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System size dependence of the transport coefficients and Stokes–Einstein relationship of hard sphere and Weeks–Chandler–Andersen fluids

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Abstract

Molecular dynamics simulations have been used to calculate the self-diffusion coefficient, D , and other transport coefficients of the hard sphere and Weeks–Chandler–Andersen (WCA) fluids over a wide density range. Simulations were carried out with different numbers of particles, N , in the range between 500 and 273 375 for the WCA and up to 10 976 for the hard sphere fluid. These data were fitted to the relationship $D = D_\infty - AN^{-\alpha}$, where the parameters D_∞ , A and α were all allowed to be density dependent. The self-diffusion coefficient in the thermodynamic limit was obtained for both fluids. The Stokes–Einstein (SE) relationship stick–slip parameter, $c = k_B T / \pi D \eta_s$, where k_B is Boltzmann’s constant, T is the temperature and η_s is the shear viscosity, was calculated for the two fluids at each state point as a function of N . Because of the relatively strong N dependence of D , the parameter c is also shown to be sensitive to N . It is shown that data taken for a few hundred particles can significantly overestimate the value of c . At liquid-like densities, with increasing system size, c tends towards the slip value of 2. The same trend is observed for hard spheres and WCA particles. Therefore for any study of the SE stick–slip parameter it is important to perform several simulations for different system sizes and extrapolate the self-diffusion coefficient to the thermodynamic limit, and it is this value which should be used to compare with theory. At the same packing fraction the self-diffusion coefficient of the WCA fluid is larger than the value for the hard sphere fluid in the thermodynamic limit by, for example, 10% at a packing fraction of 0.3 and 60% at a packing fraction of 0.49. The trend for the shear viscosity is the reverse, both of which could be attributed to the softness of the potential in the WCA case and its effect in inducing more cooperative interparticle trajectories than for the hard sphere.

1. Introduction

Molecular dynamics simulation has proved a useful tool for calculating the transport coefficients of simple model fluids. One area of interest has been testing the extent to which the Stokes–Einstein (SE) relationship applies to these simple fluids. The Stokes–Einstein relationship is

$$D\eta_s = \frac{k_B T}{c\pi\sigma}, \quad (1)$$

where k_B is Boltzmann’s constant, T is the temperature, D is the self-diffusion coefficient and η_s is the shear viscosity. c is a boundary condition parameter, which ranges between $c = 2$ (‘slip’) and $c = 3$ (‘stick’) for macroscopic spheres in a Newtonian solvent. The results of numerous simulations have revealed that c typically ranges in between these extremes for fluids at liquid-like densities, tending towards the slip limit with increasing density (e.g. see [1] and [2], p 262). These conclusions have typically been based on molecular dynamics (MD) simulations of less than a few thousand particles (often only on a few hundred), which is unsatisfactory as, although the shear viscosity has a relatively weak system size dependence (above about 500 particles), the self-diffusion coefficient is strongly system size dependent [3]. Therefore, in order to make meaningful comparisons with theory (which are implicitly in the thermodynamic limit) the value of the self-diffusion coefficient in the limit of infinite system size (or $N \rightarrow \infty$, where N is the number of molecules in the simulation cell) is required. Because of the inevitably finite computer resources the thermodynamic limit for D is not accessible directly by means of MD, and the value of D in the $N \rightarrow \infty$ limit must be obtained by extrapolation of the finite N data [3].

Dunweg and Kremer [4] and more recently Fushiki [5] and Yeh and Hummer [6] derived an expression for the N dependence of the self-diffusion coefficient of arbitrary liquids, taking into account the effects of the periodic images using a hydrodynamics model which is, formally at least, valid at any fluid density. The packing fraction ζ is a convenient measure of the density and is defined as $\zeta = \pi N\sigma^3/6V$ where N is the number of hard spheres in volume V . This theory predicts

$$D(\zeta, N) = D_\infty(\zeta) + A(\zeta)N^{-\alpha(\zeta)}, \quad (2)$$

where $D_\infty(\zeta)$ is the ζ -dependent self-diffusion coefficient in the thermodynamic limit. The exponent in the theory is $\alpha = 1/3$ and $A = -\xi k_B T \zeta^{1/3}/6^{2/3} \pi^{4/3} \eta_s$, where $\xi \simeq 2.837\,297$ [6]. Equation (2) has also been used to extrapolate to infinite N the self-diffusion coefficient of liquid *para*-hydrogen computed using ring-polymer molecular dynamics [7]. We recently carried out a test of this formula for the hard sphere fluid over a range of packing fractions [3], and showed that for N up to 10 976, while the analytic form in equation (2) applied very well for each ζ considered, the optimum exponent α was higher than $1/3$ in the low and high density extremes, and that $A(\zeta)$ also deviated from the above formula in these cases. Nevertheless, the equation (2), with α chosen as a free parameter, does represent the simulation data rather well at all densities. The D_∞ , A and α data were fitted to low order polynomials in ζ whose analytic forms and parameter values are reported in [3].

The purpose of this work is to explore further the implications of the formula in equation (2), this time concentrating on the Stokes–Einstein (SE) relationship. Clearly as c depends on D , the system size dependence of D will have an effect on c . In order to test SE we chose two interaction potentials where the effective diameter of the particle is relatively unambiguous, which then allows us to focus on c itself. We use two purely repulsive

interactions. The first, the hard sphere potential, $\phi(r)$, is

$$\phi(r) = \begin{cases} \infty, & r \leq \sigma \\ 0 & r > \sigma, \end{cases} \quad (3)$$

where r is the interparticle separation and σ is the hard sphere diameter. Also considered here is the steeply repulsive but nevertheless continuous interaction for a model fluid, namely the Weeks–Chandler–Andersen (WCA) potential [8]:

$$\phi(r) = \begin{cases} 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) + \epsilon, & r \leq 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma, \end{cases} \quad (4)$$

which is the Lennard-Jones (LJ) potential, shifted upwards by ϵ and truncated at the LJ potential minimum of $2^{1/6}\sigma$. The WCA fluid was originally devised as a reference fluid for a perturbation treatment of the LJ fluid [8] (see also [9, 10]), but it has subsequently found use as a generic fluid for simulation which is economical to employ, due to the short range of this potential. The WCA potential has been chosen largely for computational convenience in handling the very large system sizes, but noting that the treatment in [4–6] is independent of intermolecular potential, it is to be expected that the conclusions should be generally applicable to other systems. Simulations were carried out mainly in the NVT ensemble using a molecular dynamics code written by the author. Calculations were carried out at various densities for a range of numbers of particles, N , in the range between 500 and 273 375 for the WCA fluid, and 10 976 for the hard sphere fluid. The WCA simulations were carried out with $k_B T/\epsilon = 1$, or $T^* = 1$ in more usual notation.

A temperature-rescaled effective diameter, σ_e , of the WCA potential is given by the empirical formula $\sigma_e = 2^{1/6}\sigma/(1 + \sqrt{T^*})^{1/6}$, as discussed in [11]. This accounts very well for the temperature dependence of the compressibility factor, $Z (=PV/nRT)$, for the pressure P , number of moles, n , the gas constant, R , and temperature T . For the present simulations, the reduced temperature is $T^* = 1$ and therefore at this temperature according to this prescription, $\sigma_e = \sigma$. It would be incorrect however to identify σ_e as an effective hard sphere diameter, because, as was shown in [11], the hard sphere and WCA compressibility factors as a function of density do not overlap (although they are close) when this temperature-scaled effective diameter is used to define the packing fraction. The hard sphere and WCA systems follow a somewhat different equation of state line (i.e. Z versus ζ using σ_e to define ζ in the WCA case).

2. Results and discussion

The SE coefficient, c , is obtained from

$$c = \frac{k_B T}{\pi \sigma D \eta_s}. \quad (5)$$

The hard sphere fluid is considered first. The shear viscosity of the hard sphere fluid can be conveniently written in the form $\eta_s = \eta_E f(\zeta)$, where η_E is the Enskog kinetic theory prediction for the shear viscosity (e.g., see [12]) which is analytic. The correction factor $f(\zeta) \rightarrow 1$ for $\zeta \rightarrow 0$, indicating that the Enskog prediction becomes increasingly more accurate with decreasing density. The function $f(\zeta)$ was expressed in [3] as $f(\zeta) = 1.0 + a_1 \zeta^{a_2}$, where $a_1 = 2588 \pm 258$ and $a_2 = 11.11 \pm 0.13$, which reproduces the molecular dynamics simulation data of [3] within the statistical uncertainties of the calculations. The self-diffusion coefficients obtained from MD simulation data from [3] were fitted to equation (2) in which D_∞ , A and α were represented by low order polynomials in ζ (see [3]).

Table 1. Self-diffusion coefficient and shear viscosity of the hard sphere fluid in the thermodynamic limit, $D_{\infty,HS}$, from molecular dynamics data [3]. Data for different numbers of particles in the simulation cell, N , were extrapolated to the thermodynamic limit at each of the packing fractions, ζ , using the procedure applied to equation (6) in [3]. The units of $D_{\infty,HS}$ are $\sigma(k_B T/m)^{1/2}$ where σ is the hard sphere diameter of the hard sphere potential given in (3) and m is the mass of the hard sphere. $\eta_{s,\infty,HS}$ is the shear viscosity of the hard sphere fluid in the thermodynamic limit, using $\eta_s = \eta_E f(\zeta)$ where η_E is the analytic Enskog prediction for the shear viscosity (e.g. see [12]).

ζ	$D_{\infty,HS}$	$\eta_{s,\infty,HS}$	ζ	$D_{\infty,HS}$	$\eta_{s,\infty,HS}$	ζ	$D_{\infty,HS}$	$\eta_{s,\infty,HS}$
0.001	113	0.179	0.28	0.234	0.632	0.42	0.0702	2.16
0.01	11.0	0.181	0.29	0.218	0.680	0.43	0.0624	2.44
0.05	2.04	0.192	0.30	0.203	0.733	0.44	0.0550	2.78
0.1	0.936	0.222	0.31	0.189	0.790	0.45	0.0481	3.21
0.15	0.579	0.277	0.32	0.175	0.854	0.46	0.0417	3.74
0.175	0.478	0.318	0.33	0.162	0.923	0.47	0.0356	4.42
0.20	0.400	0.368	0.34	0.150	1.001	0.48	0.0300	5.27
0.21	0.373	0.392	0.35	0.138	1.09	0.49	0.0249	6.37
0.22	0.349	0.418	0.36	0.127	1.18	0.50	0.0201	7.78
0.23	0.327	0.446	0.37	0.116	1.29	0.51	0.0157	9.61
0.24	0.306	0.477	0.38	0.106	1.42	0.52	0.0117	12.0
0.25	0.286	0.511	0.39	0.0965	1.56	0.53	0.00815	15.1
0.26	0.267	0.548	0.40	0.0872	1.73	0.54	0.00492	19.1
0.27	0.250	0.588	0.41	0.0785	1.92	0.55	0.00206	24.3

The self-diffusion coefficients, D , for the WCA fluid were obtained by integration of the velocity autocorrelation function (VACF) evaluated in the laboratory frame of reference (e.g., see [13], p 95, and [14]). The truncation time t_c of the VACF was at least 100 reduced time units (of $\sigma(m/\epsilon)^{1/2}$), and it was ensured that the VACF decayed statistically to zero well within t_c at each state point. For the simulations, the packing fractions ζ were 0.3, 0.4, 0.45 and 0.49, which are all in the fluid phase (the last being on the fluid–solid coexistence boundary, [15]). A standard MD procedure was used with the Verlet leapfrog algorithm for the high density systems, employing link lists to speed up the computations (e.g., [16], chapter 3). At each value of N several simulations were carried out to establish the statistical uncertainty of the data.

The self-diffusion coefficients of the WCA fluid at finite N were extrapolated to the thermodynamic limit using equation (2). The parameters D_∞ , A and α were fitted to the simulation data at each packing fraction using an implementation of the non-linear least-squares Marquardt–Levenberg algorithm in the gnuplot graphics program [17]. The shear viscosity and thermal conductivity, λ , have a much weaker N dependence, and an N^{-1} extrapolation was adopted which is the same as has been used for the equation of state, which is also known to be weakly system size dependent compared with the self-diffusion coefficient (e.g. see [18]).

The hard sphere simulations were carried out in the NVE ensemble using a molecular dynamics code written by the author (as the potential energy is zero for hard spheres, the temperature was also constant to machine accuracy in this special case of an NVE system). For liquid-like states, system sizes (N) in the range 32–10976 were chosen, with typically about 30 simulations being carried out for each value of ζ . Both the hard sphere and Weeks–Chandler–Andersen fluid simulations were carried out in three dimensions with a cubic simulation cell and periodic boundary conditions in each of the three cartesian directions. The simulations represented systems in the bulk and had no free boundaries. Table 1 presents the self-diffusion coefficients and shear viscosity in the $N \rightarrow \infty$ limit for the hard sphere fluid at a series of packing fractions. The maximum equilibrium fluid density is 0.493 and the glass

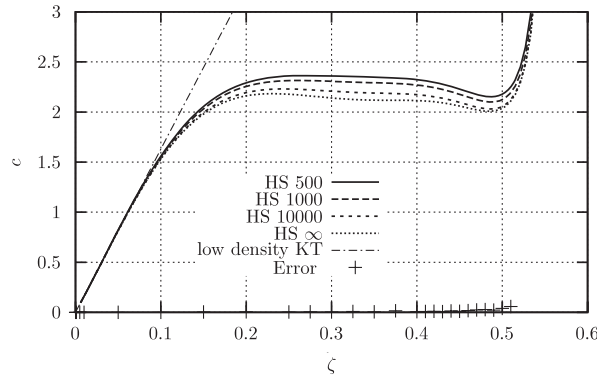


Figure 1. Packing fraction, ζ , dependence of the Stokes–Einstein boundary condition parameter $c = k_B T / \pi D(N) \eta_s(N)$ for hard spheres for selected values of N , given in the figure. $D(N)$ was fitted to equation (2) or (6) from [3]. The low density kinetic theory prediction (‘KT’) is also shown in the figure. Note that $c = 2$ and $c = 3$ correspond to the slip and stick boundary conditions respectively. The errors for the data in the thermodynamic limit are given in the figure as ‘Error’.

Table 2. Quantities associated with the self-diffusion coefficient, and other transport coefficients, of the hard sphere and WCA fluids. ζ is the packing fraction, defined in both cases as $\zeta = \pi N \sigma^3 / 6V$ (here $\sigma_e = \sigma$). The various quantities are defined in the text. The estimated errors in the self-diffusion coefficients are less than 2% in D , and 5% in the shear viscosity and thermal conductivity, and 2% in the stick–slip parameter, c .

ζ	$D_{\infty,HS}$	$D_{\infty,WCA}$	A_{WCA}	α_{WCA}	$\eta_{\infty,s,HS}$	$\eta_{\infty,s,WCA}$	$\lambda_{\infty,WSA}$	$c_{\infty,HS}$	$c_{\infty,WCA}$
0.3	0.203	0.226	−0.254 96	0.413 90	0.73	0.613	2.75	2.14	2.36
0.4	0.0872	0.109	−0.051 903	0.216 01	1.73	1.40	5.37	2.11	2.22
0.45	0.0481	0.0664	−0.034 501	0.221 89	3.21	2.43	7.44	2.06	2.09
0.49	0.0249	0.0393	−0.037 336	0.333 33	6.37	4.12	9.50	2.01	2.03

transition is between 0.57 and 0.58 [19] indicating that some of the states modelled were in the metastable two-phase regime. Table 2 presents key parameters characterizing the hard sphere and WCA fluids in the thermodynamic limit at four packing fractions. The shear viscosity and thermal conductivity of the WCA fluid were obtained by the Green–Kubo time correlation method [20, 21].

Figure 1 shows the density dependence of c as a function of ζ for the hard sphere fluid for N between 500 and 10976 and in the thermodynamic limit. The errors in these data arise from both the η_s and D terms in equation (5). The shear viscosity has a typical statistical error of ~ 3 –5% up to about $\zeta = 0.47$, and increases steadily for higher packing fractions. This quantity is assumed to be relatively independent of N here, and plays a role subsidiary to that of the self-diffusion coefficient, which has a more significant N dependence. The statistical error in D at a given packing fraction is maximum in the thermodynamic limit, which was obtained by extrapolation of the finite N data for D . The errors in c due solely to those in D_{∞} are shown in figure 1 (the contribution from the shear viscosity is the same for each N value at a given packing fraction). It is seen that the statistical uncertainties only becomes significant and comparable to the N dependence itself for densities much higher than about $\zeta = 0.51$. The various curves for different N values in the figure are therefore statistically distinguishable.

In the zero-density limit, kinetic theory gives $c = 256\zeta / 5\pi$ using definitions for the self-diffusion coefficient and shear viscosity of hard spheres in the zero-density limit given in, for example, [12]. The figure shows that the simulation data agree well with this formula for

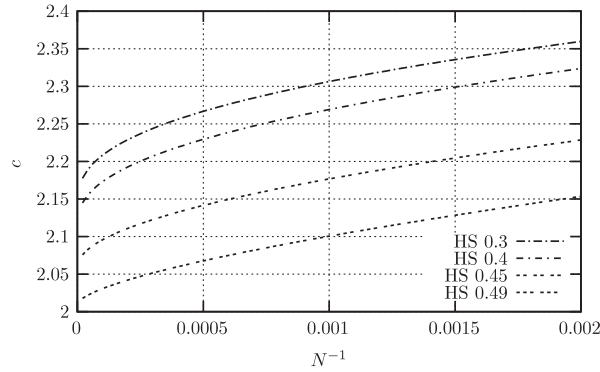


Figure 2. N dependence of the Stokes–Einstein boundary condition parameter $c = k_B T / \pi D(N) \eta_s(N)$ as a function of packing fraction for hard spheres.

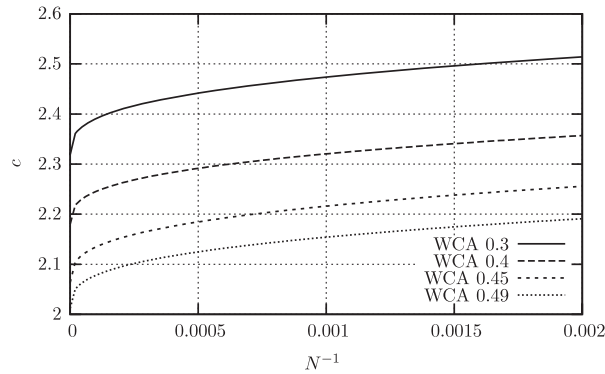


Figure 3. As for figure 2 except that the WCA fluid was considered and $\alpha = 1/3$.

densities up to about 0.1. The SE parameter reaches a maximum for all N at about $\zeta \simeq 0.2$ and then slowly decreases with increasing packing fraction up to about 0.5 before increasing rapidly again in the metastable fluid region, indicating that the self-diffusion coefficient decreases more rapidly than the viscosity increases with increasing density in this regime. There is a decrease in c with increasing N which is most pronounced for $0.2 < \zeta < 0.4$. For example at $\zeta = 0.3$ the decrease in c is about 0.3 from $N = 500$ to ∞ , which is significant in the context of comparing simulation data with any theory, as simulation data are implicitly taken to be ‘exact’ and used to test the adequacy of theory.

Figure 2 presents the dependence on N and ζ of c for the hard sphere fluid case in a different way, with this time c plotted against N^{-1} to provide a clearer indication of convergence to the thermodynamic limit (i.e., $N^{-1} \rightarrow 0$). Curves for four densities, $\zeta = 0.3, 0.4, 0.45$ and 0.49 are given in the figure. It can be seen that even for $N > 2000$ there is a significant decrease in c as N increases further. The same trends are seen for the WCA fluid, in figure 3, although the values of c are a little higher than for the hard sphere at the corresponding density and value of N . Some more insights into the origin of this can be seen in table 2, which shows various quantities in the thermodynamic limit. In the table, $D_{\infty,HS}$ is the value of the hard sphere self-diffusion coefficient in the $N \rightarrow \infty$ limit. A_{WCA} and α_{WCA} are the constants in equation (2) for the WCA fluid. $\eta_{s,WCA}$ is the value of the shear viscosity of the WCA fluid in the thermodynamic limit obtained using equation (2) with an $\alpha = 1$

extrapolation to $N \rightarrow \infty$. $\lambda_{\infty, \text{WCA}}$ is the value of the thermal conductivity of the WCA fluid in the thermodynamic limit obtained using equation (2) with an $\alpha = 1$ extrapolation to $N \rightarrow \infty$. $\eta_{\infty, s, \text{HS}}$ is the shear viscosity of the hard sphere fluid in the thermodynamic limit. $c_{\infty, \text{HS}}$ and $c_{\infty, \text{WCA}}$ are the values of the Stokes–Einstein parameter, c , in the thermodynamic limit for the WCA fluid. The values of c were determined at each N and ζ , then extrapolated to $N \rightarrow \infty$. The functional form $c_{\text{WCA}} = c_{\infty, \text{WCA}} - A_{\text{WCA}} N^{-\alpha_{\text{WCA}}}$ was fitted to the simulation data. The parameters $c_{\infty, \text{WCA}}$, A_{WCA} and α_{WCA} were fitted to the simulation data at each packing fraction using an implementation of the non-linear least-squares Marquardt–Levenberg algorithm in the gnuplot graphics program [17].

Table 2 shows that the self-diffusion coefficient of the WCA fluid is a little higher than that of the hard sphere fluid at the same density, and the shear viscosity is correspondingly lower than the hard sphere value. This is consistent with previous simulations in which the softness effect has been shown to enhance the fluidity of the system, presumably because the longer range of the potential enables the particle trajectories to be more cooperative. In the case of the hard sphere the particles have totally uncoordinated trajectories unless they collide. The two opposite trends tend to cancel each other out in their effects on the stick–slip parameter. Nevertheless there is an effect. The self-diffusion coefficients in this limit are somewhat larger for the WCA fluid than for the hard sphere fluid, yet the corresponding c values are also larger, especially at low densities. This reveals that the effect of softness is a little stronger in decreasing the shear viscosity than in increasing the self-diffusion coefficient. The thermal conductivities of the WCA fluid are also given in table 2.

3. Conclusions

To conclude, the N dependence of the Stokes–Einstein stick–slip coefficient is significant for the hard sphere and the WCA fluids, and presumably other simple liquids. The system size dependence of the shear viscosity is relatively weak for systems in excess of about 500 particles, whereas the self-diffusion coefficient has a more pronounced and relatively slowly converging convergence to the thermodynamic limit. It is therefore important to use the self-diffusion coefficient and shear viscosity values in the thermodynamic limit, D_{∞} and $\eta_{\infty, s}$, respectively, to compare with theory. D_{∞} can be readily and accurately estimated by extrapolation of D according to equation (2), in which α is employed as a free parameter in the fitting process (although as has been proved in [3], for not too low densities, the value of D_{∞} is relatively insensitive to the value of α in a reasonable range near 1/3).

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