


Dependence on the thermodynamic state of self-diffusion of pseudo-hard-sphere and Lennard-Jones potentials

L. Marchioni , M. A. Di Muro , and M. Hoyuelos *

Instituto de Investigaciones Físicas de Mar del Plata (IFIMAR – CONICET), Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Deán Funes 3350, 7600 Mar del Plata, Argentina

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Self-diffusion D in a system of particles that interact with a pseudo-hard-sphere or a Lennard-Jones potential is analyzed. Coupling with a solvent is represented by a Langevin thermostat, characterized by the damping time t_d . The hypotheses that $D = D_0\varphi$ is proposed, where D_0 is the small concentration diffusivity and φ is a thermodynamic function that represents the effects of interactions as concentration is increased. Molecular dynamics simulations show that different values of the noise intensity modify D_0 , but do not have an effect on φ . This result is consistent with the assumption that φ is a thermodynamic function since the thermodynamic state is not altered by the presence of damping and noise.

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I. INTRODUCTION

The Chapman-Enskog transport theory [1] predicts self-diffusivity of a general system of interacting particles at small concentration; it reduces to the Boltzmann theory for dilute gases when particles are hard spheres. Several approximate theories were proposed to extend the description to moderate and large concentrations, such as free volume or excess entropy theories. They were successfully applied to fluid models and real substances for the description of transport properties, usually requiring around 2–4 adjustable parameters.

In particular, free-volume theories propose relationships between transport coefficients of a dense fluid and the free volume defined as $V_f = V - V_i$, where V is the volume and V_i is an intrinsic molar volume. The equations are simple and can usually be applied over wide ranges of pressure and temperature. We mention a few examples and focus attention on the expressions for the self-diffusion coefficient. The Dymond-Hildebrand-Batschinski [2–4] model considers the self-diffusion coefficient as proportional to the free volume, $D \propto V_f$; this simple proposal can describe systems with small attractive forces at small or moderate densities. The Doolittle-Cohen-Turnbull [5,6] model, with $D \propto \exp(-C/V_f)$, incorporates the behavior at a glass transition; an improvement was proposed by Turnbull and Cohen [7], where $D \propto (C + V_f) \exp(-C'/V_f)$. The proposal of Macedo and Litovitz [8], $D \propto \exp(-C/V_f - C'/k_B T)$, has been important in the description of polymer fluids. In all cases, C and C' are constants of the models that have to be adjusted for each substance. In the van der Waals theory of transport properties, self-diffusivity at large concentrations is calculated using hard-sphere expressions at low concentration with a variable core size σ [2,9–11].

Following the works of Rosenfeld [12,13], several semiempirical formulas of the form $D \propto \exp(Cs_{\text{ex}}/k_B)$, where s_{ex} is

the excess entropy per particle, have been proposed for models and real systems; see Dzugasov [14] (again, we focus on the diffusivity, but equivalent formulas also apply to viscosity and thermal conductivity). The excess entropy can be computed from the equation of state, usually represented by the compressibility factor. Although successful in describing transport properties at large and moderate concentration in different fluids, Rosenfeld observed that based on hard-sphere results, the analytical form of transport coefficients in the whole concentration range is probably not an exponential of the excess entropy; he extended the analysis to small concentrations (or the Enskog domain) and obtained a different dependence for transport coefficients [15]. Despite its simplicity, the thermodynamic and transport properties of the hard-sphere model do not yet have exact solutions in the whole range of concentration. Accurate mathematical representations of self-diffusivity for hard spheres are, in general, obtained from the interpolation of molecular dynamics results; see Sec. 9.4 in [16] for a review and see Pieprzyk *et al.* [17] for more recent numerical simulations.

The purpose of this paper is to elucidate qualitative aspects of self-diffusion of hard spheres in three dimensions assuming, as a starting point, the following hypotheses: the self-diffusion coefficient D can be written as the product of two terms, one including the dependence on factors such as mass of particles, size of particles, or mean velocity (or temperature), and the other corresponding to macroscopic or thermodynamic aspects associated to the presence of interactions. It is assumed that the effects of interactions, that manifest themselves when the concentration is increased, are represented by the second term. For brevity, we refer to the “self-diffusion coefficient” as “diffusivity.” We identify the first term with the diffusivity at small concentration, D_0 , so that

$$D = D_0\varphi, \quad (1)$$

where φ is the factor representing the effects of interactions as concentration is increased. According to the hypotheses,

*hoyuelos@mdp.edu.ar

whose justification is given in Sec. II, only the information of interactions at the thermodynamic level is needed to describe diffusivity in the whole concentration range.

The proposal is similar to Rosenfeld's since the excess entropy exponential is, of course, a thermodynamic function. The question that we wish to address is, however, if it is possible to express the diffusivity in terms of a thermodynamic function, without knowing it in advance. We developed a method to answer this question, in which no specific form is provided for φ (as Rosenfeld observed, the excess entropy exponential does not hold for small concentration in the hard-sphere system). Moreover, we wish to know if the proportionality of the diffusivity with a thermodynamic function also holds in the presence of noise and when the noise intensity is modified.

The method proposed to check the hypothesis is as follows. Noise corresponding to a Langevin thermostat is added; the system can be seen as a colloidal suspension of hard spheres where hydrodynamic forces are neglected [18]. The noise modifies D_0 , but not the thermodynamic state. Molecular dynamics simulations are carried out using the continuous pseudo-hard-sphere potential proposed in Ref. [19] that accurately reproduces results of the hard-sphere potential; see Sec. III. Simulations are performed, using LAMMPS software [20], to verify that the equation of state does not change with the noise intensity (represented by the damping time t_d); see Sec. IV. This means that the presence of noise does not modify the thermodynamic state and, therefore, it should not modify φ which is supposed to be a thermodynamic function. The Stoermer-Verlet time integration algorithm for constant particle number, volume, and energy (NVE ensemble) is used; the fluctuation dissipation theorem determines the relationship between the stochastic force amplitude and damping time. In Sec. V, the form of diffusivity at small concentration is determined as a combination of Einstein and Boltzmann diffusion coefficients. Simulation results of D/D_0 for hard spheres against concentration for different values of the noise intensity are presented in Sec. VI. The results show that as expected, φ does not change for different noise intensities. Simulation results for the Lennard-Jones potential are shown in Sec. VII. Summary and conclusions are presented in Sec. VIII.

II. THE HYPOTHESES

Let us suppose that the system of particles is divided into cubic cells of size a . Two neighboring cells, labeled 1 and 2, have n_1 and n_2 particles, respectively. In this coarse-grained picture, a general expression for the transition rate, W_{n_1,n_2} , from cell 1 to cell 2, as a function of the the excess chemical potential has been recently derived [21],

$$W_{n_1,n_2} = \nu \psi_{n_1,n_2}, \quad (2)$$

where ν is the jump attempt frequency and

$$\psi_{n_1,n_2} = \frac{e^{-\beta(\mu_{\text{ex},n_2} - \mu_{\text{ex},n_1})/2}}{\sqrt{\Gamma_{n_1} \Gamma_{n_2}}} \quad (3)$$

represents the effects of interactions at the thermodynamic level, where μ_{ex,n_i} is the excess chemical potential for n_i particles and $\Gamma_{n_i} = 1 + \beta n_i \frac{\partial \mu_{\text{ex},n_i}}{\partial n_i}$ is the thermodynamic factor,

with $\beta = 1/(k_B T)$; T is the temperature and k_B is the Boltzmann's constant. W_{n_1,n_2} is the average transition rate for any of the n_1 particles in cell 1.

In the limit of small concentration interactions can be neglected, $\mu_{\text{ex},n_i} \simeq 0$, $\Gamma_{n_i} \simeq 1$, and

$$W_{n_1,n_2}^0 = \nu, \quad (4)$$

where superindex 0 indicates small concentration. In this case, a tagged particle performs a random walk between cells of size a , with constant transition rate ν , and the tracer diffusivity coefficient is $D_0 = \nu a^2$. If, for example, the system is a dilute gas, then D_0 is obtained with the Boltzmann theory and, besides temperature and concentration, ν depends on microscopic properties such as the mass and size of particles. If, instead, the system is composed of Brownian particles, ν depends on the particle's mass and on the damping time (or the friction coefficient).

Then, Eq. (2) consists of two parts: one, represented by ν , contains microscopic details, while the other, given by ψ_{n_1,n_2} , represents the thermodynamic aspects. Interactions usually include a repulsive part at short distances; this repulsion is reflected in an increase of the thermodynamic factor as concentration is increased, resulting in a decrease of the transition rate (and the diffusivity). This behavior of the transition rate is represented by ψ_{n_1,n_2} . In contrast, the jump attempt frequency ν is obtained, as mentioned before, from the tracer diffusivity at small concentration D_0 ; the expression for ν obtained in this way holds for any concentration.

An important difficulty appears when the transition rate is used to obtain the tracer diffusivity for any concentration. In general, spatial correlations must be taken into account as concentration is increased. The transition rate of a tagged particle may not be equal to the average transition rate of all particles in the cell, but may depend on its position before its last jump. If this dependence can be neglected, a mean-field approximation can be applied; see Ref. [21] for some examples. Nevertheless, in general, a correlation factor has to be included.

We can still assume that the separation between microscopic and thermodynamic aspects that holds for the transition rate, given by Eq. (2), also holds for the tracer diffusivity. This assumption leads to the hypotheses given by Eq. (1) in Sec. I. Then, the hypothesis is based on the structure of the transition rate; it says that this structure should also be present in the tracer diffusivity. In Eq. (1), D_0 plays the role of ν and φ plays the role of ψ_{n_1,n_2} . In this expression, the form of D_0 is relevant for the whole range of concentration (although it is derived at small concentration), and the effects of interactions are only present in φ .

III. PSEUDO-HARD-SPHERE POTENTIAL

The Mie potential, as the Lennard-Jones potential, is repulsive at short radial distance r and has an attractive well of energy ϵ at intermediate distances. It generalizes the Lennard-Jones potential by considering exponents λ_r and λ_a of the repulsive and attractive terms,

$$u_{\text{Mie}}(r) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right], \quad (5)$$

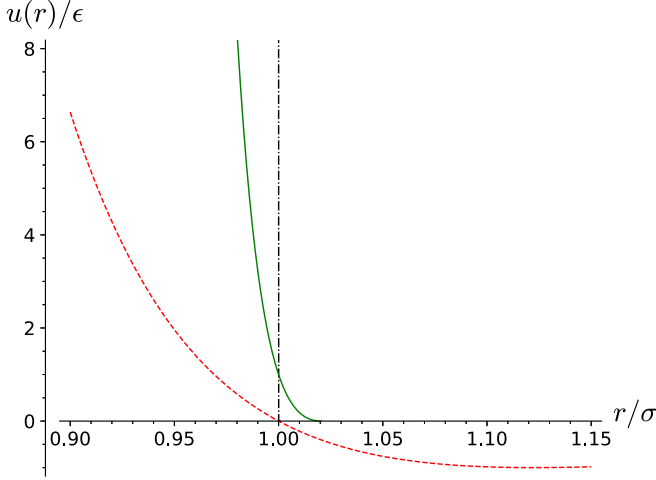


FIG. 1. Comparison between Lennard-Jones (dashed), hard-core (dash-dotted), and WCA ($\lambda_r = 50$, $\lambda_a = 49$) (solid) potentials.

where the size parameter σ is related to the diameter of the spherically symmetric particles. Weeks, Chandler and Andersen (WCA) [22] proposed a cut and shifted version of the Lennard-Jones potential in order to consider a purely repulsive core. The same procedure applied to the Mie potential, with $\lambda_r = 50$ and $\lambda_a = 49$, results in

$$u(r) = \begin{cases} 50\left(\frac{50}{49}\right)^{49}\epsilon\left[\left(\frac{\sigma}{r}\right)^{50} - \left(\frac{\sigma}{r}\right)^{49}\right] + \epsilon, & r < \sigma\frac{50}{49} \\ 0, & r \geq \sigma\frac{50}{49}. \end{cases} \quad (6)$$

This potential is known as the WCA potential.

This is the continuous potential used in Ref. [19] to reproduce the results of hard spheres. They have shown that the correspondence with hard spheres is fulfilled for a reduced temperature, $T^* = k_B T / \epsilon = 1.5$. The particle mass m , the energy ϵ , and the size σ are combined to cancel units in reduced quantities identified with an asterisk. In Fig. 1, we show a comparison between Lennard-Jones, WCA, and hard-sphere potentials.

IV. EQUATION OF STATE

Carnahan and Starling [23] obtained an approximate equation of state (EOS) for the hard-sphere fluid that is widely used due to its simplicity and accuracy. It is an expression for the compressibility factor, defined as

$$Z = \frac{PV}{Nk_B T}, \quad (7)$$

where P is the pressure, V is the volume, N is the number of particles, and the particle density is $\rho = N/V$. The Carnahan and Starling EOS is

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (8)$$

where η is the packing fraction; the equation holds for $\eta < 0.55$. The hard-sphere EOS does not depend on temperature. However, the EOS for the pseudo-hard-sphere potential (6) is not athermal. Therefore, in order to reproduce the hard-

sphere behavior, temperature has to be fixed at $T^* = 1.5$, as mentioned in the previous section.

We consider that the hard-sphere system is immersed in a background solvent modeled by a Langevin thermostat. Two forces are introduced by the thermostat: a friction force given by $-m\mathbf{v}/t_d$, where \mathbf{v} is the particle's velocity and t_d is the damping time, and a stochastic force represented by white noise of intensity, $2mk_B T/t_d$. Since temperature is fixed, both forces are determined by the value of the damping time (equal to the inverse of the friction coefficient). The reduced damping time is $t_d^* = t_d \sigma^{-1} \sqrt{\epsilon/m}$.

Temperature, number of particles, and volume are preserved when the thermostat is introduced. The pressure may, in principle, change, giving a different EOS, but this is not the case. According to the virial equation, the pressure in three dimensions can be written as (see [24, Sec. 3.7] or [25, Sec. 2.2])

$$P = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle, \quad (9)$$

where \mathbf{r}_i is the position of particle number i and \mathbf{F}_i is the force applied to it. The force is given by

$$\mathbf{F}_i = \mathbf{f}_i - m\mathbf{v}_i/t_d + \boldsymbol{\xi}_i, \quad (10)$$

where \mathbf{f}_i is the interaction with other particles; the other two terms are produced by the thermostat: friction, $-m\mathbf{v}_i/t_d$, and a stochastic force $\boldsymbol{\xi}_i$. The contribution of the thermostat to the pressure is given by

$$-\frac{1}{3V} \left(\left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \boldsymbol{\xi}_i \right\rangle - \frac{m}{t_d} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{v}_i \right\rangle \right) = 0. \quad (11)$$

Both terms are zero. In the first term, the stochastic force $\boldsymbol{\xi}_i$ and the position \mathbf{r}_i , evaluated at the same time, are uncorrelated and $\langle \boldsymbol{\xi}_i \rangle = 0$. On the other hand, for the second term, the equilibrium probability distributions of position and velocity are independent, and $\langle \mathbf{v}_i \rangle = 0$ due to isotropy. The independence between position and velocity is a consequence of the form of the Boltzmann distribution; if $\mathbf{v} = (\mathbf{v}_1, \dots, \mathbf{v}_N)$ and $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$, the equilibrium probability distribution is $P(\mathbf{r}, \mathbf{v}) \propto e^{-\beta[K(\mathbf{v})+U(\mathbf{r})]}$, where $K(\mathbf{v})$ and $U(\mathbf{r})$ are the kinetic and potential energies; then, $P(\mathbf{r}, \mathbf{v})$ is written as the product of the probability distributions for position and velocity.

Therefore, the final result for the pressure,

$$P = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle, \quad (12)$$

is independent of the presence of the thermostat and the EOS is not modified.

The pressure was numerically calculated to obtain the compressibility factor for concentrations in the fluid range and for different values of t_d^* ; see Fig. 2. The figure shows that the EOS is not altered by the presence of damping and noise. This result means that according to our hypotheses, the value of φ in (1), being a thermodynamic function, should not change with t_d^* .

The connection between the compressibility factor $Z = \beta P / \rho$ and the thermodynamic factor Γ is as follows. The thermodynamic factor in terms of the chemical potential μ

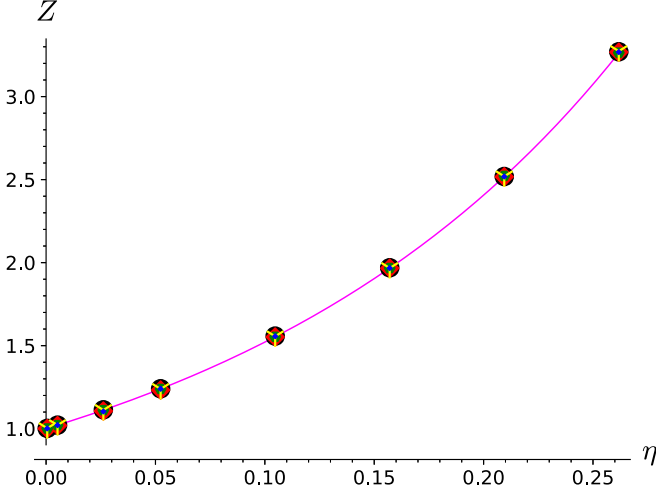


FIG. 2. Compressibility factor Z against packing fraction η for pseudo-hard-spheres ($T^* = 1.5$). The symbols represent different values of the damping time t_d^* : 0.01, 0.1, 1, and 10 (dots for each t_d^* overlap almost exactly). The curve corresponds to the Carnahan and Starling EOS, given by Eq. (8).

and the density ρ is $\Gamma = \beta\rho \frac{\partial\mu}{\partial\rho}$ or, in terms of the excess chemical potential, $\Gamma = 1 + \beta\rho \frac{\partial\mu_{\text{ex}}}{\partial\rho}$. The pressure P and the chemical potential can be written in terms of the free energy per particle, f (a function of ρ and T), as $P = \rho^2 \frac{\partial f}{\partial\rho}$ and $\mu = f + P/\rho$. Then,

$$\begin{aligned}\Gamma &= \beta\rho \left(\frac{\partial f}{\partial\rho} + \frac{\partial(P/\rho)}{\partial\rho} \right) \\ &= \beta P/\rho + \rho \frac{\partial(\beta P/\rho)}{\partial\rho} = Z + \rho \frac{\partial Z}{\partial\rho}.\end{aligned}\quad (13)$$

The excess chemical potential can also be written in terms of Z . The chemical potential and the free energy per particle for the ideal fluid are $\mu_{\text{id}} = \mu^\circ + \beta^{-1} \ln N$ and $f_{\text{id}} = \mu_{\text{id}} - \beta^{-1}$, and the residual or excess quantities are $\mu_{\text{ex}} = \mu - \mu_{\text{id}}$ and $f_{\text{ex}} = f - f_{\text{id}}$. Then,

$$P = \rho^2 \frac{\partial f_{\text{ex}}}{\partial\rho} + \rho\beta^{-1}, \quad (14)$$

$$\mu_{\text{ex}} = f_{\text{ex}} + P/\rho - \beta^{-1}. \quad (15)$$

(See, for example, Eqs. (9) and (11) in [26].) Rewriting the previous expressions in terms of the compressibility factor, we get

$$\beta \frac{\partial f_{\text{ex}}}{\partial\rho} = (Z - 1)/\rho, \quad (16)$$

$$\beta\mu_{\text{ex}} = \beta f_{\text{ex}} + Z - 1, \quad (17)$$

and, combining these equations, we obtain

$$\beta\mu_{\text{ex}} = \int \frac{Z-1}{\rho} d\rho + Z - 1, \quad (18)$$

where an integration constant is set with the condition $\mu_{\text{ex}} = 0$ in the small concentration limit.

V. DIFFUSIVITY AT SMALL CONCENTRATION

In order to numerically determine the behavior of φ , we need to calculate the ratio D/D_0 . The diffusivity at small concentration, D_0 , is well known for the two extreme values of the damping time. If $t_d^* \rightarrow \infty$, noise and damping are absent and, according to Boltzmann's theory, the diffusivity at small concentration is given by

$$D_B = \frac{3}{8\rho\sigma^2} \sqrt{\frac{k_B T}{\pi m}}. \quad (19)$$

The reduced diffusivity is $D^* = D\sigma^{-1} \sqrt{m/\epsilon}$, then

$$D_B^* = \frac{\sqrt{\pi T^*}}{16\eta}. \quad (20)$$

At the other end, for small t_d^* , noise and damping dominate the hard-sphere behavior and, according to Einstein's theory, the diffusivity is

$$D_E = \frac{k_B T t_d}{m} \quad (21)$$

or

$$D_E^* = T^* t_d^*. \quad (22)$$

For intermediate values of t_d^* , D_0 is given by a combination of D_E and D_B . We formulate a functional form for $D_0(D_B, D_E)$ by establishing an analogy between the particle current given by Fick's law, $j = -D \frac{\partial n}{\partial x}$, and the current I in an electric circuit with a potential $\mathcal{V} = IR$, with R the resistance; $\mathcal{V} \rightarrow -\frac{\partial n}{\partial x}$ and $I \rightarrow j$, hence $R \rightarrow 1/D$. When collisions between hard spheres and interactions with the background solvent are both relevant, the analogy corresponds to a series circuit in which the associated resistances are added. The small concentration diffusivity is

$$\frac{1}{D_0^*} = \frac{1}{D_B^*} + \frac{1}{D_E^*} \quad (23)$$

or

$$D_0^* = \frac{T^* t_d^*}{16\eta t_d^* \sqrt{T^*/\pi} + 1}. \quad (24)$$

For the two extreme values of the damping time, we have $D_0^* \simeq D_E^*$ (small t_d^*) and $D_0^* \simeq D_B^*$ (large t_d^*).

The validity of Eq. (23) was checked with numerical simulations at small concentration for 500 000 particles. Figure 3 shows D_0^* against the damping time t_d^* for $\eta = 0.0052$. Numerical values of D_0^* agree with Eq. (23).

VI. NUMERICAL RESULTS OF D/D_0

According to our hypotheses, the diffusivity D is proportional to D_0 for the whole concentration range; see Eq. (1). The correction factor φ is equal to 1 for small concentration. As the concentration increases, diffusion decreases and φ decays to zero due to clogging of the system. The point that we wish to verify is that this decay, characterized by φ , depends on the thermodynamic state, which is unchanged by the presence of noise. Therefore, φ should not depend on t_d^* .

Simulation results of D against concentration were obtained for different values of the damping time. The particles

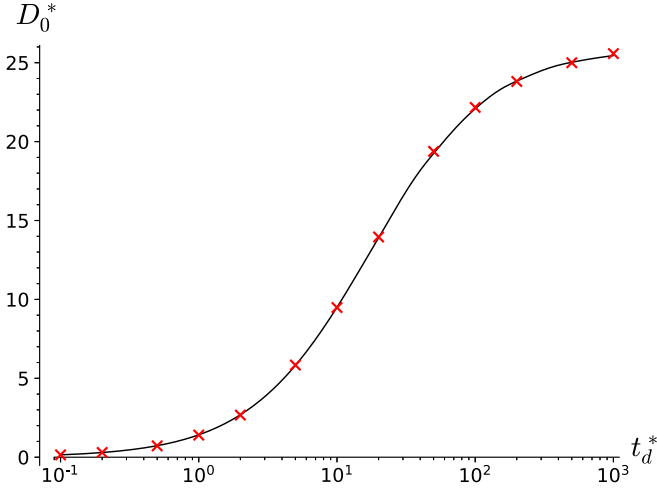


FIG. 3. Reduced diffusivity at small concentration for pseudo-hard-spheres, D_0^* , against damping time t_d^* for $\eta = 0.0052$. Crosses are numerical results and the curve corresponds to Eq. (23). Parameters of the simulations: Number of samples = 10, number of time steps (after thermalization) = 100, time step = 0.001, and number of particles per sample = 500 000.

number was fixed at 500 000. The method used to calculate diffusivity was the integration of the velocity autocorrelation (Green-Kubo formula); the mean-square displacement (MSD) was also used to check the results. Self-diffusion D^* against packing fraction η is shown in Fig. 4 for different values of t_d^* ; as expected, an increase of t_d^* (or a decrease in the friction coefficient) produces an increase in the diffusivity. But this increase is restricted only to the small concentration diffusivity D_0 (which is consistent with Fig. 3). Figure 5 shows values of D/D_0 against the packing fraction. It can be seen that the behavior is not modified by changing noise and damping; values of D/D_0 for different t_d^* agree within numerical errors. Numerical results of Pieprzyk *et al.* [17] for hard spheres (without noise) are also plotted for comparison.

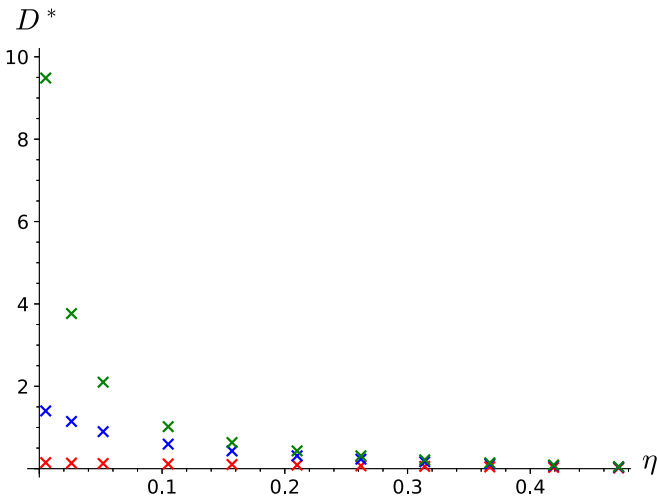


FIG. 4. Diffusivity for pseudo-hard-spheres, D^* , against packing fraction η for different values of the damping time t_d^* : red for 0.1, blue for 1, and green for 10. See Fig. 5 for the details of the simulation.

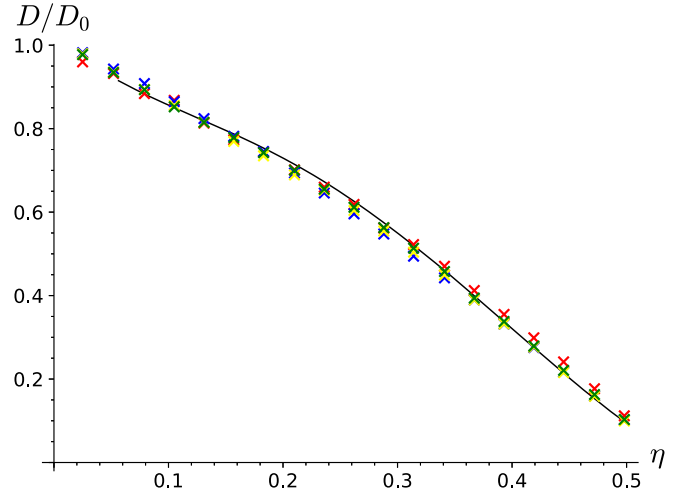


FIG. 5. D/D_0 against packing fraction η for different values of the damping time t_d^* : red for 0.1, blue for 1, yellow for 5, and green for 10. The superimposed curve corresponds to the numerical results of Pieprzyk *et al.* [17] for hard spheres. Parameters of the simulations: Number of samples = 10, number of time steps (after thermalization) = 100, time step = 0.001, and number of particles per sample = 500 000. For η greater than 0.35, the time step was changed to 0.0001.

Figure 5 shows that the diffusivity decay is slower for the intermediate packing fraction. When D is plotted relative to the Enskog diffusion coefficient (see, for example, Fig. 9.17 in Ref. [16]), the effect is enhanced since the diffusivity is actually larger than the theoretical prediction of Enskog, a result that can be attributed to the long-time tail of the velocity autocorrelation function, first reported by Alder and Wainwright [27,28].

VII. LENNARD-JONES POTENTIAL

Following the same line of thought as in Secs. V and VI, we can now work on the case where the particles interact via the Lennard-Jones potential,

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (25)$$

where σ is the radius where the potential becomes zero and ϵ is the potential well depth. We wish to verify, as in the previous sections, that the functional form of D/D_0 , characterized by ϕ , only depends on the thermodynamic state, which is not modified by the presence of noise.

According to the Chapman-Enskog theory [1,29], the small concentration diffusivity of particles interacting via the Lennard-Jones potential, D_{LJ} , is as in Eq. (19), but including the correction factor of the reduced collision integral Ω_{11} ; see, also, [30]. The equation, using dimensionless quantities, is

$$D_{\text{LJ}}^* = \frac{\sqrt{T^* \pi}}{16 \eta \Omega_{11}(T^*)}, \quad (26)$$

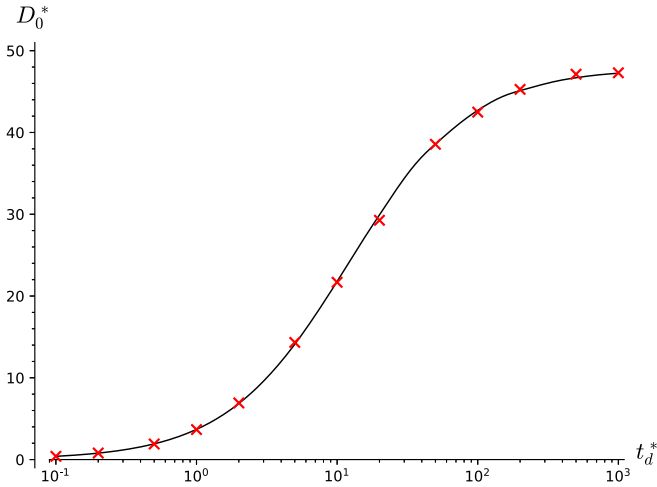


FIG. 6. Reduced diffusivity at small concentration for the Lennard-Jones potential, D_0^* , against damping time t_d^* for $\eta = 0.0052$ and temperature $T^* = 4$. Crosses are numerical results and the curve corresponds to Eq. (29). Parameters of the simulations: Number of samples = 100, number of time steps (after thermalization) = 200, time step = 0.001, and number of particles per sample = 108 000.

where $\eta = \rho^* \pi / 6$ and $\rho^* = \rho \sigma^3$; see Eq. (20). Using the approximation of Ref. [31], the collision integral is

$$\Omega_{11}(T^*) = \exp\left(-\frac{1}{6} \ln(T^*) + \sum_{i=0}^5 a_i T^{*-i/2}\right), \quad (27)$$

with $a_0 = 0.125431$, $a_1 = -0.167256$, $a_2 = -0.265865$, $a_3 = 1.59760$, $a_4 = -1.19088$, and $a_5 = 0.264833$.

We propose again that the diffusivity at small concentrations, D_0 , is a function of both D_{LJ} and D_E (Einstein's theory diffusivity),

$$\frac{1}{D_0^*} = \frac{1}{D_{LJ}^*} + \frac{1}{D_E^*} \quad (28)$$

or

$$D_0^* = \frac{T^* t_d^*}{16 \eta t_d^* \Omega_{11} \sqrt{T^* / \pi} + 1}. \quad (29)$$

The velocity autocorrelation integration method was used to calculate the diffusivity with the Lennard-Jones potential, and these results were verified with the MSD method. MD simulations were carried out using 108 000 particles.

In Fig. 6, we compare Eq. (29) with numerical simulations at small concentration and observe that there is a good agreement for all values of the damping time.

Moreover, in Fig. 7, we show $\phi = D/D_0$ as a function of η and for different values of the damping time. The collapse of the curves suggests that ϕ only depends on the thermodynamic state, as it does not seem to depend on the noise intensity.

VIII. CONCLUSIONS

Self-diffusion in a system of particles that interact through pseudo-hard-sphere and Lennard-Jones (LJ) potentials is analyzed. Particles are in a solvent whose effects are represented by a Langevin thermostat. The thermodynamic state is independent of the coupling with the thermostat, given by the

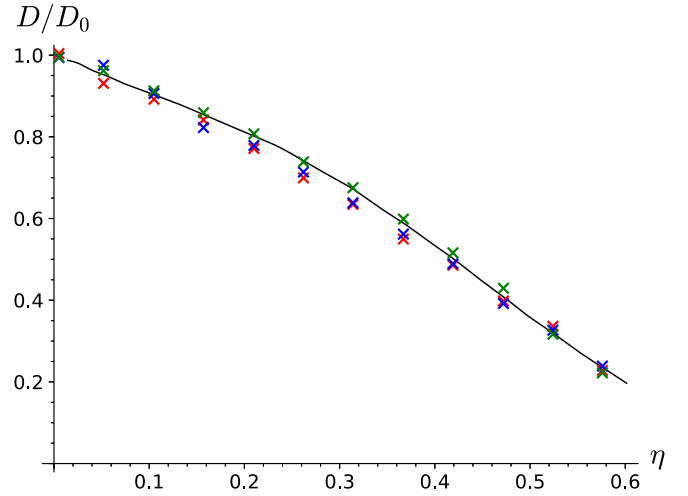


FIG. 7. D/D_0 against packing fraction η for different values of the damping time t_d^* : red for 0.1, blue for 1, and green for 10. The solid line corresponds to numerical simulations from Meier [30] for the Lennard-Jones potential, all with temperature $T^* = 4$ and cutoff radius $r_c = 3$. Parameters of the simulations: Number of samples = 100, number of time steps (after thermalization) = 200, time step = 0.001, and number of particles per sample = 108 000. For η greater than 0.35, the time step was changed to 0.0001, and for η greater than 0.5, the number of steps was changed to 500.

damping time t_d^* . Numerical simulations were performed to verify that the equation of state is independent of t_d^* and also to verify that the small concentration diffusivity D_0 can be written as a combination of the diffusivities from Boltzmann (or Chapman-Enskog) and Einstein theories, for pseudo-hard-spheres and also for the LJ potential. We obtained the connection between D_0 and the diffusivities from Boltzmann and Einstein theories using a general argument based on an analogy with an electric circuit; Figs. 3 and 6 show a very good agreement with the numerical simulations for pseudo-hard-spheres and LJ potential, respectively.

It is proposed, as a hypothesis, that the self-diffusion coefficient is proportional to D_0 and that the proportionality factor ϕ is a thermodynamic function; see Eq. (1). In the limit of small concentration, ϕ goes to one. Numerical simulations are consistent with this hypothesis. Values obtained for D/D_0 against the packing fraction are independent of the damping time t_d^* . This result is compatible with the assumption that ϕ is a thermodynamic function.

We have considered the Langevin thermostat as an intrinsic part of the system. It is frequently used as an artificial method for temperature control in molecular dynamics simulations; in these cases, it cannot be used to calculate transport properties, such as the diffusion coefficient, since it interferes in the momentum transport (the same problem occurs with other thermostats, such as Andersen's, [32, p. 146]). Nevertheless, we have shown that for pseudo-hard-spheres, the ratio D/D_0 remains independent of the thermostat (within numerical errors).

Knowing that ϕ is a thermodynamic function is a useful guide for the development of a theory for the diffusion of hard spheres. As mentioned in Sec. I, the concentration dependence of ϕ is an open problem. Factor ϕ contains information about

the influence of interactions on diffusion, but microscopic details of the interaction potential are not needed. We can expect that the interaction information contained in the excess chemical potential is important for the determination of φ for hard spheres and for the LJ potential.

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