

## A quasi-universal scaling law for atomic transport in simple fluids

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 5415

(<http://iopscience.iop.org/0953-8984/11/28/303>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 12:08

Please note that [terms and conditions apply](#).

## A quasi-universal scaling law for atomic transport in simple fluids

Yaakov Rosenfeld

Nuclear Research Centre Negev, PO Box 9001, Beer-Sheva 84190, Israel

Received 23 March 1999

**Abstract.** A semi-empirical ‘universal’ corresponding-states relationship, for the dimensionless transport coefficients of *dense fluids* as functions of the reduced configurational entropy, was proposed more than twenty years ago and established by many simulations. Here it is shown *analytically*, by appealing to Enskog’s original results for the inverse-power potentials, that the quasi-universal entropy scaling can be extended also to *dilute gases*. The analytic form and the possible origin for the entropy scaling for dense fluids are discussed in view of this unexpected result. On the basis of the entropy scaling we predict a *minimum in the shear viscosity* as a function of temperature for all soft inverse-power potentials, in quantitative agreement with the available simulations.

### 1. Introduction: excess-entropy corresponding states for the transport coefficients of dense fluids

Transport coefficients are defined in terms of the response of a system to a perturbation [1–3], e.g. the diffusion coefficient  $D$  relates the particle flux to a concentration gradient, and the shear viscosity  $\eta$  is a measure of the shear stress induced by an applied velocity gradient (see table 1). In computer simulations, transport coefficients can be calculated from: (a) equilibrium time correlation functions, e.g.

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \quad (1)$$

involving the velocity autocorrelations  $\mathbf{v}_i(t)$ , or the corresponding Einstein relations, e.g.

$$2Dt = \frac{1}{3} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad (2)$$

averaging over all particles  $i$  of the system, or (by going back to first principles) from (b) non-equilibrium simulation of the perturbation, with generally good agreement between the methods. Dimensional analysis employing the elementary concepts from kinetic theory,

**Table 1.** The flux-to-gradient relation via transport coefficients (see the text).

Flux type	Flux = –(coefficient)(gradient)	Gradient type
Particles	$j_x = -D dc/dx$	Concentration
Heat	$q_x = -\kappa dT/dx$	Temperature
Momentum	$\Pi_x = -\eta du/dx$	Flow velocity

i.e. the mean free path  $l = 1/(\rho A_\sigma)$ , the mean thermal velocity  $v = (k_B T/m)^{1/2}$ , and the collisional cross section  $A_\sigma = \pi(2R)^2 = \pi\sigma^2$ , leads to simple estimates of the transport coefficients (see table 2). Very sophisticated theory is required for significant quantitative improvements on these simple estimates [1], especially for dense (strongly coupled) fluids, and up to now there is no unifying quantitative description of atomic transport in condensed matter.

**Table 2.** Simple estimates of the transport coefficients obtained by dimensional analysis using the mean free path  $l = 1/(\rho A_\sigma)$ , the mean thermal velocity  $v = (k_B T/m)^{1/2}$ , and the collisional cross section  $A_\sigma = \pi(2R)^2 = \pi\sigma^2$ .  $C$  is the heat capacity.

$D$	$\sim vl$	$\sim v/\rho A_\sigma \sim (k_B T/m)^{1/2}/(\rho\sigma^2)$
$\kappa$	$\sim vC\rho/N_A$	$\sim vC/A_\sigma N_A$
$\eta$	$\sim m\rho vl$	$\sim mv/A_\sigma \sim (mk_B T)^{1/2}/\sigma^2$

In turn, many simulations for the transport coefficients of strongly coupled one-component fluids can be correlated with equilibrium thermodynamic properties, according to the plot of a reduced (dimensionless) coefficient as function of the reduced excess (i.e. configurational, over the ideal-gas value) entropy,  $S^E/(Nk_B)$  [2–5]. *Macroscopic* reduction parameters (density and temperature) were chosen for the transport coefficients, namely a mean interparticle distance,  $d = (V/N)^{1/3} = \rho^{-1/3}$ , and the thermal velocity,  $v_{th} = (k_B T/m)^{1/2}$ . Specifically, from the coefficients of thermal conductivity,  $\kappa$ , viscosity,  $\eta$ , and diffusion,  $D$ , one defines the corresponding reduced (dimensionless) quantities:

$$\begin{aligned}\kappa^* &= \kappa \frac{\rho^{-2/3}}{k_B(k_B T/m)^{1/2}} \\ \eta^* &= \eta \frac{\rho^{-2/3}}{(mk_B T)^{1/2}} \\ D^* &= D \frac{\rho^{1/3}}{(k_B T/m)^{1/2}}.\end{aligned}\tag{3}$$

This form of the reduced transport coefficients is suggested by an elementary kinetic theory for a dense medium of particles with thermal velocities but with a mean free path between collisions which is of the order of the average interparticle distance. The plots of hundreds of simulation results for the reduced transport coefficients, of systems with quite disparate pair interactions, as functions of (minus) the reduced excess entropy,  $s = -S^E/(Nk_B) > 0$ , show quasi-universal behaviour, of the type [2–5]

$$\begin{aligned}\kappa^* &\approx 1.5e^{0.5s} \\ \eta^* &\approx 0.2e^{0.8s} \\ D^* &\approx 0.6e^{-0.8s}\end{aligned}\tag{4}$$

for all strongly coupled simple fluids,  $s \gtrsim 1$  (freezing corresponds to about  $4 \lesssim s \lesssim 5$ ). Different potentials can be fitted better by somewhat different exponential arguments (e.g. for hard spheres,  $D^* \propto \sim e^{-0.65s}$ ) but, nevertheless, using these plots the diffusion coefficients, which vary by about two orders of magnitude, can be estimated within about 30% by using *corresponding-states* values based on the excess entropy [2–5]. More recently, the excess-entropy corresponding-states consideration was extended to moderately and strongly coupled plasma *mixtures* [6]. Because of the choice of *macroscopic* reduction parameters for the transport coefficient rather than microscopic potential parameters, the excess-entropy corresponding-states relation [4] can be applied directly to real materials. From this point of

view it can be an even more effective recipe than Enskog's approximation [7] that relates the transport coefficients to the thermal pressure.

The excess-entropy corresponding-states consideration for transport coefficients was originally motivated [4] by the success of the variational hard-sphere (HS) thermodynamic perturbation theory [8] for simple fluids in which the hard-sphere radius, or equivalently the excess entropy, was used to parametrize the structure of equilibrium fluids. This underlying connection to the hard-sphere results is also reflected by the fact that the diffusion and viscosity coefficients for all dense fluids approximately obey the Stokes–Einstein relation as originally found for hard spheres of diameter  $\sigma$  [1, 9]:

$$D\eta\frac{\sigma}{k_B T} = D^*\eta^*(\rho\sigma^3)^{1/3} \simeq \frac{2}{q\pi} \quad (5)$$

where  $q \simeq 5$ . This holds provided that the ratio of the effective hard-sphere diameter of the particles to the Wigner–Seitz radius,  $a = (3/(4\pi\rho))^{1/3}$ , is independent of temperature, and given approximately by

$$\frac{\sigma}{a} = \frac{2}{5\pi} \left(\frac{4\pi}{3}\right)^{1/3} \frac{1}{0.12} \approx 1.7 \quad (6)$$

which is usually obeyed quite well. The magnitude of the deviations from the universal relations (equations (4)) is of the order of the variations of  $q$  between slip ( $q = 4$ ) and stick ( $q = 6$ ) boundary conditions. Quasi-harmonic cell-model approaches also suggest the macroscopic reduction parameters, and are even able to predict [2, 3, 5] universal exponential dependences of the transport coefficients on the excess entropy, like those found empirically (equations (4)), but they do not yield the correct parameters. Specifically, as shown by Hoover and co-workers [2, 3, 5] following Harrocks and McLaughlin, for the heat conductivity, and Andrade for the viscosity, the reduced transport coefficients can be crudely related to the Einstein frequency,  $\omega_E$ . The result is

$$\kappa^* \propto \eta^* \propto \left(\frac{m\omega_E^2 d^2}{k_B T}\right)^{1/2} \quad (7)$$

where, in the Einstein approximation,

$$\left(\frac{m\omega_E^2 d^2}{k_B T}\right)^{1/2} \propto \exp\left(-\frac{S^E}{3Nk_B}\right) = e^{s/3}. \quad (8)$$

However, this reasoning leads to an incorrect result:  $D^* \propto (m\omega_E^2 d^2 / (k_B T))^{1/2}$ , and it cannot be applied to the completely anharmonic hard spheres.

The simplified models can provide only some intuitive feeling for the scaling as established empirically by the simulations, and better understanding of the entropy scaling is needed. The excess-entropy scaling relation is a semiquantitative model (like the van der Waals equation of state), rather than a theory. Like any corresponding-states relationship that links non-scaling force laws, it can only be approximate. However, in view of the absence of a unifying quantitative description of atomic transport in condensed matter, the excess-entropy scaling is important for estimating unknown transport coefficients and for providing guidelines for theoretical analysis. Such a point of view was also taken by a recent article in *Nature* [10] where a variant of the entropy scaling was considered, which was tailored specifically for the diffusion coefficient.

The present work addresses several questions regarding the entropy scaling. It is first shown (section 2) that the quasi-universal excess-entropy scaling can be extended also to a regime where it is least expected, namely for describing Enskog's famous results [7] for dilute gases. This demonstrates that the excess-entropy corresponding states can result from a

combination of various mathematical and physical causes, and cannot be explained completely in terms of either a hard-sphere-type modelling or cell-theory arguments. The empirical validity of an excess-entropy scaling then (section 3) enables one to draw certain general conclusions as well as to obtain specific results about transport coefficients, in particular concerning the *minimum in the shear viscosity* as a function of temperature for inverse-power potentials. The result as obtained analytically for dilute gases is a power-law dependence of the reduced transport coefficients as a function of the excess entropy. This raises the question of the analytic form for dense fluids: is it exponential, and if so can we predict the exponent? By considering in detail the hard-sphere results it is shown (section 4) that the analytic form is probably not exponential, yet an exponential form can provide a good numerical representation of the function. Finally (section 5), by appealing to the fundamental Green–Kubo formalism [1], a conjecture is offered as regards how the excess-entropy corresponding-states relationship for the reduced transport coefficients for strongly coupled fluids can be related to a well known scaling relation for the equilibrium structure.

## 2. Excess-entropy scaling for the transport coefficients of dilute gases

It turns out that the excess-entropy scaling is valid also where it is least expected, namely for dilute gases. This can be demonstrated by using Enskog’s famous results [7] for the class of inverse-power potentials of the form  $\phi(r) = \epsilon(\sigma/r)^\mu$ . This class includes the hard-sphere ( $\mu = \infty$ ) and Coulomb (the one-component plasma,  $\mu = 1$ ) potentials as two extreme cases. These systems provide starting points for thermodynamic perturbation theories, where their homogeneity facilitates the theoretical treatment [11]. The excess thermodynamic properties of these systems thus depend only on a reduced temperature–density variable,  $y = (\rho\sigma^3)(k_B T/\epsilon)^{-3/\mu}$ , and in particular the reduced excess entropy is given by

$$S^E/(Nk_B) \equiv -s = -s_\mu(y).$$

For dilute gases of particles interacting via the inverse-power potentials  $\mu > 3$ , Enskog obtained the following results [7]:

$$\eta = \left( \frac{(mk_B T)^{1/2}}{\sigma^2} \right) \left[ \frac{5}{8} \left( \frac{1}{\pi} \right)^{1/2} \left( \frac{2k_B T}{\mu\epsilon} \right)^{2/\mu} / \left\{ A_2(\mu) \Gamma \left( 4 - \frac{2}{\mu} \right) \right\} \right] \quad (9)$$

$$D = \left( \frac{(k_B T/m)^{1/2}}{\rho\sigma^2} \right) \left[ \frac{3}{8} \left( \frac{1}{\pi} \right)^{1/2} \left( \frac{2k_B T}{\mu\epsilon} \right)^{2/\mu} / \left\{ A_1(\mu) \Gamma \left( 3 - \frac{2}{\mu} \right) \right\} \right] \quad (10)$$

$$\kappa = \frac{5}{2} \eta \frac{3k_B T}{2} \quad (11)$$

where  $\Gamma(x)$  is the standard Gamma function, and  $A_1(\mu)$  and  $A_2(\mu)$  are slowly varying functions of  $\mu$ , of the order of 0.5 (see table 3). These results look like those for hard spheres but with a temperature-dependent effective hard-sphere diameter:  $\sigma_{eff}/\sigma \sim (\epsilon/(k_B T))^{1/\mu}$ . Enskog’s expressions exhibit strong  $\mu$ -dependence, and no universal behaviour has been anticipated. Yet, we shall see now that in fact these are quasi-universal provided that the *macroscopic* reduction parameters and the reduced excess entropy are involved. Indeed, for dilute inverse-power gases, in the second virial approximation, the excess entropy is linear in  $y$ , and is given by [12]

$$s = s_\mu(y) = \frac{2\pi y}{3} \left( \frac{\mu-3}{\mu} \right) \Gamma \left( \frac{\mu-3}{\mu} \right). \quad (12)$$

Combining this relation with the Enskog results for  $\mu > 3$ , we obtain a universal form for the reduced coefficients:

$$\begin{aligned}\kappa^* &= \frac{4}{15}\eta_0 s^{-2/3} \\ \eta^* &= \eta_0 s^{-2/3} \\ D^* &= D_0 s^{-2/3}\end{aligned}\quad (13)$$

for all  $\mu > 3$ . The prefactors  $\eta_0 \simeq 0.27$ ,  $D_0 \simeq 0.37$  are nearly universal for all  $\mu \gtrsim 4$  (almost monotonic variation of less than 10% and of less than 15% between  $\mu = 4$  and  $\mu = \infty$ , for  $\eta_0$  and for  $D_0$ , respectively; see table 3). For the one-component plasma ( $\mu = 1$ ) Enskog's general formulae still hold provided that we introduce Spitzer's correction [13]

$$A_1(\mu = 1) = \ln \lambda \equiv \ln \left[ 1 + \left( \frac{2}{3s} \right)^2 \right] \quad (14)$$

where  $s = (3\Gamma)^{1/2}\Gamma/6$  and here  $\Gamma = (Ze)^2/(ak_B T)$  is the standard plasma coupling parameter. Thus, the Enskog–Spitzer result for  $\mu = 1$  can be written as

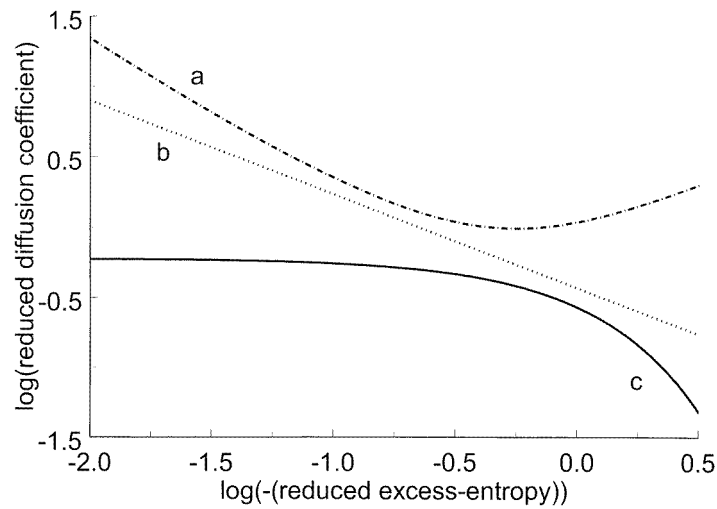
$$\begin{aligned}D^* &\simeq 0.4s^{-4/3} / \ln \left[ 1 + \left( \frac{2}{3s} \right)^2 \right] \\ \eta^* &\simeq 0.35s^{-4/3} / \left\{ \ln \left[ 1 + \left( \frac{2}{3s} \right)^2 \right] - \frac{4}{4 + (3s)^2} \right\}.\end{aligned}\quad (15)$$

**Table 3.** Parameters for transport coefficients of dilute gases of particles interacting via the inverse-power potentials,  $r^{-\mu}$  (see the text).

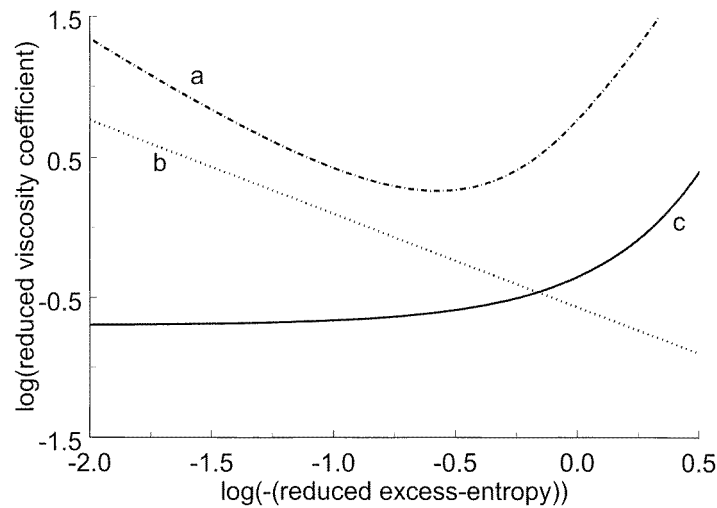
Power $\mu$	$A_1$	$A_2$	$D_0$	$\eta_0$
4	0.436	0.422	0.409	0.264
6	0.357	0.385	0.382	0.258
8	0.332	0.382	0.371	0.258
10	0.319	0.383	0.367	0.262
$\infty$	0.333	0.500	0.346	0.288

The quasi-universal behaviour for dense fluids (equations (4)), which holds also for the Coulomb case, is replaced for dilute inverse-power fluids by two different behaviours for the ‘neutral’ ( $\mu \gtrsim 4$ ) and ‘charged’ ( $\mu = 1$ ) particles (see figures 1 and 2). Note in figures 1 and 2 that for  $\mu \gtrsim 4$  the dilute-gas and the dense-gas expressions for  $D^*(s)$  almost merge at  $s \simeq 1$ . In addition, for  $\mu = 1$  the weak-coupling equation expression  $D^*(s)$  gives a minimum for  $s \simeq 0.3$ . It is worth noting that the region around  $s \simeq 1$  is indeed the transition region between weak- and strong-coupling behaviours for fluids from the point of view of the equation of state also.

The origin of the excess-entropy quasi-universal scaling, as derived for the reduced transport coefficients of dilute inverse-power fluids, is mathematically very similar to the excess-entropy scaling for their second virial coefficients [12], by which the *variational* thermodynamic perturbation theory (physically expected to ‘work’ for dense fluids) is unexpectedly found to be almost as accurate also for dilute gases. It may be the case that these excess-entropy scalings for the static and dynamic properties are generally related (see section 5).



**Figure 1.** A log-log plot of the reduced diffusion coefficient  $D^*$  for the inverse-power potentials,  $\phi(r) = \epsilon(\sigma/r)^\mu$ , as a function of (minus) the reduced excess entropy,  $s$ :  $\log_{10}(D^*)$  versus  $\log_{10}(s)$ . The curves labelled a, b, and c correspond to the expressions given, respectively, by: (curve a) equation (15) for the dilute Coulomb one-component plasma ( $\mu = 1$ ), (curve b) equation (13) for the dilute inverse systems with  $\mu \gtrsim 4$ , and (curve c) equation (4) for general dense simple fluids. Curves a and b are valid for dilute gases,  $\log_{10}(s) \lesssim -1$ , and curve c is valid for dense fluids,  $\log_{10}(s) \gtrsim 0$ , while the full picture is obtained by a smooth crossover interpolation between these limiting behaviours. See the text.



**Figure 2.** As figure 1, but for the reduced viscosity,  $\eta^*$ .

### 3. Some consequences of the excess-entropy scaling

The assumption (which is exact for the inverse-power potentials) that the reduced coefficients depend on the density and on the temperature only via their dependence on  $s$ , e.g.  $D^*(\rho, T) =$

$D^*(s(\rho, T))$ , can be used to infer some general trends. Recall that  $s$  is minus the excess entropy, and thus we can expect that for simple fluids

$$\begin{aligned} \left(\frac{\partial s}{\partial T}\right)_\rho &< 0 \\ \left(\frac{\partial s}{\partial \rho}\right)_T &> 0. \end{aligned} \quad (16)$$

For the extreme case of hard spheres, we have  $\partial s/\partial T = 0$ . If we further assume (see figure 1) that  $\partial D^*(s)/\partial s < 0$ , then

$$\begin{aligned} \left(\frac{\partial D}{\partial T}\right)_\rho &> 0 \\ \left(\frac{\partial D}{\partial \rho}\right)_T &< 0. \end{aligned} \quad (17)$$

Considering (figure 2) the qualitative behaviour of  $\eta^*(s)$  and the density independence of  $\eta$  for the ideal gas, we expect that

$$\left(\frac{\partial \eta}{\partial \rho}\right)_T > 0. \quad (18)$$

The temperature dependence is, however, more interesting:

$$\left(\frac{\partial \eta}{\partial T}\right)_\rho \sim \frac{1}{2}T^{-1/2}\eta^* + T^{1/2}\left(\frac{\partial \eta^*}{\partial s}\right)\left(\frac{\partial s}{\partial T}\right)_\rho. \quad (19)$$

Thus, contrary to the expected monotonic behaviour as a function of the density, it is possible for  $\eta$  as a function of  $T$  to have a minimum when  $\partial \eta^*/\partial s > 0$ . Thus, except for the hard-sphere system for which we have  $(\partial \eta/\partial T)_\rho > 0$ , we expect that

$$\left(\frac{\partial \eta}{\partial T}\right)_\rho \begin{matrix} \geq \\ \leq \end{matrix} 0 \quad (20)$$

provided that correspondingly

$$T\left(\frac{\partial s}{\partial T}\right)_\rho \left(\frac{\partial \ln \eta^*}{\partial s}\right) \begin{matrix} \geq \\ \leq \end{matrix} -\frac{1}{2}. \quad (21)$$

Using the quasi-universal relation (equations (4)) in the region where  $\partial \eta^*/\partial s > 0$ , and simulation results for the equation of state for inverse-power potentials [11, 12], we estimate the *minimum* shear viscosity, from

$$T\left(\frac{\partial s}{\partial T}\right)_\rho \left(\frac{\partial \ln \eta^*}{\partial s}\right) = -\frac{1}{2}.$$

This predicted minimum as a function of the temperature can be understood as follows: for high temperature (weak coupling), the shear viscosity is determined by the kinetics of pair collisions and it decreases as the temperature goes down. For low temperatures (strong coupling), near freezing, the viscosity is determined mainly by interaction effects, and goes down as the temperature increases. The minimum is predicted to occur in the intermediate-coupling region, connecting these two types of behaviour.

The repulsive inverse-power potentials can be written also as

$$\frac{\varphi(r)}{k_B T} = \frac{\Gamma}{(r/a_{WS})^\mu}$$



where  $a_{WS} = (3/(4\pi\bar{\rho}))^{1/3}$  is the Wigner–Seitz radius, and  $\Gamma = ((4\pi/3)y)^{\mu/3}$  is the coupling parameter. For strongly coupled inverse-power fluids it was recently shown [14] that the potential energy can be written as an asymptotic  $\Gamma \rightarrow \infty$  expansion of the form

$$\frac{U}{Nk_B T} = C_{\text{fluid}}\Gamma + \left(\frac{\Gamma}{\Gamma_0}\right)^{2/5} + \dots \quad (22)$$

where the *fluid Madelung constant*,  $C_{\text{fluid}}$ , for  $n > 3$  is given by the following integral:

$$C_{\text{fluid}} = \frac{1}{2^n(n-2)!} \int_0^\infty \frac{(x+2)x^{(n-1)}}{(x+2) + (x-2)e^x} dx.$$

The simulation results for the *thermal energy*  $u_{th} = U/(Nk_B T) - C_{\text{fluid}}\Gamma$  in the strong-coupling region  $\Gamma \gtrsim 1$ , can be fitted excellently by the form  $(\Gamma/\Gamma_0)^{2/5} + c$ . We get  $\Gamma_0 = 10.227, 3.1271, 5.3058, 13.921, 53.714$  for  $n = 1, 4, 6, 9, 12$ , respectively, and  $c \sim 0$ . The equation of state corresponding to  $u_{th} = (\Gamma/\Gamma_0)^\delta$  leads to

$$T \left( \frac{\partial s}{\partial T} \right)_\rho = \left( \frac{1-\delta}{\delta} \right) T \left( \frac{\partial u_{th}}{\partial T} \right)_\rho = (1-\delta)u_{th}.$$

For a behaviour of the type (equation (4))  $\eta^*(s) \propto e^{\alpha s}$  with  $\alpha \simeq \frac{1}{5}$ , and with the exponent  $\delta = \frac{2}{5}$ , the minimum is predicted to occur when the ‘thermal’ potential energy is about equal to  $k_B T$ :

$$u_{th} = \left( \frac{\Gamma}{\Gamma_0} \right)^\delta = \frac{1}{2\alpha(1-\delta)} \simeq 1 \quad (23)$$

i.e.

$$\Gamma_{\min} \sim \Gamma_0 \quad (24)$$

namely in the region where  $1 \lesssim s \lesssim 2$ .

More specifically,  $\Gamma_{\min} \sim 10$  (i.e.  $s \sim 1$ ) for the one-component plasma ( $\mu = 1$ ), and  $\Gamma_{\min} \sim 55$  (namely  $y_{\min} \sim 0.64$ , i.e.  $s \sim 2$ ) for the soft spheres ( $\mu = 12$ ). The result for the one-component plasma is in good agreement with generalized hydrodynamics calculations of Vieillefosse and Hansen (see figure 1 in [15]). If we use the best fit of Ashurst and Hoover to their data (see figure 4 in [16]), which extrapolates to Enskog’s weak-coupling limit, namely

$$\eta \propto (0.171 + 0.022(e^{6.83y/\sqrt{2}} - 1))y^{-8/3}$$

we find a minimum at  $y \simeq 0.69$  (i.e., in terms of the variable used in [16],  $x = y/\sqrt{2} \simeq 0.49$ ). This result is close to our prediction. It would be interesting to check our prediction further for a minimum shear viscosity as a function of temperature for inverse-power potentials.

#### 4. Concerning the exponential scaled form for dense fluids

As mentioned above, quasi-harmonic cell-model approaches [2, 3, 5] suggest exponential scaled forms for the transport coefficients upon using macroscopic reduction parameters, e.g.  $\eta^* \propto e^{s/3}$ . A recent variant of the entropy scaling, tailored specifically for the diffusion coefficient [10] of dense matter, introduces *microscopic* reduction parameters, and obtains another universal scaling relation:

$$D^+ \approx 0.05e^{-s} \quad (25)$$

for a reduced diffusion coefficient,  $D^+$  (see below). Using the hard-sphere system as a detailed example, it will be now explained how this new result just reflects the previous results, namely  $D^* \approx 0.6e^{-0.8s}$ , and that the exponential forms only provide a good numerical representation

to results which are fundamentally of a rational form which stems from series in powers of the density.

Enskog's theory for hard spheres [7], which is based on binary collisions, is remarkably accurate when compared with the simulations [9]. For the self-diffusion coefficient in a one-component system of hard spheres of diameter  $\sigma$  and number density  $\rho$ , he obtained

$$D_E = \frac{D_{\text{gas}}}{g(\sigma)} \quad (26)$$

where  $g(\sigma) = Z_c/(4\xi)$  is the value of the radial distribution function  $g(r)$  at  $r = \sigma$ ,

$$\xi = \frac{4\pi}{3} \left(\frac{\sigma}{2}\right)^3 \rho$$

is the packing fraction,  $D_{\text{gas}}$  is the result for a dilute gas given by equation (10):

$$D_{\text{gas}} = \frac{3}{8\rho\sigma^2} \left(\frac{k_B T}{m\pi}\right)^{1/2} \quad (27)$$

and  $Z_c$  represents the equation of state ( $P$  is the pressure),  $Z_c = P/(\rho k_B T) - 1$ . The simulation results for the hard-sphere fluid ( $\xi \lesssim 0.5$ ) equation of state can be well represented by [8]

$$\frac{P}{\rho k_B T} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \quad (28)$$

from which it follows that

$$s = \frac{4\xi - 3\xi^2}{(1 - \xi)^2}. \quad (29)$$

These expressions were obtained as small corrections to the analytic expressions from the scaled-particle and Percus–Yevick theories [17], and similar rational expressions can be obtained as Padé approximants for the virial expansion. Enskog's result can thus be written as

$$\frac{D_E}{D_{\text{gas}}} = \frac{1}{g(\sigma)} = \frac{(1 - \xi)^3}{1 - \xi/2} \quad (30)$$

while a fit to the relatively small corrections to Enskog, as obtained from the most recent simulations for the hard-sphere fluid [9], is given by

$$\frac{D_{HS}}{D_E} = 1.01896(1 + 0.073\xi + 11.6095\xi^2 - 26.951\xi^3). \quad (31)$$

Finally, the reduced coefficient is obtained from

$$D_{\text{gas}}^* = D_{\text{gas}} \frac{\rho^{1/3}}{(k_B T/m)^{1/2}} = \frac{3(\pi/6)^{2/3}}{8\pi^{1/2}} \xi^{-2/3} \simeq 0.137\xi^{-2/3}. \quad (32)$$

The new reduced diffusion coefficient [10]  $D^+$  is related to our  $D^*$  by the following relation:

$$\frac{D^+}{D^*} = \frac{2}{\sqrt{\pi}} \left(\frac{\pi}{6}\right)^{4/3} \left/ \left[ \left(\frac{\sigma}{a}\right)^4 g(\sigma) \right] \right. \quad (33)$$

i.e. it uses [10]  $\sigma$  as the unit of length and

$$\tau_E = (4\sigma^2 g(\sigma) \rho \sqrt{\pi k_B T/m})^{-1}$$

as the unit of time, instead of the corresponding macroscopic values,  $\rho^{-1/3}$  and  $\rho^{-1/3}/(k_B T/m)^{1/2}$ , respectively. For general potentials,  $\sigma$  is interpreted [10] as the position

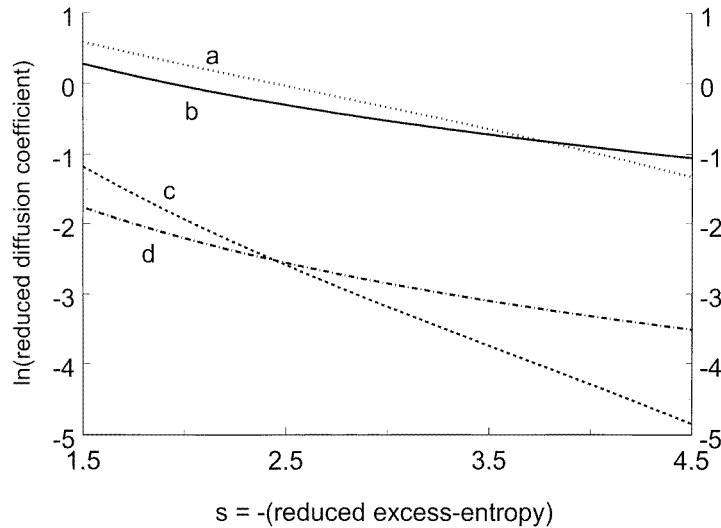
of the first maximum of the radial distribution function  $g(r)$ , and it is thus clear that  $D^+$  is not meant to provide proper scaling for dilute gases. For hard spheres of diameter  $\sigma$ ,

$$\left(\frac{D^+}{D^*}\right)_{HS} \simeq \frac{\xi^{-4/3}}{16.8g(\sigma)}. \quad (34)$$

The reduced coefficients  $D_E^* = (D_E/D_{\text{gas}})D_{\text{gas}}^*$  and  $D_{HS}^* = (D_{HS}/D_E)D_E^*$  along with  $D^+$  and the ratio  $(D^+/D^*)_{HS}$  are presented in figure 3. All of these dimensionless quantities are obtained from the manifestly rational expressions above, yet we see from figure 3 that they can all be approximated by an exponential. Specifically,  $D_E^* \propto e^{-0.42s}$ ,  $D_{HS}^* \propto e^{-0.65s}$ ,  $(D^+/D^*)_{HS} \propto e^{-0.5s}$ , so  $D^+ \propto e^{-1.1s}$ . For soft interactions, like the Coulomb one-component plasma, because  $\sigma/a$  and  $g(\sigma)$  vary more slowly as a function of the excess entropy, the ratio (not shown in figure 3)

$$\frac{D^+}{D^*} \propto \frac{1}{(\sigma/a)^4 g(\sigma)} \propto e^{-0.2s}$$

features a smaller argument of the exponent, so  $D^+ \propto e^{-s}$ . Note that the value of the exponent also depends on the accuracy of the approximation for the excess entropy, and differences of 10% in the argument (like between  $e^{-s}$  and  $e^{-1.1s}$ ) can be expected between results based on simulation results for the two-particle approximation (as employed in [10]) and those based on simulation results for the equation of state. It can be expected that other choices of reduction parameters involving the dimensionless quantities  $g(\sigma)$  and  $\sigma/a$  can also provide quasi-universal excess-entropy scalings involving other arguments of the exponent. Likewise, replacing  $\tau_E$  by  $\rho^{-1/3}/(k_B T/m)^{1/2}$  in the scaling of the Kolmogorov–Sinai entropy,  $h_{KS}$ , will only change the functional form of the apparently quasi-universal dependence [18] of  $h_{KS}$  on the excess entropy.



**Figure 3.** A semi-log plot of reduced diffusion coefficients for the hard-sphere system as a function of (minus) the reduced excess entropy,  $s$ , using equations (26)–(34). The curves labelled a, b, c, and d correspond, respectively, to: (curve a)  $\ln(D_{HS}^*)$ , (curve b)  $\ln(D_E^*)$ , (curve c)  $\ln((D^+/D^*)_{HS})$ , and (curve d)  $\ln(D^+)$ . See the text.

### 5. The conjectured relation between the ‘static’ and ‘dynamic’ excess-entropy scalings

In view of the analytic derivation of the entropy scaling for dilute gases, it is of interest to try to explore whether there is a formal way to derive the entropy scaling for dense fluids. One such possibility is perhaps through the Green–Kubo formalism [1, 19, 20] where the transport coefficients are given in terms of the time integral of an autocorrelation function for the appropriate current, e.g. the velocity autocorrelation for the coefficient of self-diffusion. In turn, these functions can be expanded for short times as a Taylor series in powers of the time with coefficients that are given in terms of space integrals involving the equilibrium correlation functions of the system, and the pair interactions and their derivatives. The success of the variational perturbation theory with hard-sphere or other inverse-power potentials as reference can be formally shown to be equivalent to the following statement [12]: from the standpoint of integrals of the pair correlation functions, of the type which appear in expressions for the energy or virial pressure, the pair correlation functions  $g_\phi(r; \rho, T)$  of any dense fluid of particles, with pair interaction  $\phi(r)$ , can be well approximated by a single universal set,  $g(r/a, s)$ , with the reduced excess entropy  $s$  as the single scaling parameter. This scaling holds exactly for any single inverse-power potential. The approximation of universality means using the exact set of any inverse-power potential as the approximate for any other dense fluid. Similar entropy scaling of integrals of higher-order correlation functions can also be expected to be valid. To the extent that this kind of information is dominant in determining the Green–Kubo integral, we can formally expect the entropy scaling for the transport coefficient. It cannot be ruled out that this is the underlying mathematical reason for the emergence of that scaling, but the complexity of the expressions involved and the slow convergence of the time series essentially prohibit a direct test of this conjecture. The flavour of such an approach can be demonstrated, however, by a specific example where the convergence of the time series is ‘enhanced’ using a model memory function [1, 20] as given below for the diffusion coefficient of the one-component plasma [21].

For the one-component plasma, choosing the inverse of the plasma frequency  $\omega_p^{-1}$  as the unit of time, the dimensionless self-diffusion coefficient can be written as

$$D^* \propto \frac{D}{\omega_p a^2} = \frac{1}{3\Gamma} \int_0^\infty \psi(t) dt \quad (35)$$

where

$$\psi(t) = \frac{\langle v_i(t') v_i(t'+t) \rangle}{\langle v_i(t') v_i(t') \rangle} \quad (36)$$

is the normalized velocity autocorrelation function,  $\Gamma$  is the standard coupling parameter, and the averaging is carried out over all particles  $i$  of the system and over the ‘zero’ of time,  $t'$ . The short-time expansion is [21]

$$\psi(t) = 1 - \frac{t^2}{2!3} + \frac{(12J+1)t^4}{4!9} - \dots \quad (37)$$

where

$$J(\Gamma) = \int_0^\infty r^{-4} g(r) dr$$

is a moment of the pair correlation function, and  $r$  is in units of  $a$ . It is customary to analyse the autocorrelation function by expressing its decay rate via a ‘memory function’  $M(t)$ :

$$\frac{d\psi(t)}{dt} = - \int_0^t M(t') \psi(t-t') dt' \quad (38)$$

Assuming a Gaussian form for  $M(t)$ , the short-time expansion can be adjusted by [21]

$$M(t) = \frac{1}{3}e^{-2Jt^2}.$$

In terms of  $M(t)$  we can write

$$D^* \propto \frac{1}{3\Gamma} \left( \int_0^\infty M(t) dt \right)^{-1} \quad (39)$$

and, using the Gaussian form above,

$$D^* \propto \frac{D}{\omega_p a^2} \simeq \frac{J^{1/2}}{0.63\Gamma}. \quad (40)$$

For  $\Gamma \gtrsim 10$ , i.e.  $s \gtrsim 1$ , this expression agrees reasonably well with the simulations [21] (deviations of less than 50% over a two-orders-of-magnitude change of  $D/(\omega_p a^2)$ ). On the other hand, moments of the type of  $J$  are approximately universal if expressed in terms of  $g(r/a, s)$ . Specifically, if we evaluate  $J$  using the hard-sphere functions  $g(r/a, s)$ , we do not introduce large errors. Thus, if the dominant contribution to the Green–Kubo integrals can be expressed via integrals of the correlation functions that can be excess-entropy scaled, the net result can be the quasi-universality as featured by equations (4).

## 6. Conclusions

A semi-empirical ‘universal’ corresponding-states relationship, for the dimensionless transport coefficients of *dense fluids* as functions of the reduced configurational entropy,  $D^*(s)$ ,  $\eta^*(s)$ ,  $\kappa^*(s)$ , was proposed more than twenty years ago [4] and established by many simulations [2,3,5]. Because of the choice of *macroscopic* reduction parameters for the transport coefficient rather than microscopic potential parameters, this relation between transport coefficients and the equation of state can be applied directly to real materials, and gains special importance in view of the absence of a unifying quantitative description of atomic transport in condensed matter. Simplified models can provide only some sort of *a posteriori* ‘justification’ for the intrinsically approximate excess-entropy scaling relation. The idea of excess-entropy scaling was rediscovered in a recent article in *Nature* [10], yet in a very restricted form. This demonstrates that the excess-entropy scaling should be better known and better understood. The present work, which is a step in that direction, extends the original excess-entropy scaling [4] also to *dilute gases*, and discusses its analytic form and origin for dense fluids in view of this unexpected result.

It was first shown analytically that the quasi-universal excess-entropy scaling can be extended also to a regime where it is least expected, namely for describing Enskog’s famous results [7] for dilute gases interacting through inverse-power potentials. Mathematically this is very similar to the excess-entropy scaling for their second virial coefficients [12], and raises the possibility that the known excess-entropy scalings for the static and dynamic properties are generally related. The empirical validity of an excess-entropy scaling, as emerges from the combination of the scalings for dense and dilute fluids, enables one to make general predictions about transport coefficients, in particular a minimum shear viscosity as a function of temperature for inverse-power potentials, in agreement with available simulations. The analytic derivation for dilute gases raises the question of the exponential form chosen to fit the data for dense fluids. By considering in detail the hard-sphere results, it was shown that the analytic form is probably not exponential, yet an exponential form can provide a good numerical representation of the function. Finally, by appealing to the fundamental Green–Kubo formalism [1], a conjecture was offered as regards how the excess-entropy corresponding-states

relationship for the reduced transport coefficients for strongly coupled fluids can be related to a well known scaling relation for the equilibrium structure.

## References

- [1] Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)
- [2] Hoover W G 1986 *Molecular Dynamics (Springer Lecture Notes in Physics vol 258)* (Berlin: Springer)
- [3] Hoover W G 1991 *Computational Statistical Mechanics* (New York: Elsevier)
- [4] Rosenfeld Y 1977 *Phys. Rev. A* **15** 2545  
Rosenfeld Y 1977 *Chem. Phys. Lett.* **48** 467
- [5] Grover R, Hoover W G and Moran B 1985 *J. Chem. Phys.* **83** 1255
- [6] Rosenfeld Y, Nardi E and Zinamon Z 1995 *Phys. Rev. Lett.* **75** 2490
- [7] Chapman S and Cowling T G 1970 *The Mathematical Theory of Non-Uniform Gases* (Cambridge: Cambridge University Press)
- [8] Mansoori G A and Canfield F B 1969 *J. Chem. Phys.* **51** 4958  
Rasaiah J and Stell G 1970 *Mol. Phys.* **18** 249  
Barker J A and Henderson D 1972 *Annu. Rev. Phys. Chem.* **23** 439  
Hansen J-P and McDonald I R 1986 *Physics of Simple Liquids* 2nd edn (New York: Academic)
- [9] Alder B J, Gass D M and Wainwright T E 1970 *J. Chem. Phys.* **53** 3813  
Kincaid J M and Erpenbeck J J 1986 *J. Chem. Phys.* **84** 3418  
Speedy R J 1987 *Mol. Phys.* **62** 509  
Erpenbeck J J and Wood W W 1991 *Phys. Rev. A* **43** 4254
- [10] Dzugutov M 1996 *Nature* **381** 137
- [11] Hoover W G, Gray S G and Johnson K W 1971 *J. Chem. Phys.* **55** 1128
- [12] Rosenfeld Y 1982 *Phys. Rev. A* **26** 3633  
Rosenfeld Y 1983 *Phys. Rev. A* **28** 3063
- [13] Spitzer L Jr 1956 *Physics of Fully Ionized Gases* (New York: Interscience)
- [14] Rosenfeld Y and Tarazona P 1998 *Mol. Phys.* **95** 141
- [15] Vieillefosse P and Hansen J-P 1975 *Phys. Rev. A* **12** 1106
- [16] Ashurst W T and Hoover W G 1975 *Phys. Rev.* **11** 658
- [17] Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1  
Reiss H, Frisch H and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369  
Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
- [18] Dzugutov M, Aurell E and Vulpiani A 1998 *Phys. Rev. Lett.* **81** 1762  
and see also an early work by  
Stoddard S D and Ford J 1973 *Phys. Rev. A* **8** 1504
- [19] Green M S 1954 *J. Chem. Phys.* **22** 398  
Kubo R 1957 *J. Phys. Soc. Japan* **12** 570
- [20] Tankeshwar K, Pathak K N and Ranganathan S 1990 *J. Phys.: Condens. Matter* **2** 5891 and references therein
- [21] Hansen J-P, McDonald I R and Pollock E L 1975 *Phys. Rev. A* **11** 1025