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Mass dependence of isotope self-diffusion by molecular dynamics

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The mass and system size dependence of the self-diffusion coefficient of a single solute particle in a Weeks-Chandler-Anderson and Lennard-Jones liquid have been determined for a wide range of solute particle mass m_B and the number of particles of the host fluid $N-1$. The self-diffusion coefficient has been calculated using the mean squared displacements, the velocity autocorrelation function of the particles, and the Gaussian memory function method. From the computer simulation results, we conclude that only for Brownian particles with a mass less than a critical value (ca. $m_B/m<25$, where m is the mass of the solvent molecule) and very small systems (ca. $N<500$) is it possible to detect a mass and system-size dependence of the self-diffusion coefficient. For more massive Brownian particles and larger systems, the self-diffusion coefficient of the Brownian particle reaches a thermodynamic limit, neither depending on its mass nor on the number of particles in the periodic solvent system. The results obtained suggest that the self-diffusion coefficient for sufficiently large isotope masses should only depend on the temperature and number density of the fluid particles.

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I. INTRODUCTION

The mass dependence of the self-diffusion coefficient of both species in a binary fluid mixture has been the subject of numerous molecular dynamics simulation studies. For example, hard disks [1] and hard spheres [2], Weeks-Chandler-Anderson (WCA) and Lennard-Jones (LJ) liquids [3] have also been studied. However, many of these publications have considered Ar-Kr mixtures in which the mass, diameter, and interaction strength parameter were all varied at the same time. Therefore it has not been easy to discern the effects of varying just one of these parameters. In this study we consider the variation in the self-diffusion coefficients of a binary mixture of particles in which the only difference between the two species is their mass. The diffusion coefficient of particle i can be computed from the linear region of the mean square displacement,

$$D_i=\lim_{t\to\infty}\frac{\langle|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2\rangle}{6t}\ , \tag{1}$$

or from the velocity autocorrelation function,

$$D_i=\tfrac{1}{3}\lim_{t\to\infty}\int_0^t\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle(1-s/t)ds\ , \tag{2}$$

where $\mathbf{v}_i$ is the velocity of particle i.

It is well known that for dilute gases the ratio of the self-diffusion coefficients of a binary mixture is equal to the reciprocal of the square roots of the masses of the two species. However, machine computations have shown that in the condensed state this ratio varies more weakly with mass ratio. For equimolar systems, changing the mass of one species has nearly the same effect on the self-diffusion coefficient of *both* species. For each species i we have $D_i\sim m_B^{-1/4}$ where m_B is the mass of the species whose mass is varied. There is nevertheless a small difference in the mass dependence in favor of the species whose mass is changing. Extensive machine computations performed by Bearman and Jolly [4] on equimolar mixtures of LJ isotopes led them to conclude that the ratio of the two species self-diffusion coefficients varied with m_B according to

$$\frac{D_B(m_B/m)}{D_S(m_B/m)}=\left[\frac{m_B}{m}\right]^{-\mu}\ , \tag{3}$$

where $0.06\le\mu\le0.1$ and m is the mass of the other (solvent) species.

These previous simulations were carried out for a limited range than previously considered of m_B/m values. The purpose of this study is to consider a much wider range of m_B/m and N values, where N is the total number of particles in the simulation. The more extreme values for these parameters help in discerning general trends and limiting behavior. The average of the squared momentum of a single solute particle depends on N as follows [5]:

$$\langle p_B^2\rangle=3kT\frac{m_B(N-1)m}{m_B+m(N-1)}\ , \tag{4}$$

where T is the temperature of the $N-1$ solvent molecules. This property of the solute particle has not been taken into account in previous studies of the mass dependence of self diffusion and is useful in determining the limiting number of solvent particles needed for the system to be in the thermodynamic limit (i.e., when $N\to\infty$).

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II. THEORETICAL BACKGROUND

The mass dependence of a single massive solute particle in a host fluid is analyzed in terms of the generalized Langevin equation (GLE),

$$m_B\dot{\mathbf{v}}(t)=-m_B\int_{t_0}^{t}M(t')\mathbf{v}(t-t')dt'+\mathbf{R}(t)\ , \tag{5}$$

where $\mathbf{R}(t)$ is a randomly fluctuating force that arises from collisions with the surrounding molecules, and $M(t')$ is the memory function. This memory function is nonlocal in time and determines the contribution to the force at time t that is proportional to the velocity at an earlier time t'. Some properties are assumed for the random force, such as a zero mean and no correlation with the velocity, i.e., $\langle\mathbf{R}(t)\rangle=\langle\mathbf{R}(t)\cdot\mathbf{v}(t)\rangle=0$. If we multiply the GLE by $\mathbf{v}(t_0)$ and take a time average, we arrive at an equation for the normalized velocity autocorrelation function $\phi(t)$, or upon Laplace transformation $\tilde{\phi}(s)$, in terms of the Laplace transformation of the memory function $\tilde{M}(s)$. Mori showed that $\tilde{M}(s)$ can be written as a continued fraction [6], in terms of the damping matrices K_n (Mori coefficients), which are the zero-time values of the memory function $M_n(0^+)$. The Mori coefficients can be obtained from the values of the moments of the time derivatives of the forces as

$$U_n=\frac{1}{N}\left\langle\sum_{i=1}^{N}\mathbf{v}_i^n\cdot\mathbf{v}_i^n\right\rangle\ , \tag{6}$$

where v_i^n represents the nth time derivative of the normalized velocity, and $\langle\ \rangle$ represents the time average. As can be seen, these Mori coefficients can be calculated directly from the simulation. If we are interested in the Brownian particle the two first Mori coefficients are given by [7]

$$K_{B1}=U_1=\frac{1}{3m_B}\left\langle\sum_{j=2}^{N}\nabla^2u(r_{1j})\right\rangle\ , \tag{7}$$

where $u(r_{1j})$ is the interaction potential between particle index 1 (assumed to be the Brownian particle) and j the index of a host liquid particle $2\leq j\leq N$, and

$$K_{B2}=\frac{U_2}{K_{B1}}-K_{B1}\ . \tag{8}$$

According to the GLE formalism, the diffusion coefficient can be obtained from the velocity autocorrelation function as [8]

$$D=\frac{kT}{m_B}\int_0^{\infty}\phi(t)dt=\frac{kT}{m_B\tilde{M}(0)}\ . \tag{9}$$

As an exact expression for the memory function is not known for simulation liquids, an assumption is made about its analytic form. According to Toxvaerd [7,9], as the isotope mass is increased, a Gaussian term in the memory function becomes the main contribution to the memory. Therefore, assuming a Gaussian memory function as

$$M(t)=K_{B1}e^{-K_{B2}t^2/2}\ , \tag{10}$$

which has a short-time relaxation given by the Gaussian term in the memory expansion, $\tau\simeq\sqrt{2/K_{B2}}$. Then,

$$\tilde{M}(0)=\int_0^{\infty}M(t)dt=K_{B1}\left[\frac{\pi}{2K_{B2}}\right]^{1/2}\ , \tag{11}$$

and so that the Gaussian contribution to the diffusion coefficient is

$$D_G=\frac{kT}{m_BK_{B1}}\left[\frac{2K_{B2}}{\pi}\right]^{1/2}\ . \tag{12}$$

III. SIMULATION DETAILS

Molecular dynamics calculations have been performed for several different classes of system. In the first class, the mass of the Brownian particle was maintained at a constant value $m_B=10m$, where m is the mass of the solvent particle, and the size of the system is changed. We used periodic boundary conditions and chose $N=32$, 108, 256, 500, 864 and 2916 in order to investigate the system size dependence of the self-diffusion coefficient. These simulations were carried out with a WCA potential, which is a potential formed out of the repulsive part of the LJ potential truncated at the potential minimum $r_m=2^{1/6}\sigma$ [3],

$$u(r)=\begin{cases}4\epsilon\left[\left[\dfrac{\sigma}{r}\right]^{12}-\left[\dfrac{\sigma}{r}\right]^{6}\right]+\epsilon & \text{for } r\leq 2^{1/6}\sigma\\ 0 \quad \text{for } r>2^{1/6}\sigma\ . \end{cases} \tag{13}$$

The WCA potential helps us establish the role of the attractive part of the LJ potential on the Mori coefficient and thus on the self-diffusion coefficient, enabling us to compare our results with those found previously [10]. Another advantage of the WCA is that, being shorter ranged, it is more economical with computer time than the LJ potential and is just as useful for the purposes of this work. In order to compare our results with previous works [9,11,12], we have chosen the state point $kT/\epsilon=0.9$ and $\rho\sigma^3=0.75$. We only have a single Brownian particle in our model, and therefore very long simulations are required to obtain acceptable statistics. Typical simulations went through $\sim5\times10^5$ time steps of $h=0.005\sigma(\epsilon/m)^{-1/2}$. In this study the Brownian particle has the same diameter as the "solvent" particles. The interaction potential between all species is that given by Eq. (13).

In the second class of simulations, the total number of particles in the system was kept constant at $N=256$ and the mass of the Brownian particle was varied. We chose the values $m_B/m=1$, 4, 10, 16, 20, 30, 40, and 50. In this series of simulations the interaction potential between all of the particles was the LJ potential with a cutoff equal to 2.5σ. The reduced temperature and density were the same as for the WCA calculations. Typical simulations went through $\sim3\times10^5$ time steps of $h=0.005\sigma(\epsilon/m)^{-1/2}$. In both cases, the Verlet leapfrog algorithm was used [13]. To help establish the "infinite" system limit, we have also compared Eq. (4) for different systems and mass ratios with the canonical expression for the squared momentum in the thermodynamic limit given by

$$\langle p_B^2 \rangle = 3kTm_B\ . \tag{14}$$

A point of importance relating to the simulation of mixtures, in which there is a large mass ratio between the species, is that although the time step must be chosen to accommodate the lighter particle, the relaxation times associated with the heavier particle are relatively long compared to that time step. Since the phenomenon studied relates to the more massive particle, the mean square displacements and time correlation functions need to be followed for a relatively large number of time steps (e.g., in excess of 2000 for $m_B/m=10$).

IV. RESULTS AND DISCUSSION

Table I shows the values of the two first Mori coefficients needed to calculate the self-diffusion coefficient in the Gaussian approximation of Eq. (12) for the WCA liquids. Apart from $N=32$ to 108, the values in the columns [especially $D_B^G(T)$] are statistically constant, the uncertainties being ca. 2% and independent of the system size.

Table II shows the results for the $N=256$ LJ systems, using several mass ratios. Using the data in the table, we see that the ratio $K_{B1}m_B/m$ is independent of the value of m_B/m as predicted in [9]. For example, at $m_B/m=1$, 20, and 50, we have $K_{B1}m_B/m=232$, 224, and 225, respectively. The mean values for K_1 and K_2 in the last row agree with the values obtained in [11], as do the K_{B1} values with those in [12] with a smaller mass ratio ($m_B/m=1$, 4, 16, and 50). However, the variation in K_{B2} between $m_B/m=1$ to 10 is very sharp, the values here being systematically higher than in our previous work [12], where it was found that $K_{B2}=352$, 370, and 369 for $m_B/m=4$, 16, and 50, respectively (with an uncertainty of ca. 7%). This systematic discrepancy could be caused by the different ensembles used in the separate studies. In the present work, the microcanonical *NVE* ensemble has been used [number of particles (*N*), volume (*V*), internal energy (*E*)], while in Refs. [11] and [12] the Nosé-Hoover [14] isothermal-isobaric *NPT* ensemble was used. It is interesting to note that in Ref. [9] the microcanonical ensemble was also used and the K_{B2} values obtained (i.e., 444 and 398 for $m_B/m=4$ and 16, respectively) are in between those obtained here and in our previous report [12]. Nevertheless, in spite of the differences in K_{B2}, the self-diffusion coefficients are relatively insensitive to these differences because $\sqrt{K_{B2}}$ is used in the calculation of the diffusion coefficient in Eq. (12). In the thermodynamic limit, the Mori theory prediction for D is 0.0632 in the present calculations has the value 0.060 in Ref. [12] and 0.063 in Ref. [9] for $m_B/m=16$. Moreover, both studies show that $D_B^G(T)$ in the Gaussian approximation is not mass dependent for a ratio $m_B/m>4$.

The ratio of the self-diffusion coefficient of the LJ fluid compared with that of the WCA fluid gives a direct measure of the influence of the attractive force on the self-diffusion coefficient [10]. From our values in Tables I and II, this ratio is 0.95, which shows that, for the state point chosen, there is only a small influence of the attractive part of the potential on the self-diffusion coefficient. Alternatively, the ratio of the relaxation times derived from the two potentials gives another way of discerning the role of the attractive part of the potential on the self-diffusion coefficients of the two systems. Straub showed that similar relaxation times should also lead to similar self-diffusion coefficients, which was found to be the case at high (i.e., liquid) densities [10]. In the present study, the ratio of the Gaussian relaxation times obtained from Eq. (12) for LJ and WCA fluids is 1.06, which confirms the small influence of the attractive part of the potential on the diffusion coefficient at this high fluid density. The results for these ratios therefore agree with those found in [10]. For most of our simulations, we use the equally valid WCA potential instead of the LJ potential, because its shorter range makes it more computationally efficient.

The generalization of these results for a Brownian particle of arbitrary mass immersed in an infinitely large solvent system was derived in a recent paper by Español and Zúñiga [5], who deduced Eq. (4) instead of the usual canonical result of Eq. (14). The "mass factor" m_f, which distinguishes Eq. (4) from Eq. (14), is given by

TABLE I. Mori coefficients, in units of $\epsilon/(m\sigma^2)$, and self-diffusion coefficient, in units of $\sigma(\epsilon/m)^{1/2}$, for the different WCA systems using $m_B/m=10$. The solvent Mori coefficients are K_1 and K_2, and the Brownian particle Mori coefficients are K_{B1} and K_{B2}. The self-diffusion coefficient $D_B^G(T)$ has been calculated using the final mean temperature of the simulation $kT/\epsilon=0.9$ in Eq. (12). The last row represents the mean values of each column and the standard errors are given in parentheses for the last significant figure. All quantities quoted in this and subsequent tables are in LJ reduced units, σ, ϵ, and m. Time is in units of $\sigma(m/\epsilon)^{1/2}$.

N	K_{B1}	K_{B2}	K_1	K_2	$D_B^G(T)$
32	23.9	477.0	241.9	756.8	0.0656
108	23.4	460.6	231.5	756.2	0.0659
256	23.1	465.3	232.7	768.2	0.0671
500	23.1	463.8	231.9	767.2	0.0669
864	23.4	466.7	232.0	768.6	0.0663
2916	23.0	460.1	229.7	759.8	0.0670
Means	23.3(3)	465.6(5.6)	233.3(4.0)	762.8(5.3)	0.0665(6)

TABLE II. The same as for Table I but using the LJ system and $N=256$ particles with different mass ratios. In the mean value for $D_B^G(T)$ we have omitted the corresponding values for $m_B/m=1$ and 4.

m_B/m	K_{B1}	K_{B2}	K_1	K_2	$D_B^G(T)$
1	231.9	684.8	232.3	695.6	0.0810
4	56.7	466.0	230.5	686.4	0.0683
10	22.5	398.5	227.9	670.3	0.0637
16	14.5	417.9	230.5	685.4	0.0633
20	11.2	396.8	229.7	683.9	0.0639
30	7.5	391.0	228.4	674.6	0.0631
40	5.7	386.2	226.2	662.6	0.0619
50	4.5	390.9	227.2	667.4	0.0631
Means			229.1(1.9)	678.3(10.5)	0.0632(6)

$$m_f=\frac{N-1}{N-1+m_B/m} . \tag{15}$$

In the thermodynamic limit, where $N\rightarrow\infty$, we find that Eq. (14) is recovered. As we are interested in the approach to the thermodynamic limit, we have applied both Eqs. (14) and (4) to the Brownian and solvent particles. It is straightforward to derive

$$\left[\frac{T_B}{T_s}\right]_{(12)}=\frac{m(N-1)}{m_B} , \tag{16}$$

where T_B and T_s are the "temperatures" associated with the Brownian and solvent particles, respectively. The subscript indicates that Eq. (14) has been used. Applying the same procedure to Eq. (4) one obtains

$$\left[\frac{T_B}{T_s}\right]_{(2)}=1+\left[\frac{T_B}{T_s}\right]_{(12)} , \tag{17}$$

or alternatively in terms of the mass factor as

$$\left[\frac{T_B}{T_s}\right]_{(12)}\Bigg/\left[\frac{T_B}{T_s}\right]_{(2)}=m_f . \tag{18}$$

The theoretical result in Eq. (18) can be directly tested by computer simulation as the kinetic energy ratio between the Brownian and solvent particles is readily calculated. Table III shows the simulation results for the several WCA systems at a given mass ratio of $m_B/m=10$. The first two columns in the table show that the ratio T_B/T_s predicted by Eq. (18) is in good agreement with that calculated from the simulation. The simulation values for T_B/T_s are almost the same as those calculated using the m_f values from Ref. [15]. As we are simulating the microcanonical ensemble, the T_s and the total energy u_B remain almost constant, as expected *a priori* for both quantities in this ensemble. Also in Table III are listed the self-diffusion coefficients obtained from the simulation using several methods. The mean square displacement method (MSD) for the self-diffusion D_B gives the same value as when the velocity autocorrelation function (VACF) method is used. Only the system of $N=32$ particles shows a significant difference from the rest by manifesting a smaller plateau value. For the intermediate size systems ($N=108$ to 500) it is easy to see that the plateaus show a dependence on system size before approaching a constant value for the larger systems ($N=864$ and 2916).

In order to calculate the diffusion coefficient using the Gaussian memory function approach, we have to decide whetherT_B or T_s should be used in Eq. (12). Two prospective diffusion coefficients can be defined: $D_B^G(T_B)$ or

TABLE III. WCA simulations using $m_B/m=10$. T_B is the "temperature" of the Brownian particle defined from the mean kinetic energy. T_S is the temperature of the solvent particles. D_B is the self-diffusion coefficient obtained from the simulations using the mean square displacements and velocity autocorrelation function. $D_B^G(T_B)$ is the self-diffusion coefficient using the Mori coefficients with a Gaussian memory function and using T_B for the temperature in Eq. (12). $D_B^G(T_S)$ uses T_S instead of T_B in (12), and u_B is the average potential energy of the Brownian particle.

T_B/T_S	m_f	N	T_S	u_B	D_B	$D_B^G(T_B)$	$D_B^G(T_S)$
0.77(1)	0.7561	32	0.9087(14)	0.633(4)	0.040	0.046	0.066
0.95(1)	0.9145	108	0.9041(8)	0.629(3)	0.060	0.062	0.065
0.96(1)	0.9623	256	0.9163(15)	0.631(5)	0.072	0.065	0.068
0.99(2)	0.9804	500	0.9122(13)	0.629(5)	0.076	0.067	0.068
1.03(2)	0.9886	864	0.9141(12)	0.637(3)	0.088	0.069	0.067
1.01(2)	0.9966	2916	0.8996(9)	0.622(3)	0.085	0.068	0.067
Means			0.909(6)	0.630(5)			0.067(1)

TABLE IV. LJ simulations using $N=256$ particles and different mass ratios. Other details as for Table III. White spaces mean that the plateau has not been reached.

T_B/T_S	m_f	m_B/m	T_S	u_B	D_B	$D_B^G(T_B)$	$D_B^G(T_S)$
1.01(1)	0.9961	1	0.8933(2)	−4.50(1)	0.068	0.081	0.080
0.99(1)	0.9846	4	0.9053(2)	−4.51(1)	0.062	0.068	0.069
0.97(3)	0.9622	10	0.8956(2)	−4.50(1)	0.058	0.062	0.063
0.97(1)	0.9410	16	0.9238(5)	−4.48(1)	0.057	0.062	0.064
0.87(2)	0.9273	20	0.8915(3)	−4.50(2)	0.044	0.055	0.063
0.88(3)	0.8947	30	0.9064(3)	−4.50(1)		0.056	0.063
0.90(3)	0.8644	40	0.8891(3)	−4.50(1)		0.055	0.061
0.84(2)	0.8361	50	0.8991(2)	−4.51(1)		0.052	0.063
Means			0.90(1)	−4.50(1)			0.063(1)

$D_B^G(T_s)$. While $D_B^G(T_B)$ shows a similar but smoother behavior to the directly computed value D_B, the $D_B^G(T_s)$ coefficient can be considered more invariant with system size even for $N=32$. Accordingly, with the T_B and T_s values in the table, one should expect a constant $D_B^G(T_B)$ that is equal to $D_B^G(T_s)$ in the limit case of $N \rightarrow \infty$. This is, in fact, what we find in the $N=2916$ row of Table III, which confirms that the simulation data are in agreement with the theory [5].

For a given LJ system of $N=256$ particles and different mass ratios, Table IV confirms that the value of (T_B/T_s) decreases with increase in mass ratio, according to Eq. (16). Comparing Tables III and IV, one can see that, as expected, even though the two interaction potentials are different, the same trend is observed. The direct method of computing the self-diffusion coefficient (MSD or VACF) produces a well defined plateau value for the first five values of m_B/m in Table IV. A plateau in $D_B(t)$ is reached, the values of which go down with the increasing of mass ratio. However, we found that the three more massive Brownian particles do not achieve a limiting value within the duration of our VACF and MSD, so we were unable to assign a value for the self-diffusion coefficient for these states. From the T_B and T_s values in the table there is evident a constant $D_B^G(T_s)$ and a $D_B^G(T_B) \rightarrow 0$ in the limiting case of $m_B/m \rightarrow \infty$, in agreement with Ref. [5]. However, note that even $D_B^G(T_s)$ is affected for the two smaller mass ratios, only tending to a constant value for $m_B/m \geq 10$.

In Tables III and IV we see that in general the D_B and $D_B^G(T_s)$ values are not the same. The most direct method of calculating the self-diffusion coefficient of a Brownian particle is by means of the MSD of the particles, and any of the other methods in use (as the VACF method) must give, in principle, the same results. However, the GM approximation should dominate for large isotope masses [9] and in some sense should be more reliable for large Brownian particle mass (bearing in mind the noted difficulty in obtaining a plateau value by the direct method for large mass). Nevertheless, one would expect that both routes should lead to the same value for the self-diffusion coefficient. What is evident from the values in the tables is that the results with both techniques do not in general agree. There are several possible origins for this discrepancy. For example, the MSD technique or the methods based on the GM technique (or both) could be subject to finite N effects or inappropriate when applied to such small systems and/or light Brownian particles. To check this possibility, we have performed further calculations for much larger systems and more massive Brownian masses, trying to find if there exists a minimum value for the system size and for the Brownian mass in which the self-diffusion calculated by both routes give, within statistical uncertainty, the same values. Table V shows the results for the WCA simulation for the chosen system and mass ratios. The MSD method for $N=500$ particles and a mass ratio of $m_B/m=15$ gives the same value for the self-diffusion coefficient as for $m_B/m=10$ in Table III, but it is still different from the GM method. However, using $m_B/m=25$, both methods

TABLE V. WCA simulations for the larger systems and mass ratios. Other details are as for Tables I–IV. Now the D_B values are the results with the mean square displacement method. In the means, the first smaller system has been omitted.

T_B/T_S	m_f	N	m_B/m	T_S	K_{B1}	K_{B2}	D_B	$D_B^G(T_S)$
0.96(2)	0.9708	500	15	0.925(1)	15.40	458.4	0.076	0.068
0.92(3)	0.9523	500	25	0.8831(5)	9.02	430.7	0.064	0.065
0.96(3)	0.9664	864	30	0.913(1)	7.80	446.8	0.069	0.066
0.94(3)	0.9717	1372	40	0.910(1)	5.84	443.5	0.068	0.065
0.96(4)	0.9762	2048	50	0.899(1)	4.59	429.7	0.070	0.065
Means				0.90(1)		437.7(7.6)	0.068(2)	0.065(1)

lead to the same value for the self-diffusion coefficient. This agreement is maintained for larger systems and for more massive Brownian particles and, moreover, the values obtained are almost constant for all the systems of $N \geq 500$ particles and mass ratios of $m_B/m \geq 25$. Consequently, within the simulation statistical uncertainty, the MSD and the GM methods give the same value for the self-diffusion coefficient of the Brownian particle, which does not depend on the number of solvent molecules nor on the mass of the Brownian particle, *provided* N and m_B are sufficiently large. The values obtained by the VACF method are similar to those using the MSD method for the first two systems, but for the other three systems they present a parallel behavior to the MSD method with slightly greater values. This behavior could possibly be caused by the approximate representation of the particle velocity in the leap-frog algorithm, which could be improved upon using a more accurate algorithm [15].

V. CONCLUSIONS

In summary, in the WCA system for a wide number of systems (from $N=32$ to 2916) and for a given value of mass ratio of $m_B/m=10$, the Mori coefficients and the self-diffusion coefficient are independent of system size (Table I). Moreover, in a fixed LJ system of $N=256$ particles, with varying mass ratio from $m_B/m=1$ to 50, the self-diffusion coefficient does not depend on the mass of the Brownian particle for $m_B/m \geq 10$ values (Table II). This conclusion is not affected by the ensemble used, whether microcanonical or isothermal-isobaric. From both tables one can notice that the attractive part of the potential, included in the LJ potential and omitted in the WCA potential, diminishes somewhat the self-diffusion coefficient [10]. In other words, the weak long ranged attractive part of the potential tends to retard the Brownian particle in the solvent.

As the computer simulation experiments are limited to finite system size far from the thermodynamic limit, any generalization from particular results is not within risk. In this sense, we have used Eqs. (4) and (14), which are valid for systems with a finite and infinite number of particles, respectively. Their comparison is a measure of how far a system is from the thermodynamic limit and thus how the behavior of a finite system simulated can be generalized to larger systems. From our results of T_B/T_s, compared with the theoretical value given by the mass factor m_f, one can conclude that the thermodynamic limit can, in fact, be very closely reached for very small systems (note, for example, how close to unity is the m_f value in Table III for $N=2916$). This result reminds us of a similar conclusion obtained in path integral theory in which the equivalence between a semiquantum particle and a ring polymer of P beads is theoretically reached when $P \rightarrow \infty$, but in many of the practical cases this equivalence is reached at a very low number of beads ($P \leq 30$, see for example [16]). Then one can estimate that the GLE, given by Eq. (5), is valid for large enough Brownian particle mass independent of system size. Moreover, if the Gaussian memory function Eq. (12) is considered to be valid for the self-diffusion coefficient, then, according to our results, this coefficient should not depend on solute mass or system size. That is, a Brownian particle should have a unique self-diffusion coefficient at a given density and temperature, no matter how massive the Brownian particle is and how many particles there are in the solvent system if they are larger than critical values. This conclusion can be considered to be in agreement with [5,9], in which the mass of the Brownian particle and the number of solvent particles were assumed to be infinity, as being the only "state" having a nonzero value for the friction coefficient by the force autocorrelation function route [5], and with the former conclusion, which states that the Gaussian memory dominates at high mass ratio [9].

An interesting generalization, which would also further check this conclusion, to be taken into account in a future study is to calculate the first two Mori coefficients for several state points (T,ρ) in order to obtain an analytical behavior for these coefficients, in a similar way to the procedure of [17] for the mass and volume changes of the Brownian particle. Then the results should be compared with previous extensive studies for different state points [18,19]. In this way, in the Gaussian approximation, the self-diffusion coefficients and other directly related coefficients, such as the friction coefficient, would be known approximately *a priori* if a functional form were found for those Mori coefficients.

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