Nucleation of long-range order in quenched Yukawa plasmas

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We discuss the nucleation from glassy to crystalline order in quenched one-component Yukawa plasmas as studied by molecular dynamics. Rapid quenches from $T \geq 4T_{\text{melt}}$ to $T \leq 0.5T_{\text{melt}}$ were studied and a range of Yukawa exponents were considered for systems with up to 10 000 particles. We report on the effect of system size on nucleation and the relevance of classical nucleation theory to the observed nonequilibrium dynamics.

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The one-component plasma (OCP), i.e., interacting charged particles in a nonresponding background of opposite charge, is of interest in areas as diverse as the astrophysics of compact objects [1], the interaction of laser radiation with condensed systems, and the kinetics of colloidal suspensions [2]. Although the equilibrium properties of this system have been studied for many years [3], it is only recently that the nonequilibrium properties have been addressed [4].

We report here on a study of the homogeneous nucleation of crystalline order in a rapidly quenched Yukawa plasma using molecular dynamics (MD) simulations. There have been a number of studies of the problem of homogeneous nucleation using MD [5–12]. Most of these have considered the Lennard-Jones system or a short ranged, hard-core potential. For shallow quenches, these studies are consistent with classical nucleation theory while for deep quenches ($T_{\text{quench}}/T_{\text{melt}} \leq \frac{1}{2}$), the interpretation has been less clear. System size is always an issue in simulations, particularly in homogeneous nucleation, since nonuniformities and boundaries induce, at an enhanced rate, catastrophic growth of the stable configuration from a metastable parent. Some authors have argued that the onset of catastrophic crystal growth is an artifact of periodic boundary conditions rather than the formation of a critical fluctuation [8,9]. Others have argued that size dependence and critical droplet morphology might be affected by the existence of a "pseudospinodal" in the phase diagram with such effects becoming more pronounced as the interaction range increases [13]. There have also been indications that for deep quenches, the nucleating droplet exhibits a ramified structure over a large portion of the computational cell [11]. The purpose of the present study has been twofold: (1) to determine the magnitude of the waiting time for the appearance of an unstable fluctuation in a rapidly quenched Yukawa OCP and (2) to determine the properties of the mode of development of long-range correlations in a system interacting with a longer-range potential.

The pair potential which we consider is given by

$$\varphi(r_{ij}) = \varepsilon(r_0/r_{ij})\exp(-\alpha r_{ij}/r_0) , \tag{1}$$

where $\varepsilon = Z^2e^2/r_0$ is the interaction strength, Ze being the ionic charge and r_0 the length scale defined in terms of the ion number density n, that is, $1/n = r_0^3/\sqrt{2} = 4\pi a^3/3$, a being the Wigner-Seitz radius. We define the usual Coulomb plasma parameter $\Gamma = \varepsilon r_0/ak_BT$, with T the temperature and k_B Boltzmann's constant. We use units such that $\varepsilon = m = n = 1$. The unit of time is then $t_0 = n^{-1/3}(m/\varepsilon)^{1/2}$ and in these units, the ion plasma frequency is given by $\omega_{\text{pl}} = 3.756t_0^{-1}$. In the limit $\alpha \to 0$, the system approaches the OCP limit for which the critical Γ at melting is $\Gamma_c = 178 \pm 1$ [14].

For $\Gamma > \Gamma_c$, the OCP is known to crystallize in a bcc lattice. The internal and Helmholtz free energies are also accurately known [15] for both phases and it is therefore possible to estimate the nucleating time, i.e., the waiting time for the onset of catastrophic growth of the phase from the metastable quenched configuration, by means of classical nucleation theory [16]. This theory typically relates the rate of formation of a critical droplet of phase B (the final state) in phase A in the metastable configuration (n, T) by an activated Arrhenius expression

$$\tau_{AB}^{-1} = \tau_0^{-1}\exp(-\Delta F^{\dagger}/k_BT) , \tag{2}$$

where τ_0^{-1} is an attempt frequency for surmounting the free energy barrier along the appropriate path in configuration space and $\Delta F^{\dagger}$ is the free energy per atom of the critical nucleus relative to that of phase A, with due account taken for the surface energy of state B:

$$\Delta F^{\dagger} = (1/N)[F_B(n,T) + F_{S,B}(n,T) - F_A(n,T)] . \tag{3}$$

If the surface tension is known, then Eq. (3) may be evaluated using the results of Slattery, Doolen, and DeWitt [15] for F_A and F_B. $\Delta F^{\dagger}$ is proportional to the cube of the surface tension, and clearly, small changes in this quantity can produce large changes in τ_{AB}. One of the major uncertainties in Eq. (2) is the surface energy,

which is not known for the Yukawa system. The purpose of this present set of simulations is to find values for τ_{AB} without relying on Eq. (2).

Our MD approach employs Nosé-Hoover dynamics [17,18] to maintain the system at constant temperature. Periodic boundary conditions were employed, and the equations of motion were solved using a central difference algorithm with a time step $\Delta t = 0.03 t_0$ in most of the runs, although time steps of $0.005 t_0$ were used in some of them. The potential was truncated at a radius $r_{\max}$ such that $\varphi(r_{\max})/\varphi(a) \leq 10^{-4}$ and was shifted by $-\varphi(r_{\max})$ to obtain a continuous potential. The number of neighbors a given particle interacts with depends on the screening parameter α; typical numbers are 1000 for $\alpha=1$ and 600 for $\alpha=2$. We start from a fluid state obtained by melting and equilibrating a bcc or fcc crystal configuration to $\Gamma=40$ for $300 t_0$. The quenching procedure consists of setting the thermostat reference temperature to the desired value and letting the system evolve at this temperature. The kinetic temperature of the particles settled to the reference value within a time of $50 t_0$, with fluctuations of order $1/N^{1/2}$. We refer to this as a *rapid quench*. We explored rapid quenches within the range $350 \leq \Gamma \leq 850$.

Figure 1 shows the times for catastrophic nucleation in $N=1024$ simulations, as determined from the onset of the sharp decrease of internal energy with time. These show a marked minimum, which for $\alpha=1$ occurs at $\Gamma \approx 400$. The final configuration for $\alpha=2$ and 3 was bcc with few defects, in agreement with the phase diagram for Yukawa systems obtained by Kremer, Robbins, and Grest [19]. For $\alpha=1$ on the other hand, the final configurations were distorted fcc structures. The range in minima of nucleation times is from $\tau=300 t_0$ for $\alpha=1$ to $\tau=800 t_0$ for $\alpha=3$, with the value of Γ at the minimum of τ ranging from $\Gamma=400$ for $\alpha=1$ to $\Gamma=800$ for $\alpha=3$. If we use $T_{\text{melt}}(\alpha)$ from Ref. [20], these values of $\Gamma_{\min}(\alpha)$ are from 2–2.5 $\Gamma_{\text{melt}}(\alpha)$. It is of interest to compare these results with the predictions of Eq. (2) for the OCP. If we assume that the surface energy is proportional to the melting temperature [21] with proportionality coefficient λ, i.e., $F_{S,B} = 2\lambda N k_B T_{\text{melt}}$ and take $\tau_0^{-1} = \omega_{\text{pl}}$, then in order for the magnitude of the waiting time to be correct, $\lambda \approx 0.72$, which results in a critical radius $r_{\text{crit}} \approx 2.6$, corresponding to a critical cluster of about 80 atoms. One may question the validity of the classical description for so small a cluster size. However, it is interesting to note that, according to this analysis, the minimum for τ for the OCP occurs at $\Gamma \approx 395$, close to the $\alpha=1$ result for our Yukawa system, and also consistent with recent Monte Carlo results for the OCP of DeWitt, Slattery and Yang [22]. A full comparison with Eq. (2) requires free energies, which are at present unavailable for the fluid state.

Estimates from classical nucleation theory give rather small critical nuclei and indicate that, at least for the initiation of growth, we are not size-dominated for a system size of $N=1024$. It is nevertheless important to assess such effects. We have therefore carried out simulations of systems with $N=432$, 1024, 3456, and 10032 particles, for $\alpha=2$ and $\Gamma_{\text{final}}=425$. We have monitored several quantities sensitive to local- and long-range order: the mean square displacement, the x-ray structure factor $S(\mathbf{q},t) = (1/N)^2 \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \rangle$, its angular average $S(q,t)$, and the pair distribution function $g(r)$.

Figure 2 shows the internal energy per particle as a function of time after quench. The final state for the largest system ($N=10\,032$) is dramatically different from the smaller size systems. For $N=432$, 1024, and 3456, the final configuration is a nearly monolithic bcc crystal. For $N=10\,032$, on the other hand, the system comes to metastable equilibrium as a mosaic crystal with microcrystalline regions of size $N \approx 500$ which remained stable: the internal energy versus time was very nearly constant (see Fig. 2) for as long as we were prepared to continue the simulation. In this configuration, there are also regions of fcc coordination. This is the predominant effect of system size in our simulations. The time at which a rapid drop in the internal energy occurs is a global measure of a nucleation time. The actual instability, we believe, occurs at earlier times. To investigate this, we divided the periodic computational cell into subcells of size $N_{\text{cell}} \approx 125$ and chose that subcell which exhibited the greatest order, as determined by the appearance of stable

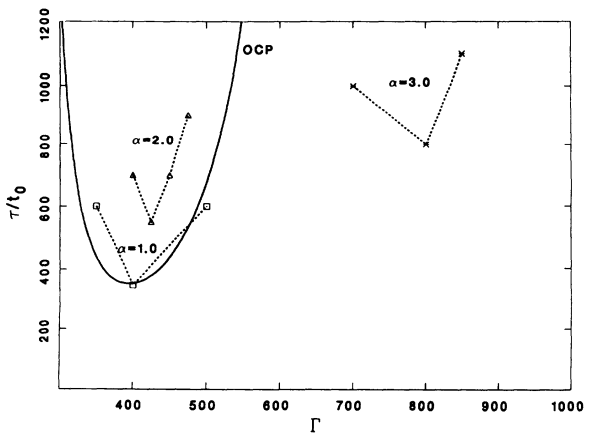

FIG. 1. Onset of catastrophic growth (τ) vs Γ:$\alpha=1$ (squares); $\alpha=2$ (triangles); $\alpha=3$ (asterisks); OCP limit ($\alpha=0$, solid line) from Eq. (2).

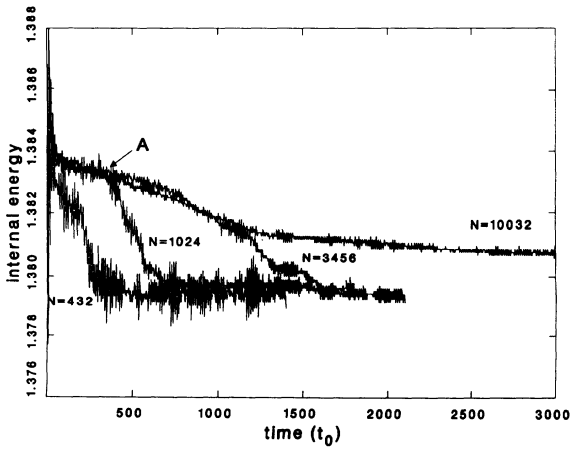

FIG. 2. Internal energy per particle, in units of ε, as a function of time for various system sizes, all with $\alpha=2$ and $\Gamma=425$.

peaks in $S_{\text{cell}}(\mathbf{q},t)$ for that subcell. For this subcell, we monitored the value of a local order parameter, $\eta_{\mathbf{q}}=\max_{\mathbf{q}}(1/N_{\text{cell}})^2\langle\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\rangle_{\text{cell}}$, where $\mathbf{q}$ ranges over a sphere of radius q and $\langle\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\rangle_{\text{cell}}$ is computed on the subcell of size N_{cell}. Figure 3(a) shows $\eta_{\mathbf{q}}(t)$ for two different-sized systems. For $N=10032$ there is an instability at $\sim 200t_0$ and for $N=1024$ at $\sim 400t_0$. The intermediate case of $N=3456$ begins to transform at an intermediate time, $\sim 300t_0$. In all systems there is a delay from the time of quench to the time at which an instability occurs. This is to be contrasted with what is observed in Lennard-Jones systems, where nucleating droplets appear soon after quench [9–11]. In the smaller-size system, growth leads to a single crystallite. We conclude that the sudden catastrophic crystallization into a nearly monolithic bcc crystal observed in the smaller systems ($N=432$, 1024, and 3456) is caused by system size dependencies and possibly triggered when single crystallites grow to sizes comparable to the size of the computational cell. The size of the largest system is sufficient to allow the boundary energies of independent crystallites to adjust and stabilize a polycrystal. This system-size behavior can be seen more clearly in Fig. 3(b), which shows the angle-integrated structure factor $S(q_{\text{bcc}},t)$ as a function of time t for three different system sizes. There is a growth region with nearly the same rate (slope) in all three cases and a transition region, which seems to depend on system size. (The linear slope is consistent with a domain growth law of the Lifshitz-Slyozov type [23] in which linear domain size increases at $t^{1/3}$. We do not

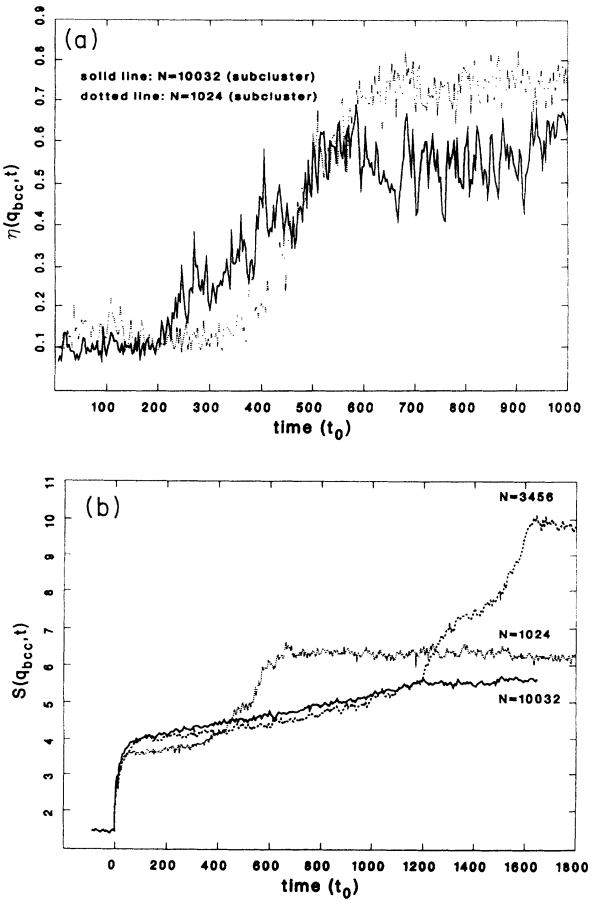

FIG. 3. (a) Parameter $\eta_{\mathbf{q}}$ as a function of time for a subcluster in two different systems for $N=10032$ (solid line), and $N=1024$ (dotted line); the curves have been smoothed for clarity. (b) Angular-averaged structure factor $S(|\mathbf{q}|=q_{\text{bcc}},t)$ for $N=10032$ (solid line), $N=3456$ (dashed line), $N=1024$ (dotted line).

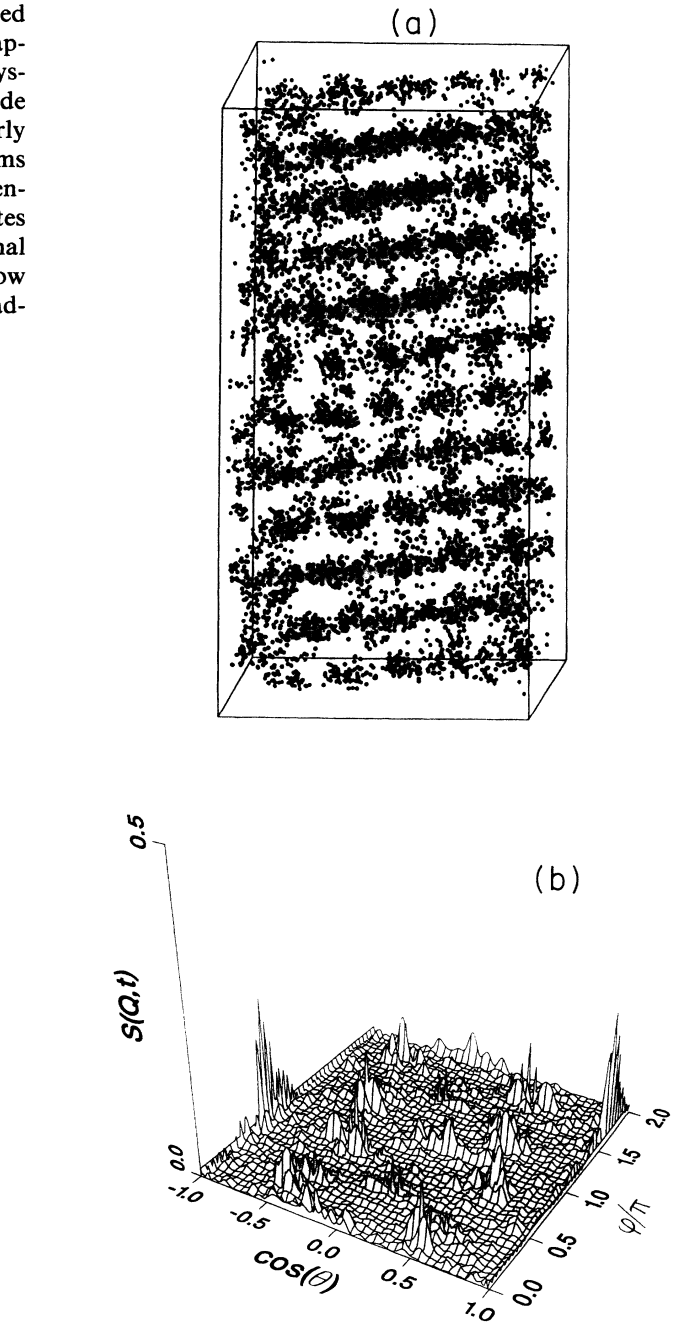

FIG. 4. (a) Section of $N=1024$ system showing superimposed atomic positions from 20 frames in the time interval $(340–400)t_0$; the section has edges [5,10,10] and the viewpoint is at (87, −5, −9). (b) X-ray structure factor $S_{\text{cell}}(\mathbf{q},t)$ for the region shown in (a) at $t=396t_0$ and with $|\mathbf{q}|=q_{\text{bcc}}=7.052\,64$.

know the detailed nature of the "domain" that is growing, however). The transition into a nearly perfect crystal occurs earlier for the smaller $N=1024$ system than for the $N=3456$ case. The picture which emerges from the size-dependent studies is that for systems of size $N>1000$, an instability occurs at times in the range $200t_0-400t_0$ and that smaller systems with a reduced phase space may give an upper bound to homogeneous nucleation times, provided the range of the potential is sufficiently small relative to the periodic computational cell size.

Simulations such as these are capable of shedding light on the modes of instability which are important in constructing continuum, or Landau-Ginzburg theories of the kinetics of crystallization. In the fluid state, real-space variables are appropriate, and in the ordered phase, spectral weight is concentrated in a reduced space of modes indexed with $\mathbf{q}$. In the Yukawa systems for the range of α studied, we have found a striking tendency to form planar order and twist boundaries as precursors to full bcc order. This is particularly apparent in the $N=1024$ system. Figure 4(a) shows a view of a remapped section of the original computational cell containing 512 atoms. it is a time lapse exposure, i.e., a composite of 20 snapshots taken every $3t_0$ from $t=340t_0-400t_0$ (around the position labeled A in Fig. 2). If we had a crystalline system, properly oriented, this figure would show Debye-Waller spheres of points with the spheres arranged on a lattice. In this time interval, although there is clearly no lattice and there is substantial diffusive motion, planes are already evident. Figure 4(b) shows $S(\mathbf{q},t)$ at time $t=396t_0$ averaged over $9t_0$ for $|\mathbf{q}|=q_{\rm bcc}$. The $(\mathbf{q},-\mathbf{q})$ pair of peaks correspond to the set of planes evident in Fig. 4(a). As time progresses, the planes become more coherent. and a twist boundary appears, separating two regions of [110] planes, with a twist angle of $\sim 81°$. One of these regions grows at the expense of the other, until at the latest stage ($t=1800t_0$), eight of the eleven [110] planes have perfect bcc coordination while three are defective. These defective planes are the reason that the final value of $S(q,t)$ in Fig. 3(b) is ~ 6 rather than the value 10 reached by the $N=3456$ system, where the final configuration is a nearly perfect bcc crystal. In the larger systems, the fluctuating boundary regions on a local scale make this kind of analysis more complicated. It is interesting to note in this context that in these Coulomblike systems, the transverse and longitudinal phonon frequencies differ substantially [20] and shear motion is relatively easy.

In conclusion, we have carried out simulations for deep quenches in one-component Yukawa plasmas in the range $\Gamma=350-850$ and for exponents $\alpha=1-3$. The majority of these simulations have been done in the canonical ensemble (constant volume V and constant temperature T). A smaller number of runs were done in the isobaric-isothermal ensemble (constant hydrostatic pressure P and constant T), as a further check on boundary or system size effects. The results in all cases showed no qualitatively significant differences. We find rapid nucleation times $\leq 10^3\,\tau_{\rm plasma}$ and polycrystalline final states for the largest systems, with bcc grain sizes of order $N\sim 500$. The nucleation time for fixed screening α is a strong function of Γ and shows a minimum, which for smaller α approaches that predicted by classical nucleation theory for the one-component plasma. In the transition region where long-range order is nucleating, we find a tendency for planar formation, rather than droplet growth mediated by a diffusive surface. System sizes of order $N\sim 1000$ are sufficient to estimate this instability for the range of α considered, but in order to describe the later stage domain growth, larger systems ($N>4000$) are necessary.

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