Excess-entropy and freezing-temperature scalings for transport coefficients: Self-diffusion in Yukawa systems

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A semiempirical ''universal'' corresponding states relationship, for the dimensionless transport coefficients of dense fluids as functions of the reduced configurational entropy, was proposed more than 20 years ago and established by many simulations. Recent density functional analysis predicts a universal freezing-temperature scaling for the excess entropy. Combining these properties we derive an approximate corresponding states relationship for the dimensionless transport coefficients of dense fluids as functions of the temperature scaled by the freezing temperature. The temperature scaling observed in recent computer simulation results for self-diffusion in Yukawa systems is just one more case of our general result.

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Up to now there has been no unifying quantitative description of atomic transport in condensed matter [1–3]. However, 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 a function of the reduced excess (i.e., configurational, over ideal-gas value) entropy, S^E/Nk_B, [4,5,2,3]. 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 thermal velocity $v_{th}=(k_BT/m)^{1/2}$. Specifically, from the coefficients of thermal conductivity, κ, viscosity, η, and diffusion, D, one defines the following reduced (dimensionless) quantities:

$$\kappa^*=\kappa\frac{\rho^{-2/3}}{k_B(k_BT/m)^{1/2}},\qquad \eta^*=\eta\frac{\rho^{-2/3}}{(mk_BT)^{1/2}},$$
$$D^*=D\frac{\rho^{1/3}}{(k_BT/m)^{1/2}}. \tag{1}$$

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 quasiuniversal behavior of the type [4,5,2,3]

$$\kappa^*\approx 1.5e^{0.5s},\qquad \eta^*\approx 0.2e^{0.8s},\qquad D^*\approx 0.6e^{-0.8s} \tag{2}$$

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 and prefactors (e.g., for hard spheres $D^*\simeq 0.7e^{-0.65s}$) but, nevertheless, using these plots the reduced 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 [4,5,2,3]. The excess-entropy corresponding states were extended to moderately and strongly coupled plasma *mixtures* [6]. More recently it was found [8] that the excess-entropy scaling is valid also for dilute gases, where it is least expected on the basis of either hard-sphere modeling or cell-theory arguments.

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 even a more effective recipe than Enskog's approximation [7], which relates the transport coefficients to the thermal pressure. 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 nonscaling force laws, it can be only approximate. However, in view of the absence of a unifying quantitative description of atomic transport in condensed matter, excess-entropy scaling is important for estimating unknown transport coefficients and for providing guidelines for theoretical analysis, and should be further checked against any new available data.

An extensive set of simulation results for the self-diffusion of Yukawa systems was obtained very recently [9] which should enable us to test further the excess-entropy scaling mentioned above. These simulations where analyzed, however, for another scaled diffusion coefficient D^+, which was shown [9] to obey a linear behavior as a function of the temperature reduced by the melting temperature. Using recent density functional theory results [10–12] we first recast the excess-entropy scaling for D^* in the form of freezing (or melting) temperature scaling. We then use this result to derive the new linear scaling relation for D^+, thus demonstrating that it represents just one more case of general excess-entropy scaling.

On the basis of the fundamental-measure free energy functional [10,11] for hard spheres and thermodynamic perturbation theory [13,14], a *unified analytic description* of classical bulk solids and fluids was obtained [12], predicting correctly the major features of their equations of state and freezing parameters as obtained by simulations. The same singularity in the hard-sphere free energy functional yields a fundamentally different fluid and solid asymptotic high-

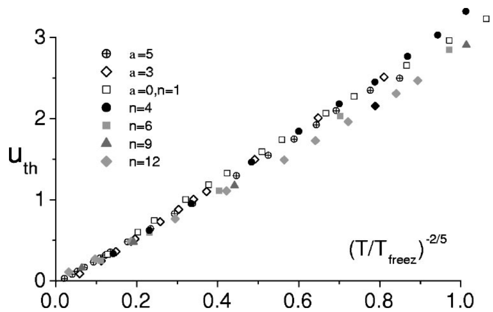

FIG. 1. The simulation results [15] for the ''thermal'' potential energy $u_{th}=U/Nk_BT-C_{fluid}\Gamma$ of the inverse power potentials $\varphi(r)/k_BT=\Gamma/(r/a_{WS})^n$ and of the Yukawa potentials $\varphi(r)/k_BT=\Gamma/(r/a_{WS})e^{-\alpha(r/a_{WS})}$ (α denoted by a in the figure) as a function of $(T/T_{freez})^{-2/5}$. See the text.

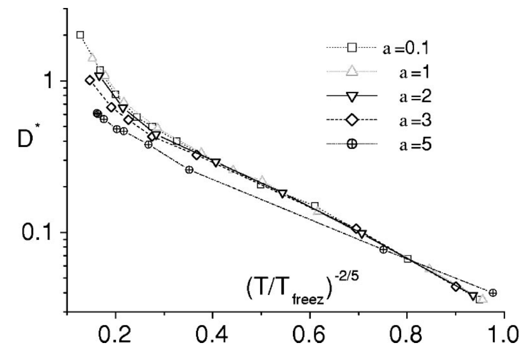

FIG. 3. Simulation results [9] for the reduced coefficient of the self-diffusion D^* for the Yukawa potentials $\varphi(r)/k_BT=\Gamma/(r/a_{WS})e^{-\alpha(r/a_{WS})}$ as a function of $(T/T_{freez})^{-2/5}$ for several values of the screening parameter α (denoted by a in the figure). The inset shows the same results as a function of $(T/T_m)^{-2/5}$. See the text.

density expansions for the potential energy: featuring a static-lattice Madelung term and the harmonic $\frac{3}{2}k_BT$ correction, for the solid, and a fluid Madelung energy with a $\sim T^{3/5}$ thermal energy correction, for the fluid. This result for the the bulk fluid turns out to be one particular possibility of the variational perturbation theory which was considered in the past [13].

Focusing our attention on the repulsive inverse power potentials $\varphi(r)/k_BT=\Gamma/(r/a_{WS})^n$, with $n\leqslant 12$, and screened Coulomb (Yukawa) potentials $\varphi(r)/k_BT=\Gamma/[r/a_{WS}]e^{-\alpha(r/a_{WS})}$, where $a_{WS}=(3/4\pi\overline{\rho})^{1/3}$ is the Wigner-Seitz radius and Γ is the coupling parameter, note that the classical Coulomb one-component plasma (OCP) corresponds to an inverse power potential with $n=1$ or to a Yukawa potential with zero screening parameter $\alpha=0$. The analytic theory based on the fundamental measure free energy functionals yields also an approximate new freezing ''law'' in the form [12]

$$\Gamma_{freez}\simeq 0.7/(C_M-C_{fluid}), \tag{3}$$

where C_M is the Madelung constant of the crystal structure and C_{fluid} is the fluid Madelung constant (see below). This ''law'' compares well [12] with the simulation results [15,17]. For these potentials the asymptotic high-density expansion for the fluid thermal energy takes the form

$$u_{th}=\frac{U}{Nk_BT}-C_{fluid}\Gamma\simeq O(\Gamma^{2/5}), \tag{4}$$

where the fluid Madelung constants C_{fluid} are given explicitly in [12]. In particular, for the $n>3$ inverse power potentials,

$$C_{fluid}=\frac{1}{2^n(n-2)!}\int_0^\infty\frac{(x+2)x^{(n-1)}}{(x+2)+(x-2)e^x}dx, \tag{5}$$

and for the $\alpha>0$ Yukawa fluids,

$$C_{fluid}(\alpha)=\frac{\alpha(\alpha+1)e^{-\alpha}}{(\alpha-1)e^{\alpha}+(\alpha+1)e^{-\alpha}}. \tag{6}$$

In Fig. 1 we present the simulation results [15,17] for $u_{th}=U/Nk_BT-C_{fluid}\Gamma$, as a function of $(\Gamma/\Gamma_{freez})^{2/5}=(T/T_{freez})^{-2/5}$. We find that to high accuracy the thermal energy can be represented by

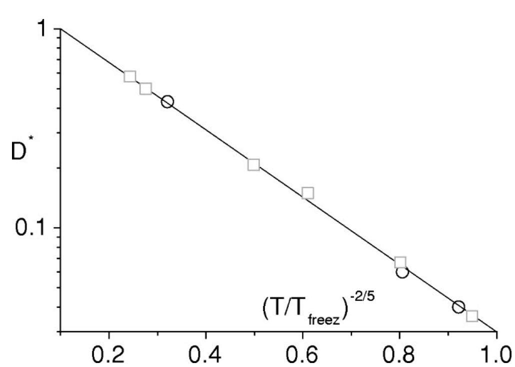

FIG. 2. Simulation results [[9] (squares), [18], [6] (circles)] for the reduced coefficient of the self-diffusion D^* for the one-component plasma (OCP) as function of $(T/T_{freez})^{-2/5}$, compared with the fit (10). See the text.

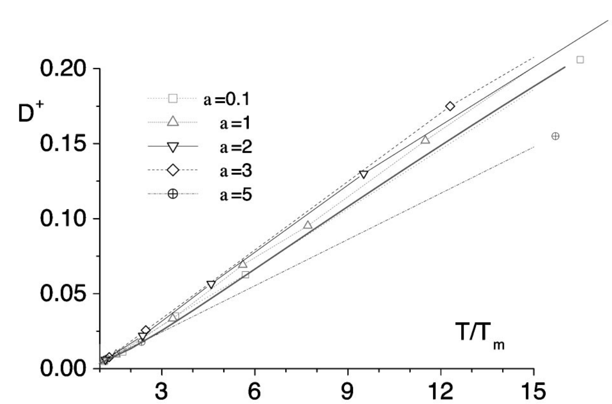

FIG. 4. Simulation results [9] for the reduced coefficient of the self-diffusion D^+ for the Yukawa potentials $\varphi(r)/k_BT=\Gamma/(r/a_{WS})e^{-\alpha(r/a_{WS})}$ as a function of $(T/T_m)^{-2/5}$ for several values of the screening parameter α (denoted by a in the figure) compared with our prediction (14) given by the heavy solid line. See the text.

$$u_{th} \simeq 3\left(\frac{T}{T_{freez}}\right)^{-2/5} = 3\left(\frac{\Gamma}{\Gamma_{freez}}\right)^{2/5} \tag{7}$$

almost all the way to $(T/T_{freez})^{-2/5} \simeq 0$, so that the excess entropy can be well represented by the form

$$s - s_{freez} \simeq \frac{9}{2}\left[\left(\frac{T}{T_{freez}}\right)^{-2/5} - 1\right] = \frac{9}{2}\left[\left(\frac{\Gamma}{\Gamma_{freez}}\right)^{2/5} - 1\right]. \tag{8}$$

It should be noted that s_{freez} is about the same, $s_{freez} \simeq 4$, for all soft inverse power potentials and Yukawa potentials. As the potentials become steeper the asymptotics does not extend so well to small values of Γ, and other terms in the expansion interfere. It is remarkable that these terms contribute such that the linear dependence on $\Gamma^{2/5}$ is still well perserved down to low values of Γ. The $T^{-2/5}$ dependence of the excess entropy was also observed in very recent simulations for Lennard-Jones fluids [16].

By combining the semiempirical excess entropy scaling of the reduced transport coefficients [4,5,2,3] with the freezing temperature scaling of the excess entropy [12], we obtain the following quasiuniversal relations:

$$t^* \simeq A_t \exp\left[B_t\left(\frac{T}{T_{freez}}\right)^{-2/5}\right] \simeq A_t \exp\left[B_t\left(\frac{(C_M - C_{fluid})\Gamma}{0.7}\right)^{2/5}\right], \tag{9}$$

where t^* is a reduced transport coefficient ($t=\kappa,\eta$, or D) and the corresponding parameters A_t, B_t are weakly dependent on the potential. It should be emphasized that to within the expected few percent accuracy of the quasiuniversality of the excess-entropy scaling for the Yukawa potentials, as we find also in this work, the melting and freezing temperatures T_m and T_{freez} are almost interchangable in the scaling relation (9).

The recent results for the self-diffusion of Yukawa systems [9] provides a test for the scalings mentioned above. These new results [9] are in agreement with a limited set of results obtained earlier (see [18,19,17(b),6] and references therein). Like other scaling properties of Yukawa potentials [12,20] the parameters in relations like Eq. (9) are expected to be weakly dependent on the screening parameter α for all Yukawas with $\alpha \lesssim 5$. In particular, the results are expected to be well approximated by those available for the OCP ($\alpha = 0$). Simulation results for the self-diffusion coefficient from various sources for the OCP ($\alpha=0$) or near the OCP ($\alpha=0.1$) are presented in Fig. 2 which can be well fitted by the following expression of the form of Eq. (9):

$$D^* = 1.48 \exp\left[-3.9\left(\frac{T}{T_{freez}}\right)^{-2/5}\right]. \tag{10}$$

The new simulation results [9] for several values of the screening parameter are given in Fig. 3 where it is clear that they follow closely our scaling prediction and in particular Eq. (10). In this paper we use for T_m the simulations based values given in [9], while for T_{freez} we take our estimate (3).

Returning to Eq. (8) we obtain

$$D^* = 1.48 e^{-3.9(1-2s_{freez}/9)} e^{-7.8s/9} \simeq 0.9 e^{-0.87s} \tag{11}$$

in accordance with the early work [4] and its results of the type (2). Following [17(b)], Ohta and Hamaguchi analyzed their recent simulations [9] by considering the reduced diffusion coefficient

$$D^+ = \frac{D}{\omega_E a_{WS}^2}, \tag{12}$$

where ω_E is the Einstein frequency of the solid, and find that it is linear in T/T_m all the way to large values of $T/T_m \sim 100$, and only weakly dependent on the sceening parameter $\alpha \lesssim 5$. This behavior they can explain near melting, i.e., for $T/T_m \sim 1$, but there is no physical reason to incorporate ω_E when $T/T_{melt} \gg 1$. We find, however, that the scaling employed by [9] represents just a special case of our general results. In particular, we note that the coefficient D^+ is related to our D^* by

$$D^+ = \frac{D^*}{\left(\frac{3}{4\pi}\right)^{1/3}\left(\sqrt{3}\,\frac{\omega_E}{\omega_P}\Gamma_{freez}\right)^{1/2}}\left(\frac{T}{T_{freez}}\right)^{1/2}, \tag{13}$$

where ω_P is the plasma frequency. Specifically, using Eq. (10) for the OCP we obtain

$$D^+ = \left[\frac{\left(\frac{T}{T_{freez}}\right)^{1/2}}{7.9}\right] 1.48 \exp\left[-3.9\left(\frac{T}{T_{freez}}\right)^{-2/5}\right], \tag{14}$$

which turns out to be almost linear, $D^+ \simeq 0.01 T/T_{freez}$, all the way to $T/T_{freez} \sim 100$, and compares well (see Fig. 4) with the simulation results of [9].

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