Generalized Viscoelastic Theory of the Glass Transition for Strongly Coupled, Classical, One-Component Plasmas

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We present a new theory of dynamic correlations for a classical one-component plasma in strong Coulomb coupling within the generalized viscoelastic formalism. The dynamic structure factor and the coefficient of shear viscosity for the one-component plasma in a metastable supercooled state are investigated and the possibility of a glass transition is predicted. Relevance to laboratory experiments is pointed out through analyses of the metastable-state lifetimes against homogeneous nucleation of the crystalline state.

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The classical one-component plasma (OCP) is a system consisting of a single species of charged particles, obeying the classical statistics embedded in a uniform background of neutralizing charges. The law of binary interaction is set to be Coulombic; the system is characterized by a single dimensionless parameter,[1,2] $\Gamma=(Ze)^2/ak_BT$, where Ze is the electric charge and $a=(4\pi n/3)^{-1/3}$ is the Wigner-Seitz (ion-sphere) radius. The correlation properties of such an OCP have been extensively studied by the Monte Carlo and molecular-dynamics (MD) simulation techniques,[3-5] as well as by numerical solutions to integral equations.[6,7] Recent experimental developments[8,9] lead us to expect that a classical OCP in strong coupling ($\Gamma \gg 1$) may soon be realized in a laboratory setting.

It has been predicted[3] that the OCP may undergo a phase transition into a crystalline state (Wigner crystallization) at $\Gamma_m=178\pm1$. Since the transition is of the first order, the plasma may remain in a metastable fluidlike state[10] when it is supercooled below the corresponding transition temperature. If a sufficiently "rapid quench" is applied to such a plasma, a possibility exists that the plasma may turn into a glassy state. In light of both the theoretical significance and the practical feasibility of the experimental study, it is essential to clarify the nature of the OCP in the supercooled state and to explore the possibility of a glass transition.

In the present paper we wish to develop a theory of dynamic correlations in the strongly coupled OCP within the generalized viscoelastic formalism,[11] in such a way that the existing MD simulation data for $\Gamma\leq160$ *both* on the dynamic structure factor[4] $S(k,\omega)$ and on the coefficient of shear viscosity[5] η are accurately reproduced. We then extend the theory to those plasmas in the supercooled state, and thereby investigate the behaviors of the radial distribution function $g(r)$, the static structure factor $S(k)$, and most importantly η; the possibility of a glass transition at $\Gamma=900$–1000 will be revealed in the dynamic properties through the variation of η. The lifetime of a metastable fluid state against a homogeneous nucleation of crystals is evaluated; the rate of rapid quench necessary for the formation of a glass is thereby estimated. These theoretical findings are finally compared with the experimental possibilities.

The improved hypernetted chain (IHNC) scheme[7] has reproduced almost exactly the existing Monte Carlo data[3] of $g(r)$ for $\Gamma\leq160$. In Fig. 1 we exhibit the results of the IHNC calculations extended to those plasmas in the supercooled state. We clearly observe a splitting of the second peak and structural developments around the third peak in $g(r)$ as Γ increases to and beyond 500. We have also computed the Wendt-Abraham ratio[12] $g_{\min}/g_{\max}$ between the first minimum and maximum in $g(r)$ for various Γ values, to find a slight but unmistakable kink at a Γ value between 300 and 400. Those indications may be interpreted as precursors in the static correlations signaling a dynamic glass transition at a still larger value of Γ. We add a remark that the IHNC results for $S(k)$ have also exhibited features quite analogous to Fig. 1.

The strong Coulomb-coupling effects are described in the present theory by the dynamic local-field correction $G(k,\omega)$, which is introduced via the wave-vector-**k**– and frequency-ω–dependent linear-response

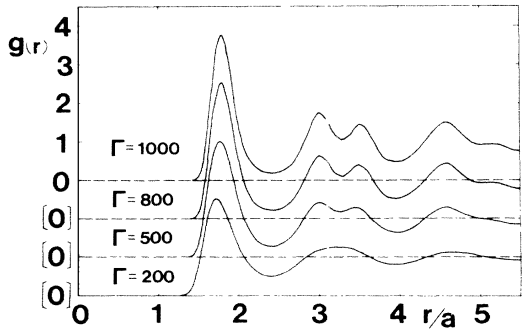

FIG. 1. The radial distribution function of the OCP at various values of Γ in the supercooled state calculated in the IHNC scheme (Ref. 7).

relation between the external potential $\phi_{\rm ext}(\mathbf{k},\omega)$ and the induced density fluctuations $\delta n(\mathbf{k},\omega)$ [2,13]:

$$\delta n(\mathbf{k},\omega)=\chi_0(k,\omega)\{\phi_{\rm ext}(\mathbf{k},\omega)+v(k)[1-G(k,\omega)]\delta n(\mathbf{k},\omega)\}.$$

Here $v(k)=4\pi(Ze)^2/k^2$ and $\chi_0(k,\omega)$ is the retarded free-particle polarizability[2]; the dynamic structure factor is calculated in terms of these functions and $G(k,\omega)$.

A solution to the kinetic equation with the collision term[14] (where $\mathbf{p}=m\mathbf{v}$),

$$\left.\frac{\partial F(\mathbf{p})}{\partial t}\right|_c = i\int d^3k\frac{v(k)}{(2\pi)^3}\int_{-\infty}^{\infty}d\omega\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{p}}\left[\frac{F(\mathbf{p})\delta(\omega-\mathbf{k}\cdot\mathbf{v})}{\tilde\epsilon(k,\omega)} + \frac{v(k)}{|\tilde\epsilon(k,\omega)|^2}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{p}}\frac{1-G(k,\omega)}{\omega-\mathbf{k}\cdot\mathbf{v}+i0}\int d^3p'F(\mathbf{p}')\delta(\omega-\mathbf{k}\cdot\mathbf{v}')\right], \quad (1)$$

yields the expression for the dimensionless shear viscosity, $\eta^*\equiv\eta/mn\omega_p a^2$, with $\omega_p=[4\pi n(Ze)^2/m]^{1/2}$; that is,

$$1/\eta^*=A_R+A_I, \quad (2)$$

where

$$A_R=\frac{12\sqrt{3}}{5\pi}\Gamma^{5/2}\int_0^\infty\frac{dx}{x}\int_0^\infty dz\frac{1-\mathrm{Re}G(x/a,\omega_0xz)}{|\tilde\epsilon(x/a,\omega_0xz)|^2}\exp(-z^2), \quad (3)$$

$$A_I=\frac{\sqrt{3}}{5\pi^2}\Gamma^{5/2}\int_0^\infty\frac{dx}{x}\int_{-\infty}^\infty dy\int_{-\infty}^\infty\frac{dz}{y-z}\left[(2z^2-2yz+3)\frac{\mathrm{Im}G(x/a,\omega_0xy)}{|\tilde\epsilon(x/a,\omega_0xy)|^2} - (2y^2-2yz+3)\frac{\mathrm{Im}G(x/a,\omega_0xz)}{|\tilde\epsilon(x/a,\omega_0xz)|^2}\right]\exp\left[-\frac{y^2+z^2}{2}\right], \quad (4)$$

$\omega_0=(k_BT/m)^{1/2}/a$, and $\tilde\epsilon(k,\omega)=1-v(k)[1-G(k,\omega)]\chi_0(k,\omega)$ is a dielectric screening function. Once $G(k,\omega)$ is known, η^* can be calculated through Eqs. (2)–(4). The function $G(k,\omega)$ and especially its imaginary part, in turn, depend on the values of η^* [see Eqs. (8) and (9) below]. A self-consistency requirement is thus imposed on Eq. (2), which is to be solved numerically by iteration.

The linearized viscoelastic equations of motion in the low-frequency and long-wavelength regime take a form[11]

$$mn\frac{\partial}{\partial t}\mathbf{u}(\mathbf{r},t)=-\frac{\partial}{\partial\mathbf{r}}\Pi(\mathbf{r},t),$$

$$\left(1+\tau_m\frac{\partial}{\partial t}\right)\left[\frac{\partial}{\partial\mathbf{r}}\Pi(\mathbf{r},t)-\frac{\partial}{\partial\mathbf{r}}P(\mathbf{r},t)+Zen\mathbf{E}(\mathbf{r},t)\right]=-\eta\frac{\partial}{\partial\mathbf{r}}\cdot\frac{\partial}{\partial\mathbf{r}}\mathbf{u}(\mathbf{r},t)-\left(\zeta+\frac{\eta}{3}\right)\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{u}(\mathbf{r},t).$$

Here the fluctuating quantities, $\mathbf{u}$, Π, P, and $\mathbf{E}$, represent the flow velocity, the isotropic part of the momentum flow tensor, the pressure, and the electric field, respectively; ζ and τ_m are the bulk viscosity and the viscoelastic relaxation time. In this formalism we find that

$$G(k,\omega)=\frac{k^2}{k_D^2}\left[1-\frac{1}{k_BT}\left(\frac{\partial P}{\partial n}\right)_T+\frac{i\omega}{nk_BT}\frac{\eta_l}{1-i\omega\tau_m}\right], \quad (5)$$

where $k_D^2=4\pi n(Ze)^2/k_BT$ and $\eta_l=\frac{4}{3}\eta+\zeta$ refers to the longitudinal viscosity. In the ensuing calculations we shall ignore ζ since it has been found[5,15] that ζ is negligible compared to η in the OCP.

In the viscoelastic theory the dynamic structure factor contains the quasielastic peak

$$S(k,\omega)\simeq\left(\frac{k}{k_D}\right)^4\frac{\eta_l}{\pi k_BT[1+(\tau_m\omega)^2]}. \quad (6)$$

In the limit of $\tau_m\to\infty$, which also implies that $\eta_l\to\infty$ [see Eq. (8) below], $S(k,\omega)\to nS_0(k)\delta(\omega)$. This limit thus corresponds to a frozen state[16] in which the local structure does not vanish even after an infinite time, or the expectation value $\langle\delta n(\mathbf{r},t)\delta n(0,0)\rangle$ stays finite for $t=\infty$; these features point to a dynamic transition to a glassy state.

We now generalize the viscoelastic formalism into a finite k and ω regime, so that $\eta_l(k)$ and $\tau_m(k)$ are

functions of k. In light of the compressibility sum rule[1,2] we note that

$$\frac{k^2}{k_D^2}\left[1-\frac{1}{k_B T}\left(\frac{\partial P}{\partial n}\right)_T\right] \rightarrow G(k)=1+\frac{k_B T}{n v(k)}\left[1-\frac{1}{S(k)}\right]. \tag{7}$$

The third frequency-moment sum rule[1,2] sets the relation

$$\eta_l(k)/\tau_m(k)=nk_B T(k_D/k)^2[G(k)-I(k)], \tag{8}$$

with

$$I(k)=\frac{1}{n}\int\frac{d^3q}{(2\pi)^3}\left(\frac{\mathbf{k}\cdot\mathbf{q}}{q^2}+\frac{\mathbf{k}\cdot(\mathbf{k}-\mathbf{q})}{|\mathbf{k}-\mathbf{q}|^2}\right)\frac{\mathbf{k}\cdot\mathbf{q}}{k^2}[1-S(|\mathbf{k}-\mathbf{q}|)].$$

Substitution of Eqs. (7) and (8) in Eq. (4) yields

$$G(k,\omega)=\frac{G(k)-i\omega\tau_m(k)I(k)}{1-i\omega\tau_m(k)}. \tag{9}$$

The only function that remains to be determined is $\tau_m(k)$. The relaxation time has been introduced to remove a certain rigidity inherent in the Navier-Stokes equation with regard to temporal response of the internal energy against the viscous motion of the fluid. Without it, the viscous motion cannot be made compatible with Eq. (6) or (8). We note that $\tau_m(k)$ should vanish as the size ($\sim k^{-1}$) of the fluctuation tends to zero.

The relaxation time $\tau_m(k)$ must be a positive-definite quantity for reasons of causality. To simulate the cage effect in dense liquid,[16] where a single particle has a tendency to be trapped by the surrounding particles, we adopt a Gaussian form, $\tau_m(k)=\tau_m \times\exp[-(ak/\xi)^2]$. The free parameter is adjusted to $\xi=2.7$, so that the computed results of η closely reproduce the existing MD values[1,5] for $\Gamma\leq 100$ (see Fig. 2). We have confirmed that the resulting values of $S(k,\omega)$ likewise reproduce the MD simulation data.[1,4]

To show an approach to a glassy state at $\Gamma=900$–1000, we plot the computed values of η^* as a function of Γ in Fig. 2. For comparison we also plot in the figure the values of η^* obtained by Wallenborn and Baus[17] and by the MD simulation.[5] At $\Gamma=900$–1000 we have separately confirmed that a δ-function–like quasielastic peak has developed in the calculated results of $S(k,\omega)$.

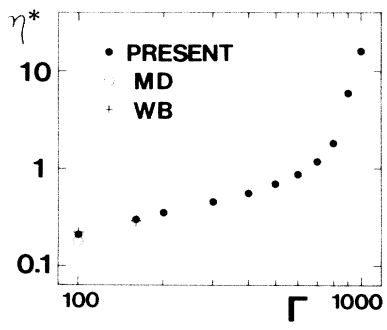

FIG. 2. The normalized shear viscosity $\eta^*=\eta/mn\omega_p a^2$ calculated in the generalized viscoelastic theory (filled circles). The crosses refer to the calculations in Ref. 17 and the open circle to the MD simulation result (Ref. 5).

The coefficient D of self-diffusion is evaluated by evoking the correspondence[2] between a strongly coupled OCP with $\Gamma\gg 1$ and a hard-core system with an effective radius σ, as established, e.g., in the variational calculation.[18] The Stokes-Einstein relation,[19] $D=k_B T/6\pi\eta\sigma$, then connects η with D.

The probability of homogeneous nucleation of crystals with radius r is analyzed in the same way as reported earlier,[10] in terms of the minimum work $R_{\min}(r)$ necessary for creation of such a nucleus and the associated critical radius of nucleation, $r_{cr}/a=k_B T(4\Gamma/3\Gamma_m)/(\mu_F-\mu_C)$. The chemical potential μ_F in the supercooled fluid phase, $200\leq\Gamma\leq 1000$, has been calculated in two ways: by extrapolation of the fluid free-energy formula of Slattery, Doolen, and DeWitt[3] and by actual performance of the coupling-constant integration of the IHNC interaction energies. The maximum discrepancy between the two is 0.15% at $\Gamma=1000$. The chemical potential μ_C in the crystalline phase has been given by Slattery, Doolen, and DeWitt.[3]

In Fig. 3 we plot the computed values of the diffusion time $t_D=r_{cr}^2/D$ and the nucleation time $t_N=t_D\exp[R_{\min}(r_{cr})/k_B T]$. We observe large discrepancies between the solid curves (the IHNC results) and the dashed curves (extrapolation of the fluid formula), despite the fact that the free-energy differences have been confined within 0.15%. To close those gaps, extremely accurate equations of state for both the supercooled-fluid and the crystalline OCP's would have to be derived, which would call for further developments in the computer simulation work and the analytic theory. We may nevertheless conclude from Fig. 3 that $\omega_p t_N$ takes on a minimum value somewhere between 10^9 and 10^{13} at $\Gamma\simeq 400$; an OCP with $\Gamma>400$ thus departs from a simple supercooled

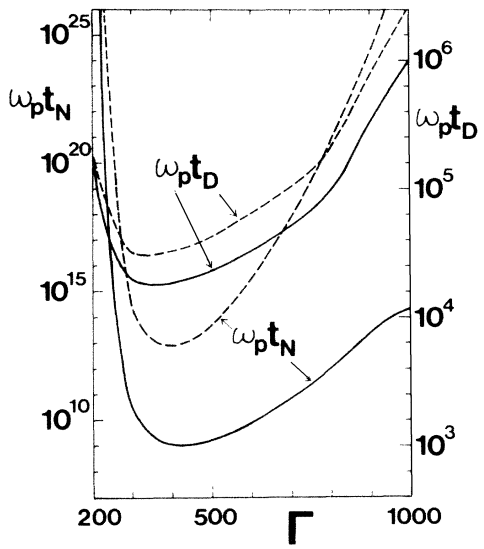

FIG. 3. The diffusion time t_D and the nucleation time t_N in units of the plasma time ω_p^{-1}. The solid curves refer to the results based on the IHNC free energies and the dashed curves to the extrapolation of the fluid formula due to Slattery, Doolen, and DeWitt (Ref. 3).

state and enters a glassy state.

Finally, we remark on the experimental possibility of realizing such an OCP glass. For such a purpose the ion plasmas produced recently by Bollinger and Wineland[9] appear most promising, because of the smallness of the plasma frequency ($\omega_p \simeq 4.4\times 10^7$ s^{-1} for a $^9Be^+$ plasma at $n \simeq 10^{10}$ cm^{-3}). Those authors have already created and stably maintained ion plasmas at $\Gamma = 5$–10 for many hours; they contemplate achieving a Γ value of $\sim 10^4$ by an ultimate use of the laser-cooling technique and the increased strength of the confining magnetic field. If the cooling can be administered sufficiently fast to overcome the minimum value of t_N in Fig. 3 [$2\times(10$–$10^5)$ s for the aforementioned $^9Be^+$ plasma], then a highly viscous glassy OCP may be realized in the laboratory. The present theoretical estimates may also provide a guide to design a molecular-dynamics simulation experiment for a glass transition in an OCP system, similar to the one performed recently in a metallic system.[20]

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