

Universal Scaling of Pair-Excess Entropy and Diffusion in Strongly Coupled Liquids

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Understanding diffusion in liquids from properties of static structure is a long standing problem in condensed matter theory. Here we report an atomistic study of excess entropy and diffusion coefficient in a strongly coupled Yukawa liquid. We observe that the pair excess entropy s_2 scales with temperature as $-3.285 (T_m/T)^{0.665}$ and contributes to about 90% of the total excess entropy close to the freezing transition T_m . We further report that at low temperatures where the diffusive transport is mediated by cage relaxation, the diffusion coefficient when expressed in natural units of the Enskog collision frequency and the effective hard sphere diameter, obeys the scaling law $0.04 e^{s_2}$ and deviates from it at high enough temperatures where cages cannot form. The scaling laws reported here may also apply to strongly coupled dusty plasmas and charged colloids.

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A unifying description of atomic diffusion in condensed matter has remained elusive so far [1–4]. For dilute gases the Chapman-Enskog solution of the Boltzmann equation applies well as the collisions in this limit, to a good approximation are assumed to be binary in nature [5, 6]. Higher densities can be addressed after a generalization of the Enskog theory [7] or by using an effective Boltzmann approach [8]. The late 1960s saw the first computer simulations on transport phenomena prompting the development of mode coupling theories which were more successful in describing diffusion in moderate to dense fluids [9–11]. For liquids that are dense or at very low temperatures, structural effects dominate over kinetic effects and change the qualitative features of atomic transport [12–14]. These structural effects manifest themselves in the form of a cage around a given particle formed by nearest neighbors [15, 16]. As temperature rises, the short range order of a liquid begins to fluctuate rapidly and eliminates any caging effect that may affect diffusive transport. Particularly at low temperatures where dynamical excitations become collective in nature, universal scaling laws emerge in both thermodynamics and transport phenomena [17, 18]. Whether such a bridge exists that can connect underlying structure with dynamics in strongly coupled liquids is the subject matter of our work.

Rosenfeld [19] proposed a connection between diffusion coefficient D and the total excess entropy per particle s in the form of a scaling law $Dn^{1/3}/(k_B T/m)^{1/2} = Ae^{Bs}$ where n is the number density. It should be noted that s which arises due to structural correlations, is over and above the ideal gas value and is therefore negative. The prefactor A and the exponential argument B vary for different inter-atomic potentials and the scaling law is able to estimate the diffusion coefficient to within 30% of the actual value. The scaling thus acts as a corresponding states like relationship and was observed to be only quasi-universal in nature. The dimensional reduction of D is macroscopic in nature as the parameters $n^{1/3}$ and $(k_B T/m)^{1/2}$ do not depend on the liquid structure. Later

works [20] showed that a microscopic reduction of D using structure dependent parameters namely the Enskog collision frequency ν and effective hard sphere diameter σ leads to a scaling law $D/(\nu\sigma^2) = 0.049e^{s_2}$. Here σ is defined as the location of the first peak in the pair correlation function $g(r)$ and ν is given by $4\sigma^2 g(\sigma)n\sqrt{\pi k_B T/m}$. The pair excess entropy s_2 is a two body approximation of the full configuration entropy and can be readily obtained once $g(r)$ is available (see text later). The scaling law which works for a range of soft potentials was seen to break down in liquid Silicon and some liquid metals [21]. To the best of our knowledge, a microscopic study of this pair excess entropy and its connection to the diffusion coefficient in strongly coupled liquids with long ranged interactions is lacking. Such a study will be immediately useful for kinetically resolved experiments in dusty plasma and charged colloids where the particle interactions to a good approximation can be considered to be the Yukawa potential. The purpose of this letter is to address this issue and provide a universal scaling of pair excess entropy (directly calculated from structure) with temperature in a strongly coupled Yukawa liquid. In what follows we also provide a scaling law that connects this pair excess entropy with liquid diffusion.

Our prototype system is a three dimensional (3D) strongly coupled Yukawa liquid which is known to be an excellent model for dusty plasma and colloidal suspension of charged particulates [22, 23]. The availability of kinetically resolved in experiments in dusty plasma [24] further brightens up the prospect of a direct comparison with our results reported here. The particles in the liquid interact through the Yukawa potential $\phi(r) = Q^2(4\pi\epsilon_0 r)^{-1}e^{-r/\lambda_D}$ where Q is the particle charge and λ_D is the Debye length of the background plasma. We have performed molecular dynamics (MD) simulations in a canonical ensemble with periodic boundary conditions. We neglect neutral gas friction as it affects the diffusion dynamics only in the limit of large dissipation [25, 26]. Distance is expressed in units of the Wigner-Seitz radius

$a = (4\pi n/3)^{-1/3}$, energy in units of $Q^2/(4\pi\epsilon_0 a)$, time in units of inverse nominal dust frequency $\sqrt{3\epsilon_0 m}/(Q^2 n)$ and entropy in units of Nk_B . The system can exhibit a state of strong coupling when the dimensionless parameter $\Gamma = Q^2/(4\pi\epsilon_0 a k_B T) \gg 1$ leading to a remarkable display of collective excitations and self organization phenomena [27, 28]. The two dimensionless parameters Γ and $\kappa = a/\lambda_D$ completely describe the thermodynamics of our system. We take 10648 particles at a reduced density $n = 3/(4\pi)$. To speed up the simulations we smoothly truncate the interaction potential along with its two derivatives to zero at a cutoff distance r_c . This is done by employing a fifth-order polynomial function that is switched on when $r_m < r < r_c$ with r_m and r_c being the inner and outer cutoff distance respectively. We choose r_m and r_c subject to criteria $\phi(r_m) \approx 4.085 \times 10^{-4}$ and $\phi(r_c) \approx 9.300 \times 10^{-7}$ thus ensuring negligible perturbation to the bare Yukawa potential. A Nosé-Hoover thermostat [29] maintains constant temperature in the NVT ensemble. To improve statistics we average our

data over 30 statistically independent realizations.

We begin by first computing the total excess entropy s by performing a thermodynamic integration of the equation of state along a reversible path from some reference state Γ_0 to the desired Γ as mentioned below

$$s_{\Gamma \leftarrow \Gamma_0} = u(\Gamma)\Gamma - u(\Gamma_0)\Gamma_0 - \int_{\Gamma_0}^{\Gamma} u(\Gamma') d\Gamma' \quad (1)$$

where u is the potential energy per particle. Ideally one should take Γ_0 to be zero in order to measure entropy relative to the ideal gas state but in practice it is difficult to carry the above integration at such low values of Γ . We avoid this problem by taking $\Gamma_0 = 1$ as a reference state as all peaks in $g(r)$ disappear at this temperature. An alternate route to calculate excess entropy directly from the underlying structure is due to Wallace [30]. His method is based on the expansion of s in terms of correlation functions and gives excess entropy relative to the ideal gas state. We use Ref. [31] to write for s :

$$s = \underbrace{-\frac{1}{2}n \int [g(r)\ln\{g(r)\} + \{1 - g(r)\}] dr}_{s_2} - \underbrace{\frac{1}{6}n^2 \int \int [g^{(3)}(r)\ln\{\delta g^{(3)}(r)\} + 3g(r)^2 - g^{(3)}(r) - 3g(r) + 1] dr^2}_{s_3} + \dots \quad (2)$$

Here s_2, s_3, \dots are the two body, three body and other

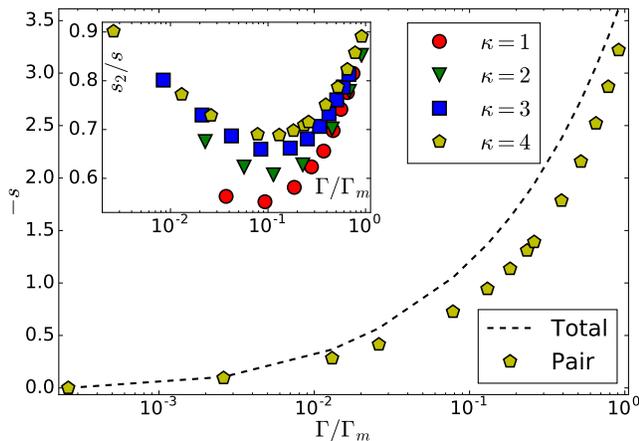


FIG. 1. (color online). Comparison of the total excess entropy [Eq. (1)] with the pair contribution [Eq. (2)] shown for the case $\kappa = 4$ and the reference state $\Gamma_0 = 1$. Inset: Fraction of the total excess entropy as a function of Γ .

many body contributions to the total entropy s respectively. In Fig. 1 we plot a comparison of s [from Eq. (1)] with s_2 keeping $\Gamma_0 = 1$ as the reference. We find that close to freezing s_2 dominates over other many

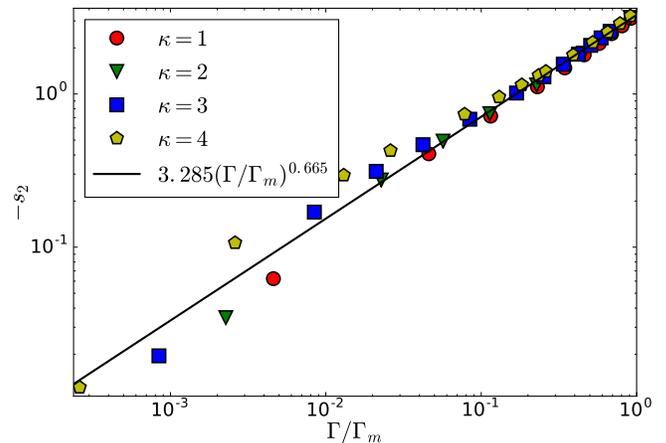


FIG. 2. (color online). Pair excess entropy as a function of reduced inverse temperature Γ/Γ_m . Data collapse indicates the accuracy of our scaling law down to Γ as low as 2% Γ_m .

body terms and contributes to over 90% of s [see Fig. 1: Inset]. Note the existence of a minimum around $\Gamma = 10\% \Gamma_m$ and highest contribution at Γ extrema. Next we show the scaling of this pair excess entropy with the reduced temperature Γ/Γ_m in Fig. 2. It should be noted that Γ_m varies by more than an order of magni-

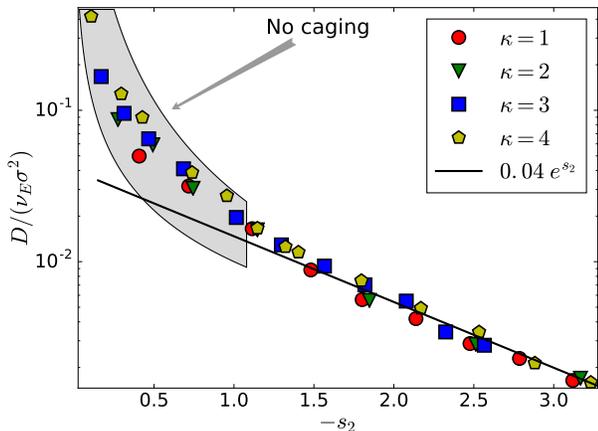


FIG. 3. (color online). Reduced diffusion coefficient vs pair excess entropy. Except when caging is absent (shaded region) we are able to collapse our data on to the simple scaling law shown by a solid line. Data inside the shaded region are taken at temperatures where the velocity auto-correlation does not cross zero [see text and Fig. 4].

tude from 217.4 to 3837 as κ goes from 1 to 4 [32] and hence we have sufficient reasons to believe the scaling law $s_2 = -3.285(\Gamma/\Gamma_m)^{0.665}$ reported here is universal in nature. The value of s_2 at melting ≈ -3.285 for all κ . Our results may thus prove to be very useful in predicting structural entropy from trajectory snapshots which are easily available in kinetically resolved dusty plasma experiments. In what follows we will provide a link to connect this structural information to the dynamics that governs transport.

Any theory that unifies dynamical properties such as diffusion with the underlying structure will need to provide ways in which the local arrangement of nearest neighbors (or cage) around a particle may affect its long time dynamics. Recently we showed that the lifetime of this cage decides the relaxation of shear stress in the liquid state [16]. Thus it is natural to expect that cage relaxation will also be necessary to produce local density fluctuations necessary for diffusive transport especially at low temperatures where the liquid exhibits strong caging behavior. Since a cage is typically formed by the nearest neighbors [particles within the first peak of $g(r)$], the momentum and energy transfer processes between particles can be expected to be short ranged just like binary collisions in a gas of hard spheres. The relevant time scale of these collisions can then be given by the inverse of Enskog collision frequency ν_E and the relevant length scale can be realized as the effective hard sphere diameter σ which is just the location of the first peak in $g(r)$. Within the classical Enskog theory we have

$$\nu_E = 4\sigma^2 g(\sigma) n \sqrt{\pi k_B T / m} \quad (3)$$

We now turn our attention to Fig. 3 where we plot

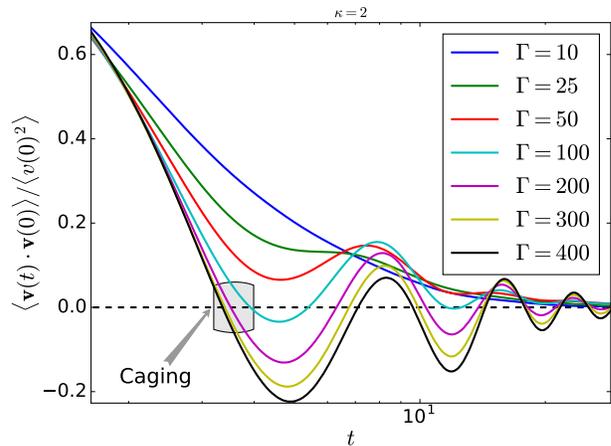


FIG. 4. (color online). Normalized velocity auto-correlation data for the case $\kappa = 2$. Zero crossing of the function indicates caging behavior. For Γ values 10, 25 and 50 where caging is absent we see deviations from the scaling law as shown in the shaded region of Fig. 3.

the diffusion coefficient in units of $\nu_E \sigma^2$ as a function of pair excess entropy and find that a scaling law $D/(\nu_E \sigma^2) = 0.04 e^{s_2}$ holds in the region $-s_2 > 1$. However when $-s_2 < 1$, a deviation from this scaling law is observed which is shown by the shaded region. Our prefactor of 0.04 which is about 18% smaller than the one used in Ref. [20] is not universal. Note that lower values of $-s_2$ imply higher temperatures. The points that deviate from the scaling law are taken at temperatures high enough to set rapid fluctuations in the short range order of the liquid thus marginalizing any role that the nearest neighbor dynamics can play in particle diffusion. Our data for velocity auto-correlation (VAC) for the case $\kappa = 2$ shown in Fig. 4 confirms this. Data for other values κ are similar (not shown here). When the liquid exhibits caging, indicated by zero-crossing of VAC, we find that the corresponding data for diffusion obeys the scaling law shown in Fig. 3. This is expected because at these temperatures cage relaxation is necessary for the onset of diffusive transport. At temperatures where the VAC does not cross zero, there is no caging and D does not obey the scaling law. These data points are shown in the shaded region of Fig. 3.

To further strengthen our argument, we provide in Fig. 5 plots of self-intermediate scattering function $F_s(k_0, t)$ at various Γ for the case $\kappa = 2$. The value of k_0 is taken to be $2\pi/\sigma$. The points $\mathcal{A}, \mathcal{B}, \mathcal{C}, \mathcal{D}$ and \mathcal{E} denote the locations of the e-folding times (t_α) in the $F_s(k_0, t)$ data. As t_α tells us how long one must typically wait for the cages to break or rearrange, it is a good measure of the structural relaxation time. Thus the diffusive regime if mediated by cage relaxation must occur at $t \gtrsim t_\alpha$. Indeed we observe this in the inset where we show the corresponding plots

of the diffusion coefficient with the same points marking the onset of cage breaking. We notice that for the cases $\Gamma = 100, 200$ and 400 where cages do form (see Fig. 4) the corresponding points \mathcal{C}, \mathcal{D} and \mathcal{E} mark the onset of diffusive regime (i.e $D \approx \text{constant}$). Diffusive transport at these values of Γ is thus mediated by cage relaxation and the diffusion data obeys our scaling law shown in Fig. 3. At $\Gamma = 10$ and 25 , the liquid does not exhibit any caging behavior and hence diffusion cannot be mediated by local structural relaxation- also confirmed from the location of points \mathcal{A} and \mathcal{B} in the inset of Fig. 5. Diffusion data at these Γ thus deviate from the scaling $D/(\nu\sigma^2) = 0.04e^{s_2}$.

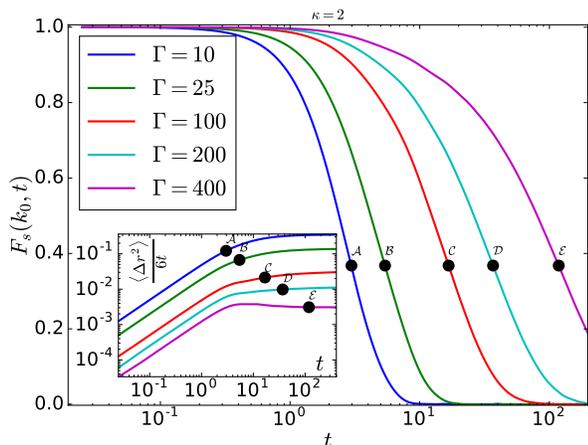


FIG. 5. (color online). Self intermediate scattering function $F_s(k_0, t)$ at various Γ for the case $\kappa = 2$. We take $k_0 = 2\pi/\sigma$ with σ being the location of the first peak in $g(r)$. Points $\mathcal{A}, \mathcal{B}, \mathcal{C}, \mathcal{D}$ and \mathcal{E} mark the e-folding times of $F_s(k_0, t)$. Inset: Diffusion coefficient shown for the same Γ .

We can conclude that the pair excess entropy s_2 in liquid dusty plasma scales as $-3.285(T_m/T)^{0.665}$ for all values of screening parameter with -3.285 being the value of s_2 at melting for all screening lengths. Especially close to the melting point T_m , we find that s_2 which arises from pair correlation contributes to almost 90% of the total entropy. Our scaling is universal as the melting points vary by more than an order of magnitude over the entire range of screening parameters used in this work. We further report that at low temperatures where the liquid exhibits caging, the diffusion coefficient when expressed in the natural units of the Enskog collision frequency and the effective hard core diameter scales as $0.04 e^{s_2}$. At higher temperatures when caging is absent, deviation from the scaling law is seen. The prefactor in our scaling law for diffusion is different from the one in past works [20] implying that the prefactor itself is not universal. The scaling laws reported here may prove to be valuable in directly computing excess entropy and diffusion coefficient in kinetically resolved liquid dusty plasma experiments where particle snapshots are easily obtained.

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