Test of the Stokes-Einstein Relation in a Two-Dimensional Yukawa Liquid

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The Stokes-Einstein relation, relating the diffusion and viscosity coefficients D and η, is tested in two dimensions. An equilibrium molecular-dynamics simulation was used with a Yukawa pair potential. Regimes are identified where motion is diffusive and D is meaningful. The Stokes-Einstein relation, $D\eta \propto k_BT$, was found to be violated near the disordering transition; under these conditions collective particle motion exhibits dynamical heterogeneity. At slightly higher temperatures, however, the Stokes-Einstein relation is valid. These results may be testable in strongly coupled dusty plasma experiments.

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Two-dimensional systems in crystalline or liquid states [1] are of interest in various fields of physics. Monolayer particle suspensions can be formed in colloidal suspensions [2] and dusty plasmas [3]. Electrons on the surface of liquid helium form a 2D Wigner crystal [4]. Ions in a Penning trap can be confined as a single layer of a one-component plasma [5]. Magnetic flux lines in 2D high-temperature superconductors form patterns of hexagonally correlated vortices [6]. Granular flows of discrete macroscopic particles can be confined to a 2D layer [7]. Here we are concerned with 2D liquids, with no motion in the vertical direction. (The experimental systems listed above actually have finite out-of-plane motion; this Letter is most applicable to systems such as dusty plasma where the out-of-plane displacement is small compared to the particle spacing.) As in 3D liquids [8], 2D liquids near the disordering transition are especially interesting because they exhibit dynamical heterogeneities, where the collective motion of the more mobile particles occurs in strings [9].

Our 2D system is composed of molecules or particles that interact with a Yukawa pair potential. This is a soft potential that is applicable in several fields including colloids [2,9], dusty plasmas [3,10], and some polyelectrolytes [11] in biological and chemical systems.

The Stokes-Einstein relation for 3D liquids

$$D = k_BT/c\pi\eta R \tag{1}$$

is an important hydrodynamic law relating the diffusion coefficient D of a Brownian particle and the fluid shear viscosity η. It states that the diffusion of a Brownian particle in a liquid is proportional to the liquid temperature k_BT and is inversely proportional to the viscosity of the liquid. This combines the Einstein relation $D = k_BT/\xi$ for D and the Stokes law $\xi = c\eta R$ for the frictional force ξ on a sphere in a fluid. Here, c is a constant that depends on the hydrodynamic boundary condition at the particle surface, and R is the effective radius of the Brownian particle.

For 3D liquids, the validity of the Stokes-Einstein relation is well known, even at the molecular level. Over a wide range of temperature [12], the diffusion coefficient D and the factor k_BT/η have a fixed ratio as k_BT varies. Only for deeply supercooled liquids does the Stokes-Einstein relation appear to fail [13]; such liquids typically exhibit a spatial heterogeneity [8]. The Stokes-Einstein relation is so trusted in 3D that it is routinely used to compute D from a measurement of η. However, the situation in 2D is very different.

For 2D liquids, unlike 3D liquids, tests of the validity of the Stokes-Einstein relation are lacking. Indeed, some earlier results suggest that the Stokes-Einstein relation should not be valid at all in 2D because the transport coefficients D and η are themselves not valid. These earlier results came from a 2D molecular-dynamics (MD) simulation [14] and kinetic and mode-coupling theories [15,16]. They predict that, unlike the case of 3D, the long-time tails of the velocity (VACF) and stress autocorrelation functions (SACF) have a slow $1/t$ decay. A decay this slow precludes the use of Green-Kubo relations to calculate D and η, and suggests that these transport coefficients are meaningless, at least in the context of equilibrium liquids. However, there is no universal agreement that D and η are meaningless in 2D. The shear viscosity coefficient in 2D has now been shown to be meaningful, at least for soft potentials, in a significant number of simulations [17–20], and an experimental measurement [21] of a 2D viscosity has been reported. The diffusion coefficient in 2D, on the other hand, has not been demonstrated to be meaningful over a wide range of density or temperature. As a test of this, motion is deemed to be diffusive, and diffusion coefficients are meaningful, only if the VACF decays faster than $1/t$ or if the Einstein relation MSD $\propto t$ is obeyed. Here, MSD is the time series of mean-square displacement of particle positions. Simulations [22–24], using a r^{-12} pair potential and the Einstein relation, for example, successfully yielded a diffusion coefficient, but only near the disordering transition. Identifying the conditions where a 2D diffusion coefficient is meaningful is our first goal. We do this two ways, using the Green-Kubo method and the Einstein

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relation. The expressions we used for the VACF and Green-Kubo relations were Eqs. (7.2.1) and (7.2.8), respectively, in Ref. [25], where we replace the coefficient 3 with 2 to reflect the number of dimensions.

Our second goal is to test the Stokes-Einstein relation for 2D liquids. For the regimes where D is valid we compute the product $D\eta$ and plot it versus temperature as an empirical test of the 2D Stokes-Einstein relation,

$$D = k_B T / c_{2\mathrm{D}} \pi \eta. \tag{2}$$

Equation (2) is analogous to Eq. (1), except that it does not contain the particle radius R in the denominator due to the different dimensionality of η in 2D. Finding a linear scaling of $D\eta$ on $k_B T$ would be an empirical verification of the validity of the Stokes-Einstein relation, while a deviation from linear scaling would indicate a violation. In performing this test, it is important that we obtain values of D and η independently.

We use a 2D Yukawa system. Particles are present only in a single monolayer, and they interact with a Yukawa potential energy, which for two particles of charge Q separated by a distance r is $U(r) = (Q^2/4\pi\epsilon_0 r) \times \exp(-r/\lambda_D)$. This potential changes gradually from a long-range Coulomb repulsion to a hard-sphere-like repulsion as the screening parameter $\kappa = a/\lambda_D$ is increased. Here, λ_D is a screening length, $a = (n\pi)^{-1/2}$ is the 2D Wigner-Seitz radius [26], and n is the areal number density of particles. A Yukawa system is characterized by two dimensionless parameters: κ and the Coulomb coupling parameter $\Gamma = Q^2/4\pi\epsilon_0 akT$. We use Γ^{-1} as a dimensionless temperature. The phonon spectrum of a 2D Yukawa system is characterized by a frequency $\omega_{pd} = (Q^2/2\pi\epsilon_0 m a^3)^{1/2}$ [26]. The disordering transition for a 2D Yukawa system occurs at $\Gamma = 137$ for $\kappa = 0$ [4]. At our value of $\kappa = 0.56$, the transition is at $\Gamma \approx 145$ [27], and we denote the corresponding melting temperature as T_m.

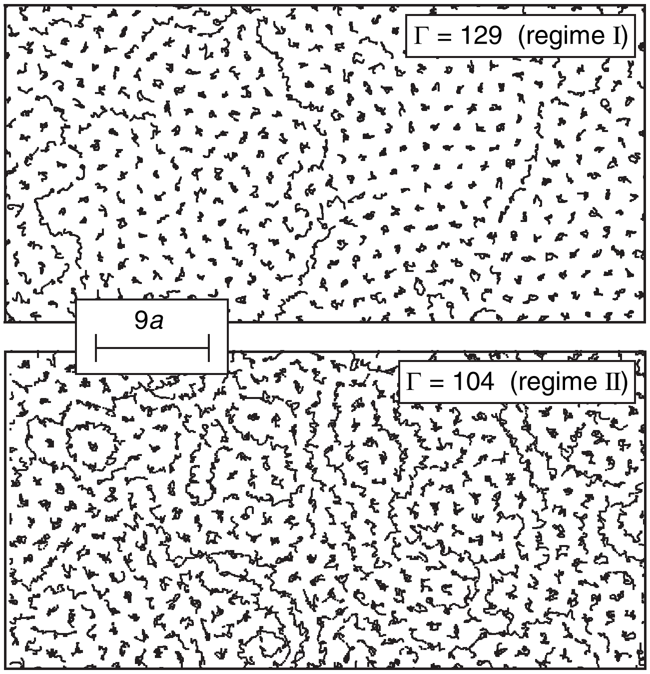

FIG. 1. Particle trajectories from the simulation. Regime I is near the disordering transition, and regime II is at a slightly higher temperature. Regime I has a dynamical heterogeneity; strings of mobile particles flow between domains consisting of less-mobile caged particles. In regime II ($\Gamma = 104$) the domains are smaller and there is a less distinctive difference between the caged trajectories and the trajectories of particles bounding the domains. Trajectories are shown for a time interval $\omega_{pd}\Delta t \approx 37$. Only a portion of the simulation box is shown here. The full simulation box was $113.98a \times 98.16a$ with 4096 particles for $\Gamma = 129$, and $56.99a \times 49.08a$ with 1024 particles for $\Gamma = 104$.

We performed an MD simulation to calculate η and D. The equations of motion for 1024 or 4096 particles were integrated using periodic boundary conditions. A Nosé-Hoover thermostat was applied to achieve a constant T. As a test, we ran simulations with the thermostat turned on or off, and verified that the thermostat does not affect η or D, for any values of Γ. The screening parameter was $\kappa = 0.56$. We recorded particle positions and velocities, and then we calculated velocity and stress correlation functions and the mean-square displacement. The system was in equilibrium, and it had no macroscopic velocity shear or density gradient. There was no friction term in the equation of motion. Examples of particle trajectories for $\Gamma = 104$ and 129 are shown in Fig. 1. Data for MSD and correlation functions were averaged over multiple runs with different initial conditions. Further details of the simulation can be found in Ref. [17].

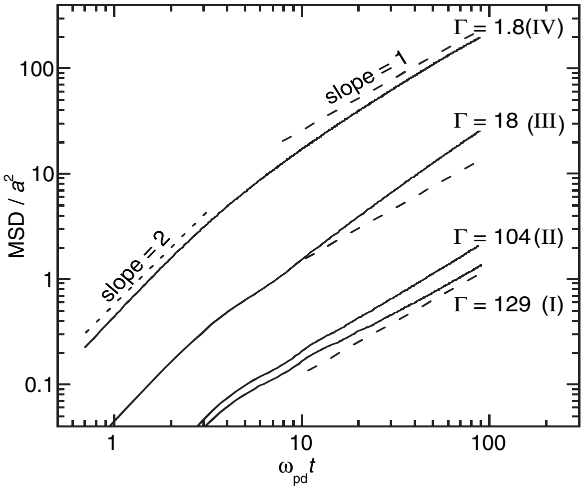

FIG. 2. Mean-square displacement (MSD). Ballistic motion at small t has MSD $\propto t^2$, with a slope of 2 on this log-log plot. Motion at later times is either diffusive, MSD $\propto t$ as indicated by a slope of 1, or nondiffusive as in regime III. By this test, we found that motion is diffusive in regimes I, II, and IV, but not III. A separate test, using the VACF, is consistent with this result.

To meet our first goal, we identify regimes where the transport coefficients D and η are meaningful. Previously [17] we found that η was meaningful, as indicated by a SACF that decayed faster than $1/t$, for a wide range of Γ. Here, we report results for the diffusion coefficient D, where the results are more complicated. We applied two tests to determine whether motion is diffusive. First, if MSD $\propto t^1$ is satisfied at times that are long (compared to the short-term ballistic motion, which has an exponent of 2, MSD $\propto t^2$), then the Einstein relation is satisfied, indicating diffusive motion. Results for this test for selected values of Γ are shown as a time series for MSD in Fig. 2. The time series has a duration that exceeds, by approximately a factor of 2, the ratio of the box width and sound speed. We tested the last portion of this time series, for an interval of $\approx 37\omega_{pd}^{-1}$, to determine whether the exponent is equal to 1. Second, if the long-time tail in the VACF decays faster than $1/t$, then the Green-Kubo theory indicates that the motion is diffusive. We found that these two tests always agreed. Details of the VACF data will be reported elsewhere.

We identified four different temperature regimes, and we characterized them according to whether the motion is diffusive or not. All four regimes have $\Gamma < 145$, i.e., they are all in the liquid state and have $T > T_m$. In regime I ($124 < \Gamma < 145$) the motion is diffusive; this regime is near the disordering transition. Motion is also diffusive in regime II ($88 < \Gamma < 124$), and the nonideal gas regime IV ($\Gamma < 5$). However, motion was not diffusive in regime III ($5 < \Gamma < 88$). That a regime exists where motion is nondiffusive is not surprising, because earlier studies of 2D liquids predicted they would be nondiffusive due to the long-time tail in the VACF, which arises from hydrodynamic modes [14–16]. What is surprising is that we found other regimes, for our frictionless atomic system, that are diffusive.

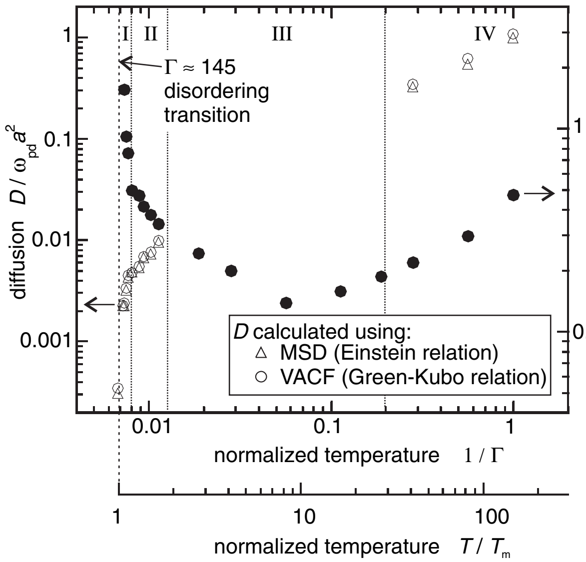

FIG. 3. Diffusion and viscosity coefficients. Diffusion coefficients (open symbols) were computed from the same simulation data using two methods, the Green-Kubo relation and the Einstein relation. For comparison to the diffusion coefficient, the viscosity coefficient data from Ref. [17] are shown as solid circles; these were computed using a Green-Kubo relation. The disordering transition for our $\kappa = 0.56$ occurs at $\Gamma \approx 145$, based on the simulation results of Ref. [27].

If a friction term were added to the equation of motion to model drag due to a solvent, the motion might more likely be diffusive. Löwen [28] used a different simulation method, Brownian dynamics, for a 2D Yukawa system with a large friction. The equation of motion in that method lacks an inertial term, and is therefore suitable for a strongly dissipated system. They reported finding diffusive motion not only in our regimes I and II, but also for one data point in our regime III. Their values for D were systematically smaller than ours by a factor of 2.3 in regime II.

Our two methods of computing D yield values that agree, as shown in Fig. 3. Note that D increases with temperature, and the rate of increase is very high in regime I, near the disordering transition at T_m.

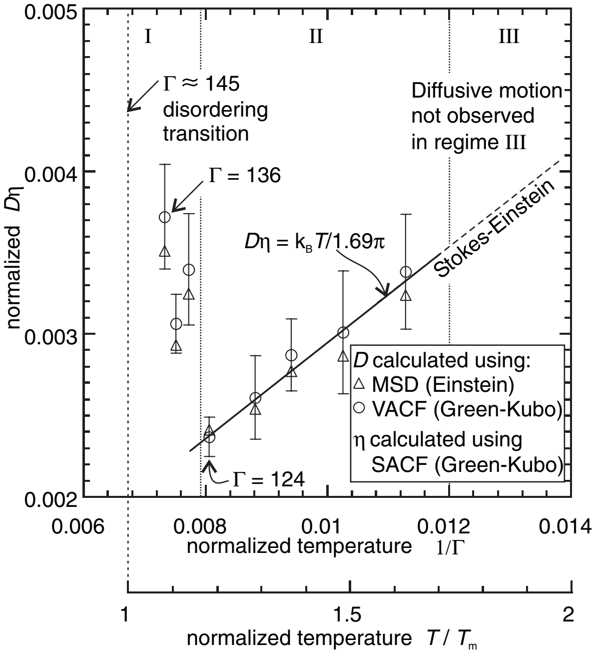

FIG. 4. Test of the Stokes-Einstein relation. Linear scaling $D\eta \propto T$ in regime II indicates the validity of the Stokes-Einstein relation. However, the deviation from the linear scaling for $\Gamma > 124$ indicates a violation of the Stokes-Einstein relation in regime I, which is near the disordering transition. Diffusive motion was not observed in regime III, so that the relation is not testable there. The vertical axis is normalized by $nm\omega_{pd}^2 a^4$. Extrapolating the Stokes-Einstein line shown here into regime IV (not shown), we found rough agreement with simulation data even though the applicability of the Stokes-Einstein relation in nonideal gas is not expected.

To meet our second goal of testing the Stokes-Einstein relation, we compute the product $D\eta$ and examine its scaling with temperature. Results, shown in Fig. 4, reveal that $D\eta$ varies almost linearly with temperature in regime II, but not regime I. We therefore conclude that the Stokes-Einstein relation is obeyed in regime II but not in regime I.

We can thus summarize our two chief results. First, the diffusion coefficient is meaningful in both regimes I and II but not regime III. Second, the Stokes-Einstein relation is valid in regime II, but it is violated in regime I.

We found the value of the coefficient in Eq. (2) relating D, η, and k_BT. Fitting the data in Fig. 4 to a straight line passing through the origin yields $c_{2D} = 1.69 \pm 0.10$. This coefficient has never been reported, to our knowledge, for 2D, although its value is well known for 3D, where $c = 4$ for stick or $c = 6$ for slip boundary conditions.

Verification of the Stokes-Einstein relation in regime II indicates a coupling of diffusion and shear viscosity in 2D just as it does in 3D simple liquids. For a macroscopic particle in a fluid, particle diffusion is a result of Brownian motion, with a friction that arises from the viscous dissipation of the associated velocity field in the surrounding liquid. In a simple liquid, validity of the Stokes-Einstein relation is an indication of a coupling of individual particle motion to collective modes. This coupling has been observed previously in 3D for strongly coupled Yukawa systems [29] and one-component plasmas [30].

The violation of the Stokes-Einstein relation that we observed in regime I, near the disordering transition, indicates a decoupling of diffusive and viscous transport. We found the diffusion coefficient is larger than would be expected if the Stokes-Einstein relation were valid. We note that in 3D a violation of the Stokes-Einstein relation is also observed in supercooled liquids [13,31], and this motivates us to suggest an explanation for our result in 2D.

The decoupling in regime I (near the disordering transition) is likely related to structural and dynamical heterogeneities in the liquids. As shown in Fig. 1, on a time scale of tens of ω_{pd} the 2D liquid develops domains of localized crystalline order with localized oscillatory motion that are separated by stringlike structures of more mobile particles. For 3D supercooled liquids, it is believed that this type of heterogeneity accounts for the failure of the Stokes-Einstein relation [31]. Our results suggest that the same effect is responsible in 2D.

The results we have reported for our test of the Stokes-Einstein relation in a 2D liquid could be tested in a future experiment. Monolayer suspensions of microspheres in a dusty plasma have a Yukawa interaction as in our simulation, and a recently developed method has been reported for measuring the shear viscosity [21]. There is no obstacle to measure the self-diffusion coefficient as well.

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