The generalized Stokes–Einstein relation for liquid sodium

Umberto Balucani†, Günther Nowotny‡ and Gerhard Kahl‡

† Istituto di Elettronica Quantistica, CNR, I-50127 Firenze, Italy
‡ Institut für Theoretische Physik, TU Wien, Wiedner Hauptstraße 8–10, A-1040 Wien, Austria

Abstract. We show that a microscopic generalization of the Stokes–Einstein relation between the diffusion and shear viscosity coefficients, previously tested in simple liquids near melting, has a much wider range of application. The practical validity of the approach is accurately checked by performing extensive computer simulations in liquid sodium at temperatures ranging from 403 K to 1003 K.

Transport properties such as the diffusion and shear viscosity coefficients are widely used in any macroscopic description of time-dependent phenomena in dense fluids and liquids such as, for example, ordinary Navier–Stokes hydrodynamics. These 'coarse-grained' approaches are, however, unable to predict in different thermodynamic states the actual magnitude of the transport coefficients, which depends on a variety of underlying microscopic events (comprising, e.g., collisions, vortices and particle trapping). In the last decade or so, considerable progress in the microdynamics of the liquid state has however been achieved by the development of comprehensive frameworks combining both kinetic and mode-coupling arguments [1, 2]. In particular, by these approaches quite satisfactory results have been obtained for the dynamics (and consequently for the transport coefficients) of several simple liquids near freezing as well as in supercooled states [1]. In comparison, less attention has instead been devoted to realistic liquids at relatively high temperatures, where the tests of the above general framework are limited, and the results still somewhat controversial.

In this work we shall explicitly consider the problem of 'predicting' the diffusion coefficient D of a simple liquid in a wide range of thermodynamic states. Specifically, we shall consider the case of molten sodium, an appropriate benchmark system because of the stability of its liquid phase over a rather large temperature interval (from the melting point at $T_m \sim 371$ K up to the boiling point at $T_b \sim 1154$ K). Although our approach is less general, it is much simpler (and equally reliable) than those referred to in the above, as will be clear in the following. We shall also compare the theoretical results for D with the experimental findings [3, 4]. In order to test the validity of the predictions as accurately as possible, we have also performed a number of subsidiary molecular dynamics (MD) simulations in a model system which mimics in a rather realistic way the features of liquid Na for the properties under consideration. The effective pair potentials acting between the Na atoms are based on pseudopotential theory: we have used the Ashcroft empty-core pseudopotential [5] along with the Ichimaru–Utsumi expression for the local field correction [6]. The only parameter in the pseudopotential is the core radius, for which we have taken the usual value reported in the literature (0.9049 Å) [7]. For state I (cf. table 1) we have used instead the effective interatomic potential proposed by Price *et al* [8] which gives

Table 1. First section: input data for the MD simulation—the temperature T, mass density ρ and time-step Δt for the integration of equations of motion; second section: results for the diffusion constant D (in $\text{Å}^2 \text{ ps}^{-1}$) obtained by using equations (4) and (7); third section: results for D as obtained directly from the MD simulation (cf. text); fourth section: experimental results [3, 4].

State		I	II	III	IV	V
T (K)		403.0	602.0	803.0	900.0	1003.0
ρ (kg m^{-3})		919.2	873.5	824.4	801.0	777.0
Δt (fs)		3	1	1	1	1
D^0	(MD)	0.364	1.501	2.478	2.909	3.351
	(MF fit)	0.507	1.501	2.340	2.868	3.257
D_{free}^∞		0.075	−0.068	−0.080	−0.085	0.209
$D^0 + D_{\text{free}}^\infty$	(MD)	0.439	1.433	2.399	2.824	3.560
	(MF fit)	0.582	1.433	2.260	2.783	3.466
D^{MD}		0.615 ± 0.015	1.52 ± 0.02	2.67 ± 0.05	3.23 ± 0.03	4.0 ± 0.01
D^{exp}		0.505	1.280	2.20	2.98	3.35

slightly different (or even better) results for the diffusion constant [9, 3]. In this case the core radius was assumed to be 0.9116 Å.

Overall we have investigated five states of liquid Na; they are characterized by temperatures T and mass densities ρ which are compiled in table 1 and were taken from [4]. In our approach we require the transverse-current correlation functions (CF) $C_{\text{T}}(q, t)$ which were obtained by standard micro-canonical MD simulations of 2048-particle ensembles over 100 000 time-steps Δt. The values for Δt for the different states are also reported in table 1. Numerical and technical details about the simulation are compiled in previous papers [10, 11]. The transverse-current CFs were evaluated over a time-range of 2048 Δt. For every Na state a set of 63 q-vectors compatible with the periodic boundary conditions and up to a value q_m ranging from 8.2 to 9 Å^{-1} was chosen (the position of the main peak of the structure factor being at about 2 Å^{-1}). The simulation results for $C_{\text{T}}(q, t)$ have been fitted by a hydrodynamic model (with a q-dependent shear viscosity $\eta(q)$) and by a 'viscoelastic' memory function model, by introducing a relaxation time $\tau(q)$ [1, 10]. From the MD data, the diffusion coefficient D can be deduced both from an integral over the velocity autocorrelation function (VACF) and from the long-time behaviour of the mean square displacement [1, 12].

The starting point of our analysis is a microscopic generalization of the well-known 'Stokes–Einstein' (S–E) relation connecting D with the ordinary shear viscosity coefficient η. Such a generalization is a by-product of an approach developed by Gaskell and co-workers [13] for the VACF $\langle v(0) \cdot v(t) \rangle$ of a tagged particle in a dense monatomic fluid. The central point of this theory is the introduction of a *microscopic velocity field* around the tagged particle; from the VACF, the diffusion coefficient can eventually be obtained by a straightforward time integration. A simplified version of the theoretical result for D reads [14]

$$D = \frac{1}{3} \int_0^\infty \mathrm{d}t \ \langle v(0) \cdot v(t) \rangle \simeq \frac{1}{3\pi^2} \int_0^\infty \mathrm{d}q \ q^2 f(q) \int_0^\infty \mathrm{d}t \ C_{\text{T}}(q, t). \qquad (1)$$

Here $f(q)$ is the Fourier transform of $f(r)$, the 'form factor' of the microscopic

velocity field. As shown in [13], $f(r)$ can in practice be approximated by a step function $\Theta(a-r)$, where the length a represents an effective particle radius determined by the relation $\frac{4}{3}\pi na^3 = 1$ (n being the number density). Adopting this scheme, it is readily seen that $f(q) = (3/n)j_1(qa)/qa$, where $j_1(x) = (1/x)[\sin(x)/x - \cos(x)]$ is the spherical Bessel function of order one. Initially, $C_T(q, t = 0) = (\beta m)^{-1}$, where m is the atomic mass and $\beta = (k_B T)^{-1}$ with T the temperature of the fluid.

Strictly speaking, the velocity field approach cannot be considered as being a self-contained theory, since there is no recipe for a separate determination of all the dynamical quantities which enter the full VACF expression. However, with the resorting to simple theoretical approximations for the current correlations (for example, those provided by simple viscoelastic models [1]), the final results for the VACF compare very favourably with the simulation data in a variety of model systems, ranging from dense hard-sphere fluids to both Lennard-Jones and molten alkali metals *near the melting point* [13, 14]. Our purpose is to focus attention on the diffusion coefficient, and to test the validity of equation (1) a much wider temperature range.

As already remarked, equation (1) represents a generalization of the usual S–E relation (originally derived for a 'Brownian particle' in a solvent of much smaller particles). Inserting in equation (1) the hydrodynamic approximation $C_T(q, t) \simeq (\beta m)^{-1} \exp[(-\eta/nm)q^2 t]$, we would in fact obtain

$$D \simeq \frac{n}{3\pi^2 \eta \beta} \int_0^\infty dq \ f(q) = \frac{1}{\pi^2 a \eta \beta} \int_0^\infty dx \ j_1(x)\frac{1}{x} = \frac{1}{4\pi a \eta \beta} \equiv D_H. \quad (2)$$

The result (2) is identical with the one deducible from the S–E relation as written for a particle of radius a immersed in a continuum (and in the case of 'slip' boundary conditions). Thus, apparently the S–E relation is valid to some extent even if we deal with a fluid made of equal-mass particles. However, the roughness of the approximation (2) becomes clear if we consider that the insertion of the hydrodynamic expression for $C_T(q, t)$ would be correct if the q-integral in (1) were dominated by the small wavevectors. But, if this were the case, we should also consistently replace $f(q)$ by its 'hydrodynamic' value $f(q = 0) = 1/n$. As a result, the q-integral would diverge, signalling the relevance of wavevectors outside the hydrodynamic regime. Indeed, it is generally found that D_H substantially underestimates the actual value of the diffusion coefficient [15].

The origin of these discrepancies is clearly the incorrect insertion of the hydrodynamic expression for $C_T(q, t)$ in equation (1). To proceed, we shall make use of a formal representation of the Laplace transform $\hat{C}_T(q, z)$ of $C_T(q, t)$:

$$\hat{C}_T(q, z)/C_T(q, t = 0) = [z + \hat{K}_T(q, z)]^{-1} \quad (3)$$

which involves the Laplace transform of the (first-order) memory function $K_T(q, t)$. Adopting this 'Mori representation', it is readily seen that equation (1) can now be written as

$$D \simeq \frac{1}{3\pi^2 \beta m} \int_0^\infty dq \ q^2 f(q)[\hat{K}_T(q, z = 0)]^{-1} = \frac{n}{3\pi^2 \beta} \int_0^\infty dq \ f(q)\frac{1}{\eta(q)} \quad (4)$$

where in the last step we have introduced a *wavevector-dependent* shear viscosity coefficient $\eta(q)$ defined by $\hat{K}_T(q, z = 0) = (q^2/nm)\eta(q)$. The introduction of generalized transport coefficients is typical of the so-called 'generalized' hydrodynamical frameworks. For $q \to 0$ (the realm of ordinary hydrodynamics) the quasi-conserved character of the transverse current justifies a rapidly decaying ('Markovian') model for $K_T(q, t)$ [$\sim 2(q^2/nm)\eta\delta(t)$]; correspondingly, in equation (3), $\hat{K}_T(q, z) \simeq \hat{K}_T(q, z = 0) \to (q^2/nm)\eta$, so $\eta(q) \to \eta$. As is well known, there are many indications that ordinary hydrodynamics breaks down

at finite wavevectors: in the present context, there have been in fact several items of MD evidence [16, 17, 18] that $\eta(q)$ is a rapidly decreasing function, which for large q eventually approaches the free-particle result

$$\eta(q) = \sqrt{\frac{2}{\beta\pi m}}\frac{nm}{q}. \tag{5}$$

On a tentative basis, one may accept for the generalized viscosity the simple empirical form $\eta(q) \sim \eta[1 + A^2q^2]^{-1}$ proposed by Alley and Alder [16] for dense fluids of hard spheres of diameter d at not too high wavevectors. Inserting this expression into equation (4) we obtain

$$D \simeq D_{\mathrm{H}}\frac{1}{\pi^2a^2}\int_0^\infty \mathrm{d}q\ f(q)[1 + A^2q^2] = D_{\mathrm{H}}[1 + 2(A/a)^2f(r = 0)] = D_{\mathrm{H}}[1 + 2(A/a)^2] \tag{6}$$

which shows that the actual diffusion coefficient should indeed exceed D_{H}. From the estimate $A \simeq 0.3d$ [16] and some reasonable assumptions, one can also obtain a remarkably good (even if somewhat fortuitous) agreement for D [19].

For a less empirical theory, it is clear that at finite q one should ideally work out a model for $K_{\mathrm{T}}(q, t)$ that is more realistic than the Markovian one. For example, the above-mentioned 'viscoelastic model' assumes for $K_{\mathrm{T}}(q, t)$ a simple exponential decay, with a time constant $\tau(q)$ which governs the transition of the response from solid-like (the 'elastic' q-dependent rigidity modulus $G(q) = K_{\mathrm{T}}(q, t = 0)$) to fluid-like (the generalized viscosity $\eta(q) = G(q)\tau(q) = (nm/q^2)\hat{K}_{\mathrm{T}}(q, z = 0)$). Unfortunately, there is no serious theoretical approach for assessing the time $\tau(q)$, and consequently the quantity $\eta(q)$ to be inserted in equation (4).

In view of this situation, we have preferred to check the validity of the result (4) by a direct MD evaluation of $\eta(q)$. Although formally less appealing, the recourse to MD data has the merit of providing a stringent test of equation (4), free of the approximations inherent to any theoretical model for $K_{\mathrm{T}}(q, t)$. On a practical basis, at large wavevectors the finiteness of the integration step limits the accuracy of the MD data for $C_{\mathrm{T}}(q, t)$, which decreases more and more rapidly as q increases. Consequently, it is convenient to limit the MD investigation to a q-range below a suitable value q_m. Equation (1) is accordingly split into two contributions

$$D = D^0 + D_{\mathrm{free}}^\infty \tag{7}$$

where the two quantities on the r.h.s. refer to integration ranges $[0, q_m]$ and $[q_m, \infty]$, respectively (in the present study $q_m \sim 8.2$–9.0 Å^{-1}). The contribution D^0 can be evaluated from equation (1) by directly using the MD data for $C_{\mathrm{T}}(q, t)$. On the other hand, we may choose q_m large enough that $\eta(q)$ is practically given by the expression (5). In such a case from equation (4) one deduces that

$$D_{\mathrm{free}}^\infty = \frac{1}{(2\pi^3)^{(1/2)}na}\sqrt{\frac{1}{\beta m}}\int_{q_m}^\infty \mathrm{d}q\ j_1(qa) = \frac{1}{(2\pi^3)^{1/2}na^2}\sqrt{\frac{1}{\beta m}}j_0(q_ma) \tag{8}$$

where $j_0(x) = \sin(x)/x$.

The overall results of this procedure are reported in table 1. D^0 has been evaluated in two ways: (i) directly by inserting the MD data for $C_{\mathrm{T}}(q, t)$ in equation (1) and evaluating these integrals; (ii) via equation (4) using a value for $\eta(q)$ which is obtained from a viscoelastic fit to the MD data (i.e., $\eta(q) = G(q)\tau(q)$, where $G(q)$ is calculated from the static properties

[12] and $\tau(q)$—mentioned above—is determined from a fitting procedure). The comparison with the values of D obtained directly from the simulation appears to be quite good for both the procedures adopted. Furthermore, the agreement of the theoretical results with experimental data [3, 4] is also satisfactory. Having in mind the different nature of the relevant mechanisms ruling the diffusive process [20, 21], it is remarkable that the simple velocity field approach is able to describe rather well the overall features of single-particle motion in a range of conditions where D changes considerably (by more than a factor of 6). Viewed in perspective, this success is likely to be due to an important ingredient correctly incorporated in the approach, namely the exploitation of a separation of time-scales between the current and the positional coordinates. Owing to the close-packed character of the fluid (see table 1), this separation is approximately valid even at relatively high temperatures. This circumstance suggests that the approach may also be able to account for the temperature evolution of the 'minor' dynamical features of the VACF. Further work in this direction is in progress.

Acknowledgments

References

[1] Balucani U and Zoppi M 1994 *Dynamics of the Liquid State* (Oxford: Clarendon)
[2] Sjölander A 1987 *Amorphous and Liquid Materials* ed E Lüscher, G Fritsch and G Jacucci (Dordrecht: Nijhoff)
[3] Stangl A 1993 *PhD Thesis* Technische Universität München
[4] Ohse R W (ed) 1985 *Handbook of Thermodynamic and Transport Properties of Alkali Metals* (Oxford: Blackwell Scientific)
[5] Ashcroft N W 1966 *Phys. Lett.* **23** 48
[6] Ichimaru S and Utsumi K 1981 *Phys. Rev.* B **24** 7381
[7] Hafner J 1987 *From Hamiltonians to Phase Diagrams* (Berlin: Springer)
[8] Price D L, Singwi K S and Tosi M P 1970 *Phys. Rev.* B **2** 2983
[9] Balucani U, Torcini A, Stangl A and Morkel C 1995 *Phys. Scr.* T **57** 13
[10] Kambayashi S and Kahl G 1992 *Phys. Rev.* E **46** 3255
[11] Kahl G and Kambayashi S 1994 *J. Phys.: Condens. Matter* **6** 10 897
[12] Boon J-P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)
[13] Gaskell T and Miller S 1978 *J. Phys. C: Solid State Phys.* **11** 3749, 4839
   Gaskell T and Woolfson M S 1982 *J. Phys. C: Solid State Phys.* **12** 2705
   Balucani U, Vallauri R, Murthy C S, Gaskell T and Woolfson M S 1983 *J. Phys. C: Solid State Phys.* **16** 5605
[14] Gaskell T 1984 *J. Non-Cryst. Solids* **61+62** 913
   Gaskell T, Balucani U and Vallauri R 1989 *Phys. Chem. Liq.* **19** 193
[15] Consider, for example, liquid Na at 900 K, where $n = 0.021$ Å^{-3} and $a = 2.2485$ Å. Inserting for the shear viscosity coefficient the experimental value $\eta_{exp} = 2.01$ mP, equation (2) predicts a value $D_H = 2.187$ Å^2 ps^{-1}, considerably lower than the observed value $D \simeq 2.98$ Å^2 ps^{-1}. A similar discrepancy occurs also near the melting point ($T = 380$ K, $n = 0.024$ Å^{-3}). From $a = 2.145$ Å and $\eta_{exp} \simeq 6.579$ mP, equation (2) predicts $D_H = 0.2957$ Å^2 ps^{-1}, again substantially lower than the actual $D \simeq 0.423$ Å^2 ps^{-1}.
[16] Alley W E and Alder B J 1983 *Phys. Rev.* A **27** 3158
[17] Gaskell T, Balucani U, Gori M and Vallauri R 1987 *Phys. Scr.* **35** 37
   Balucani U, Vallauri R and Gaskell T 1987 *Phys. Rev.* A **35** 4263

[18] Shimojo F, Hoshino K and Watabe M 1994 *J. Phys. Soc. Japan* **63** 141

[19] In a real fluid with continuous potentials, d should of course be replaced by an effective temperature-dependent diameter $\sigma(T)$ which can be estimated in several ways. For instance, in liquid sodium it has been reported to have values of $\sigma \simeq 3.36$ Å at 380 K and $\sigma \simeq 3.11$ Å at 900 K [8]. Accepting in both cases as valid the 'recipe' $A \simeq 0.3\sigma(T)$ and using equation (6), one would obtain $D \simeq 0.426$ Å^2 ps^{-1} at 380 K and $D \simeq 2.939$ Å^2 ps^{-1} at 900 K, quite close to the values actually observed for the diffusion coefficient at these two points.

[20] Nowotny G and Kahl G 1996 *J. Non-Cryst. Solids* at press

[21] Balucani U, Torcini A, Stangl A and Morkel C 1996 *J. Non-Cryst. Solids* at press