distance on collision. Although this "mean" is an amorphous concept, we can (within the accuracy that we are dealing with) replace it by any other mean, preferably one in which the proper particle–particle correlations are included. Since the cluster in question can be regarded as in temporary thermal equilibrium under the pressure supplied by the rest of the system, a reasonable choice for this purpose would be obtained from the isobaric equation of state $l(\beta p)$. For one-dimensional cores, this would take the form $l = a + 1/\beta p$, and so we can define quite generally an effective mean separation

$$a(l) = l - \frac{1}{\beta p(l)}. \tag{3.1}$$

Correspondingly, Eq. (2.5a,b) would now give rise to the general estimate

$$\langle(\Delta x)^2\rangle = \frac{\langle|x|\rangle_{\rm o}}{\beta p(l)}. \tag{3.2}$$

The computation of $\beta p(l)$ for particles with a one-dimensional ordering and strictly next neighbor

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interaction is a very solvable analytical problem, although simple closed forms need not exist. Numerically exact estimates for the equation of state can be easily obtained from computer simulations.

Quite generally, the thermodynamics of such a fluid is most easily computed in an isobaric ensemble [26] and is given by

$$\beta\mu(p) = -\ln \Lambda_{\max}(\tilde{w}(\beta p)\rho) \tag{3.3}$$

where $\rho(r) = e^{-\beta u(z)}$, $\tilde{w}(z, z', \beta p) = \int_0^\infty e^{-\beta p(x-x')} e^{-\beta\varphi(r-r')}\, \mathrm{d}(x - x')$ coupled of course with

$$l = \partial\beta\mu/\partial\beta p. \tag{3.4}$$

Here p is the one-dimensional pressure, the total force on a cross-section, φ is the pair interaction potential, $\Lambda_{\max}$ refers to the maximum eigenvalue of the argument, which is an integral operator (continuous matrix).

In particular, for discs of diameter a in a channel of half-width R, we need the maximum eigenvalue $\Lambda_{\max}$ of

$$M(z, z') = \frac{1}{\beta p}\Theta\left(R - \frac{a}{2} - |z|\right) e^{-\beta p(a^2 - (z-z')^2)^{\frac{1}{2}}} \Theta(a^2 - (z - z')^2)\Theta\left(R - \frac{a}{2} - |z'|\right). \tag{3.5}$$

Since the dynamics may be very slow in the higher density regime, one would initially focus on the low density limit. In the low-pressure limit, a routine expansion results in

$$\frac{1}{v} = \beta P - \gamma(\beta P)^2 \ldots$$

where

$$\gamma = a^2 \sin^{-1}\left(\frac{2\hat{R}}{a}\right) + \frac{1}{3}(a^2 - 4\hat{R}^2)^{1/2}\frac{2\hat{R}^2 + a^2}{\hat{R}} - \frac{\frac{1}{3}a^3}{\hat{R}}; \tag{3.6}$$

$P = p/2\hat{R}$ is the usual two-dimensional pressure, and $v = 2\hat{R}l$. Hence $\beta P = 1/v - \gamma$ or

$$\beta p = \frac{1}{l - \gamma/2\hat{R}}, \tag{3.7}$$

where for small $\hat{R}$,

$$\frac{\gamma}{2\hat{R}} = a - \frac{\hat{R}^2}{3a} - \frac{2\hat{R}^4}{15a^3} - \frac{\hat{R}^6}{7a^5} \ldots \tag{3.8}$$

Comparison with simulations indicates that this is rather accurate.

RATIONALE FOR THE EQUATION OF STATE APPROXIMATION

The estimate Eq. (3.2) serves as a low order approximation to the asymptotic dynamics. In order to set the stage for a deeper analysis, it is important to present Eq. (3.2) in a stepwise fashion that is susceptible to sequential improvement. Let us consider the case of infinitesimal jumps, i.e. of traditional diffusion. For a d-dimensional system, the N particles effectively constitute an Nd-dimensional particle, $\mathbf{r}^N$, diffusing subject to boundary restrictions, which we represent by the weight function $\Pi_\alpha\Theta_\alpha(\mathbf{r}^N)$, where $\Theta_\alpha = 0$ in the αth disallowed region and otherwise $\Theta_\alpha = 1$. Thus, taking the infinitesimal jump limit, as we did in going from Eqs. (1.1) to (1.4), the N-body probability density now satisfies

$$\frac{\partial}{\partial t}\rho(\mathbf{r}^N, t) = D\Pi_\alpha\Theta_\alpha(\mathbf{r}^N)\nabla^2_{ND}\rho(\mathbf{r}^N, t) \tag{4.1}$$

$$\rho(\mathbf{r}^N, t) = \Theta_\alpha(\mathbf{r}^N)\rho(\mathbf{r}^N, t),$$

for all α, and the Neumann boundary condition, derivable from Eq. (4.1), takes the form

$$\nabla_{ND}\Theta_\alpha(\mathbf{r}^N)\cdot\nabla_{ND}\rho(\mathbf{r}^N, t) = 0, \tag{4.2}$$

for all α.

We will want to study the projection, say x_o, of the specified particle with index "o" on the longitudinal x-axis. Hence, we rewrite Eq. (4.1) as

$$\frac{\partial}{\partial t}\delta(x - x_o)\rho = D\nabla_{Nd}\cdot(\delta(x - x_o)\Pi\Theta_\alpha\nabla_{Nd}\rho) - D\delta(x - x_o)(\nabla_{ND}\Pi\Theta_\alpha)\cdot\nabla_{ND}\rho) + D\frac{\partial}{\partial x}\left(\delta(x - x_o)\Pi\Theta_\alpha\frac{\partial\rho}{\partial x_o}\right) \tag{4.3}$$

and integrate over all space, obtaining

$$\frac{\partial}{\partial t}\int\delta(x - x_o)\rho(\mathbf{r}^N, t)\,\mathrm{d}\mathbf{r}^N = D\frac{\partial}{\partial x}\int\delta(x - x_o)\Pi\Theta_\alpha(\mathbf{r}^N)\frac{\partial}{\partial x_o}\rho(\mathbf{r}^N, t)\,\mathrm{d}\mathbf{r}^N. \tag{4.4}$$

Finally, integrate Eq. (4.4) by parts, yielding (s = "self")

$$\frac{\partial}{\partial t}\rho_s(x, t) = D\frac{\partial^2}{\partial x^2}\rho_s(x, t) - D\frac{\partial}{\partial x}F(x, t), \tag{4.5}$$

where $\rho_s(x, t) = \int\delta(x - x_o)\rho(\mathbf{r}^N, t)\,\mathrm{d}\mathbf{r}^N$ and

$$F(x, t) = \int\delta(x - x_o)\sum_\alpha\frac{\partial}{\partial x_o}\Theta_\alpha(\mathbf{r}^N)\rho(\mathbf{r}^N, t)\,\mathrm{d}\mathbf{r}^N.$$

In the situation of interest, the Θ_α consist of one-particle and two-particle boundaries, so that F likewise is expressible in terms of one and two-particle terms. This is the beginning of a hierarchy in the mold of the BBGKY equations in which one would successively find the motion of n-body densities in terms of n and $n + 1$-body densities,

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and the problem is always that of discovering a reasonable closure to terminate the sequence. To apply this strategy here, we first make explicit the 2-body character of $F(x,t)$. In the present case, we have the boundaries

$$\Theta_j(\mathbf{r}^N) = \Theta(\hat{R} - |\mathbf{r}_j|)$$
$$\Theta_{ij}(\mathbf{r}^N) = \Theta(|\mathbf{r}_i - \mathbf{r}_j|^2 - a^2), \tag{4.6}$$

so that in terms of (d = "different")

$$\rho_{\mathrm{sd}}(\mathbf{r},\mathbf{r}',t) = \sum_{j\neq 0}\langle\delta(\mathbf{r}-\mathbf{r}_{\mathrm{o}}(t))\delta(\mathbf{r}'-\mathbf{r}_j(t))\rangle. \tag{4.7}$$

Equation (4.5) says that

$$\begin{aligned} F(x,t) = &\int \rho_{\mathrm{sd}}(x,r_\perp,x',r'_\perp,t) \\ &\frac{\partial}{\partial x}\Theta((x-x')^2 + |r_\perp - r'_\perp|^2 - a^2)\,\mathrm{d}\mathbf{r}_\perp\,\mathrm{d}\mathbf{r}'_\perp \\ = &\int\Big[\rho_{\mathrm{sd}}(x,r_\perp,x-(a^2-|r_\perp-r'_\perp|^2)^{1/2},r'_\perp,t) \\ &- \rho_{\mathrm{sd}}(x,r_\perp,x+(a^2-|r_\perp-r'_\perp|^2)^{1/2},r'_\perp,t)\Big] \\ &\times \mathrm{d}\mathbf{r}_\perp\,\mathrm{d}\mathbf{r}'_\perp, \end{aligned} \tag{4.8}$$

where subscript $\perp$ indicates transverse component.

Equations (4.5) and (4.8) are still exact, but require a relation between ρ_{sd} and ρ_{s} to be useful, and this depends very much on the qualitative characteristics of the system. Here, to start with, if the particles are ordered at time $t = 0$, this ordering is maintained for all time. This means that, assuming small enough $\hat{R}$ that only next neighbors can touch (the implicit assumption in Eq. (3.3) as well), the condition $(x-x')^2 + |\mathbf{r}_\perp - \mathbf{r}'_\perp|^2 = a^2$ in Eq. (4.8) restricts ρ_{sd} to next neighbor, now designated by ρ_{nn}.

An approximation now enters. We replace Eq. (4.8) by

$$\begin{aligned} F(x,t) = \rho_{\mathrm{nn}}(x, x - \langle(a^2 - |r_\perp - r'_\perp|^2)^{1/2}\rangle_\perp, t) \\ - \rho_{\mathrm{nn}}(x, x + \langle(a^2 - |r_\perp - r'_\perp|^2)^{1/2}\rangle_\perp, t), \end{aligned} \tag{4.9}$$

in obvious notation. Since Eq. (4.9) is precisely what we would obtain in the strictly one-dimensional case with a replaced by

$$\bar{a} = \langle(a^2 - |r_\perp - r'_\perp|^2)^{1/2}\rangle_\perp, \tag{4.10}$$

then for any closure relating ρ_{nn} to ρ_{s} that is modeled on the strictly one-dimensional case, we will have the asymptotic result

$$\frac{\langle(\Delta x)^2\rangle}{\langle|\Delta x|\rangle_{\mathrm{o}}} = l - \bar{a}. \tag{4.11}$$

In the approximation Eq. (4.11), only the effective diameter $\bar{a}$ remains to be determined. But according to Eq. (3.5), generalized to dimension $d > 2$, we have $\langle(a^2 - |r_\perp - r'_\perp|^2)^{1/2}\rangle_\perp = -\big(\partial/\partial\beta p\;\beta p\Lambda_{\max}\big)/(\beta p\Lambda_{\max})$ $= -1/\beta p - \partial/\partial\beta p \ln\Lambda_{\max} = -1/\beta p + l$. We conclude that under the above assumptions, one will recover Eqs. (3.1) and (3.2) as

$$\frac{\langle(\Delta x)^2\rangle}{\langle|\Delta x|\rangle_{\mathrm{o}}} \sim \frac{1}{\beta p(l)} \equiv l - \bar{a}(l). \tag{4.12}$$

where p is the equilibrium thermodynamic "pressure" of the system and an effective length $a(l)$

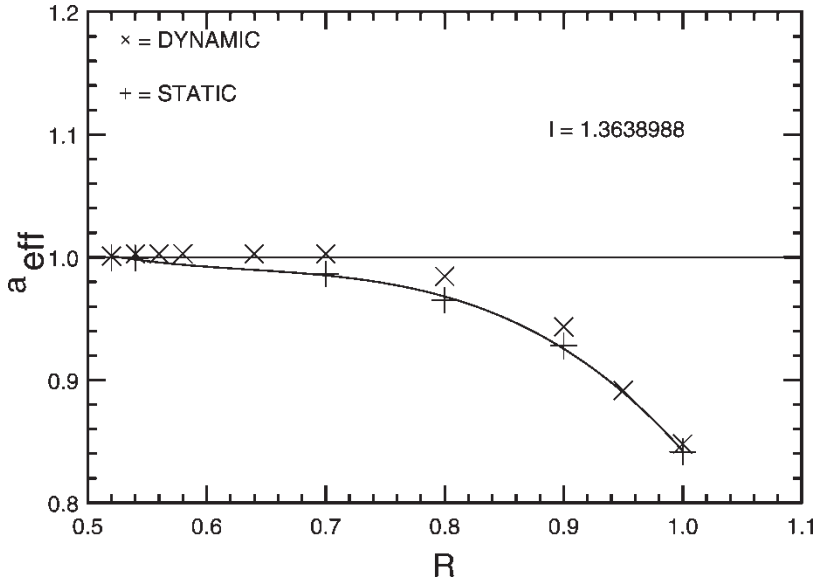

FIGURE 2 We compare the Monte Carlo result for the dynamic length of the mobility factor denoted by (x) with the static length from equilibrium equation of state denoted by (+). One thousand hard discs are used in a channel of width $2R$ with standard Monte Carlo simulation [27]. Each attempted move can be in either transverse or longitudinal direction with equal probability and a uniformly distributed step size between $(-0.1, 0.1)$. The unit of length is fixed by setting the diameter of the disc to be one. The longitudinal density is 1.3639. These are preliminary results and the estimated statistical error is about the size of the symbols.

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from the thermodynamic equation of state has been inserted into Eq. (3.1). In Fig. 2, we compare the effective length from dynamic simulations with that from the simulated equilibrium equation of state. The general trends of the two appear to be similar, but they are quantitatively different. This is very interesting, probably due to the details of the elementary dynamical moves, and forms the basis of ongoing research.

Acknowledgements

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References

[1] Gelb, L.D., Gubbins, K.E., Radhakrishnan, R. and Sliwinska-Bartkowiak, M. (1999) "Phase separation in confined system", *Rep. Prog. Phys.* **62**, 1573, See reference for reviews.
[2] Henderson, D., ed (1992) *Fundamentals of Inhomogeneous Fluids* (Dekker, New York).
[3] Hagen, M.H.J., Pagonabarraga, I., Lowe, C.P. and Frenkel, D. (1997) "Algebraic decay of velocity fluctuation", *Phys. Rev. Lett.* **78**, 3785.
[4] Goulding, D., Hansen, J.-P. and Melchionna, S. (2000) "Size selectivity of narrow pores", *Phys. Rev. Lett.* **85**, 1132.
[5] Molz, E., Wong, A.P.Y., Chan, M.H.W. and Beamish, J.R. (1993) "Freezing and melting of fluids in porous glasses", *Phys. Rev.* **B48**, 5741.
[6] Sokol, P.E., Ma, W.J., Herwig, K.W., Snow, W.M., Wang, Y., Koplik, J. and Banavar, J.R. (1992) "Freezing in confined geometries", *Appl. Phys. Lett.* **61**, 777.
[7] DiCicco, A. (1998) "Phase transitions in confined Gallium droplets", *Phys. Rev. Lett.* **81**, 2942.
[8] Xin, Q., Hiyane, I. and Siders, P. (1994) "Statistical thermodynamics of hard-spheres in a narrow cylindrical pore", *J. Chem. Soc. Faraday Trans.* **90**, 973.
[9] Wei, Q.-H., Bechinger, C. and Leiderer, P. (2000) "Single-file diffusion of colloids in one-dimensional channels", *Science* **287**, 625.
[10] Hahn, K., Karger, J. and Kukla, V. (1996) "Single-file diffusion observation", *Phys. Rev. Lett.* **76**, 2762.
[11] Finkelstein, A. (1987) *Water Movement Through Lipid Bilayers, Pore, and Plasma Membranes* (Wiley, New York), See reference for biological examples.
[12] Roux, B. (1995) In: Goodfellow, J.M., ed, *Computer Modelling in Molecular Biology* (VCH, New York).
[13] Karger, J. and Ruthen, D.M. (1992) *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York), See reference for nanoporous material applications.
[14] Ebbesen, T.W., ed (1996) *Carbon Nanotubes: Preparation and Properties* (Chemical Rubber Co., Boca Raton, FL).
[15] Levitt, D.G. (1973) "Dynamics of single-file pore: non- Fickian behavior", *Phys. Rev.* **A8**, 3050.
[16] Harris, T.E. (1965) *J. Appl. Prob.* **2**, 323.
[17] Percus, J.K. (1974) "Anomalous self-diffusion for one-dimensional hard cores", *Phys. Rev.* **A9**, 557.
[18] Schoen, M., ed, *Computer Simulation of Condensed Phases in Complex Geometry* (Springer, Berlin), See reference for a review.
[19] van Beijeren, H., Kehr, K.W. and Kutner, R. (1983) "Diffusion in concentrated lattice gases, 3", *Phys. Rev.* **B28**, 5711.
[20] Kehr, K.W. and Binder, K. (1987) In: Binder, K., ed, *Applications of Monte Carlo Method in Statistical Physics* (Springer, Berlin).
[21] Kutner, R., van Beijeren, H. and Kehr, K.W. (1984) "Diffusion in concentrated lattice gases 6", *Phys. Rev.* **B30**, 4382.
[22] Tepper, H.L., Hogenboom, J.P., van der Vegt, N.F.A. and Briels, W.J. (1999) "Unidirectional diffusion of methane in ALPO4-5", *J. Chem. Phys.* **110**, 11511.
[23] Hahn, K. and Karger, J. (1998) "Deviations from the normal time regime of single-file diffusion", *J. Phys. Chem.* **B102**, 5766.
[24] Hahn, K. and Karger, J. (1995) "Propagator and mean-square displacement in single-file systems", *J. Phys. A* **28**, 3061.
[25] Doi, M. (1996) *Introduction to Polymer Physics* (Clarendon, Oxford), Chapter 5.
[26] Hill, T.L. (1956) *Statistical Mechanics* (McGraw-Hill, New York).
[27] Allen, M.P. and Tildesley, D.J. (1987) *Computer Simulation of Liquids* (Clarendon, Oxford), See reference for discussions.

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