Plasma-Dust Crystals and Brownian Motion

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In the plasma-dust system Brownian motion replaces thermal agitation, because the strong friction of the air robs the dust of its kinetic energy almost instantly. Numerical simulation shows that, in the presence of Debye screening, a liquid-solid transition may take place when the Coulomb potential is extremely strong, in accord with experimental observations.

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In recent years there has been considerable interest in using macroscopic physical systems as models of molecular systems. Usually, a model system of this kind comprises small particles made from polymer or other material several microns in size, sandwiched between plates, suspended in a liquid or laid on an air-liquid interface [1]. Another example, which is perhaps more spectacular, involves electrically charged fine dust floating in a plasma generated by a rf electromagnetic field [2–5]. Great insight into phase transitions, including melting, condensation, etc., has been gained from these models. One the other hand, some discrepancies between experiment and theory have also become apparent. In particular, conditions for "crystallization" to take place in the plasma-dust system [3,4] appear to be vastly different from theoretical predictions [6,7]. This Letter addresses this problem; the principles involved may, however, be applied to problems in other systems.

Essentially the present study concerns the relative significance of Coulomb interaction and random agitation. At the molecular level, agitation arises from the kinetic energy of ions, and the balance between the Coulomb potential and this energy is conventionally measured by a parameter $\Gamma = Q^2/4\pi\varepsilon_0\Delta kT$, where Q is the charge of the ions, ε_0 the vacuum permittivity, k Boltzmann's constant, T the absolute temperature, and Δ the average separation between ions. It was found through experiments that if T was taken to be the so-called particle temperature, charged dust particles formed a structure described as a crystal when $2.1 \times 10^3 < \Gamma < 1.6 \times 10^4$ [3] or $\Gamma \sim 10^6$ [4]. The plasma-dust system is also characterized by another dimensionless parameter $\kappa = \Delta/\lambda$, where λ is the Debye length, and $0.6 \leq \kappa \leq 4.8$ in Ref. [3] and $\kappa \sim 9.8$ in Ref. [4]. But previous numerical simulations suggest that crystallization requires $\Gamma \approx 99$ when $\kappa = 0.7$, $160 < \Gamma < 850$ when $1 < \kappa < 5$, and $\Gamma = 4.8 \times 10^4$ when $\kappa = 10$ (using the standard definition of Γ) [6,7].

We wish to draw attention to the importance of Brownian motion in various macroscopic models where particles are not in a vacuum but in a gas or other medium, so that the very idea of kinetic energy must be treated with caution. Dust has a large surface area for its size giving significant friction: Even in a gas the viscosity coefficient reaches a typical value of about $4 \times 10^3\ s^{-1}$ at room temperature, sufficient to rob dust of its kinetic energy almost instantly. Therefore random agitation in a macroscopic system arises, not from kinetic energy, but from asymmetric molecular bombardment, which counteracts the ordering influence of the Coulomb force. We cannot use Γ as it has been used in the previous analysis. Furthermore, it is easier for the Brownian motion to destroy an ordered structure. A crystal will melt once the random displacement of its constituent particles is comparable in size to a lattice constant [8]. For a harmonic oscillator in a vacuum a definite energy barrier can never be passed, so that the displacement is strictly limited. But for a Brownian particle there is always a chance to overcome an energy barrier, regardless of its height [9]. We find through numerical simulation that when κ is relatively large ($\sim$4.8), Γ must be extremely high ($\sim 10^4$) for the plasma-dust system to become ordered, which is compatible with experiments.

We first review briefly the experiments on plasma-dust crystals [2–5], with particular reference to the work of Thomas *et al.* [3]. The pressure of the working gas was usually between 0.13 and 2.1 mbar, the plasma was generated by a rf discharge, typically of 2–5 W at 14 MHz, and the ion density was about 2×10^8-$10^{10}\,cm^{-3}$. The colloidal dust was SiO_2, TiO_2, or polymer particles, either formed in reactions in the working gas or introduced from outside. Because of the effect of electrostatic equilibrium, the dust acquired net charge, which was normally negative and large (e.g., 10^3 to 10^4 electrons on particles of 1 μm diameter). A negatively charged electrode kept the dust afloat. The dust formed a thin disk-shaped cloud, approximately 3 cm in diameter, comprising about 18 planar, horizontal layers of particles parallel to the electrode. In the layers particles tended to form lattices, mainly sixfold coordinated, in which the particles oscillated gently about fixed equilibrium positions. Occasionally a particle diffused through the structure and caused disturbance to the nearest particles. The particle temperature was around room temperature. Gravity plays no significant role in the structure and dynamics within the 2D layers, which were studied experimentally.

To simulate the above plasma-dust system, we treat mechanical friction, electrostatic repulsion, and Debye shielding separately. This treatment is justified as follows. Ac-

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cording to Thomas *et al.* [3] the electron temperature of the plasma is about 3 eV, equivalent to about 3.5×10^4 K. Although this is about 10^2 times higher than the temperature of positive ions and neutral molecules, the density of the electrons is merely 10^9 cm^{-3}, about one in every 5.4×10^7 molecules of the gas at 2 mbar [3]. Furthermore, most electrons are much cooler, due to the so-called double Maxwellian distribution of electron energy in rf discharge [10]. The bombardment of the electrons will make no noticeable difference to the movement of the dust, so that we can disregard the plasma effect in considering friction. On the other hand, it appears reasonable to assume uniform dust charge, because the dust is confined in a well-defined and stable structure, indicating that the local electrostatic field is also stable. The reason for the stability of the local field lies in the strong friction, which forces dust particles to move locally and gently, as observed experimentally [3], as well as from our numerical simulations. We may appreciate this gentleness quantitatively through Einstein's formula $\langle|\mathbf{r} - \mathbf{r}_0|^2\rangle = 6Dt$, where $\mathbf{r}_0$ is the initial position of a Brownian particle which moves to $\mathbf{r}$ after time t and D is the diffusion coefficient of the particle [9]. Typically $D = 3.4 \times 10^{-12}$ m^{2}s^{-1} giving an rms displacement of 4.5 μm in 1 s, compared to the average interparticle distance of 250 μm, and the dust cloud diameter of 3 cm [3]. Therefore neither the change of the Coulomb force due to Brownian motion nor the effects of the edge of the cloud are important. This facilitates our programming, as no difficulty has been encountered in determining a time step, during which the Coulomb force is approximately constant. In fact, the Coulomb force, if reasonably strong, is always fairly constant, because, lacking a Maxwellian demon, Brownian motion cannot pack dust particles together to cause a significant local electrostatic disturbance. Electrostatic equilibrium is thus maintained, and there is no need to link the particle charge and the Debye shielding with dust movement. Indeed various authors have calculated the particle charge without considering dust agitation [2–4].

The Brownian motion of a dust particle is determined by the Langevin equation

$$\frac{d}{dt}\mathbf{v} = -\beta\mathbf{v} + \frac{1}{m}\mathbf{F} + \mathbf{A}(t), \tag{1}$$

where $-\beta\mathbf{v}$ represents a dynamic friction experienced by the particle, m the particle mass, $\mathbf{F}$ the external force, and $\mathbf{A}$ the Brownian acceleration, which can be seen as a chain of random impulses of infinitely short duration [9]. If we integrate Eq. (1) over a time interval t, then $\mathbf{A}$ gives a chain of random speeds, which leads through the theory of Markoff chains to a nondeterministic "solution" for $\mathbf{v}$, that can take any value with probability

$$W(\mathbf{v}, t; \mathbf{v}_0) = \sqrt{\frac{m}{2\pi kT(1 - e^{-2\beta t})}} \times \exp\left[-\frac{m|\mathbf{v} - e^{-\beta t}\mathbf{v}_0 - (\mathbf{F}/m\beta)(1 - e^{-2\beta t})|^2}{2kT(1 - e^{-2\beta t})}\right]. \tag{2}$$

Here $\mathbf{v}_0$ is the initial speed of the particle, t is short enough that the external force $\mathbf{F}$ is approximately constant, and T stands either for the particle temperature or for the temperature of the medium, because they are the same in both the theory of Brownian motion [9] and experimental observations [2,3]. Equation (2) is justified by the fact that it reduces to the Maxwellian distribution when $\mathbf{F}$ is negligible and $\beta t \gg 1$. This means that, in the absence of an external force, the particles behave like gas molecules when exposed long enough to the frequent and asymmetric molecular bombardment. To further our understanding, we note that in the case of a 2D particle assembly Eq. (2) is integrable. This allows us to use the Box-Muller method [11] to represent $\mathbf{v}$ by a deterministic value and a random perturbation, so that

$$\mathbf{v} = \mathbf{v}_0 e^{-\beta t} + \frac{t}{m}\mathbf{F}\frac{1 - e^{-\beta t}}{\beta t} + \sqrt{\frac{2kT}{m}(1 - e^{-2\beta t})}(\mathbf{x}\cos\theta + \mathbf{y}\sin\theta)\sqrt{\ln\frac{1}{\rho}}, \tag{3}$$

where ρ and θ are random variables distributed uniformly in [0,1] and [0,2π], respectively. Here (and below) we retain the form βt, which is dimensionless, so that the physical meaning of various terms is more apparent. The first two terms on the right-hand side of Eq. (3) represent deterministic movement of the particle given by the mean value of the random variable in Eq. (2). The last term of Eq. (3) represents the effect of Brownian accelerations, given by the standard deviation of Eq. (2). Similarly, the position of the dust particle is found to be

$$\mathbf{r} = \mathbf{r}_0 + t\mathbf{v}_0\frac{1 - e^{-\beta t}}{\beta t} + \frac{t^2\mathbf{F}}{m\beta t}\left[1 - \frac{1 - e^{-\beta t}}{\beta t}\right] + t\sqrt{\frac{4kT}{m\beta t}\left[1 - 2\frac{1 - e^{-\beta t}}{\beta t} + \frac{1 - e^{-2\beta t}}{2\beta t}\right]} \times (\mathbf{x}\cos\theta + \mathbf{y}\sin\theta)\sqrt{\ln\frac{1}{\rho}}, \tag{4}$$

which also includes deterministic and random parts. Equations (3) and (4) are semianalytic difference equations, in which t stands for one time step. The last terms of these two equations are the integration of the random acceleration in the Langevin equation. Statistically, the outcomes of Eqs. (3) and (4) are always correct, so long as the external force $\mathbf{F}$, from Coulomb repulsion among particles, does not change significantly during the time step. Here $\mathbf{F} = -\nabla\Phi$ with

$$\Phi(\mathbf{r}_k) = \frac{Q^2}{4\pi\varepsilon_0}\int_A \frac{\exp(-|\mathbf{r}_k - \mathbf{r}'|/\lambda)}{|\mathbf{r}_k - \mathbf{r}'|} \times \sum_{j\neq k}\delta(\mathbf{r}_j - \mathbf{r}')\,d\mathbf{r}' \tag{5}$$

standing for the screened potential at the kth particle, δ is Dirac's delta function, A is the area of integration centered at $\mathbf{r}_k$, which in practice can be a circle of a finite radius, and the summation of over all but the kth particle. Equation (5) is in the form of convolution to facilitate later explanations. Equations (3)–(5) suffice to describe the plasma-dust or other macroscopic systems. Letting $\beta \to 0$, they reduce to the equations of motion in a vacuum [7]. But for the plasma-dust system $\beta \gg 1$ holds, and different results may be expected.

We evaluate Eqs. (3) and (4) numerically for a 2D assembly of 625 particles. We use periodic boundary conditions, so that "mirror" particles are added whenever the integration area A in Eq. (5) extends beyond the square area of simulation. The diameter of A equals the width of the square, which has proved more than adequate. Parameters in the simulation are chosen to be similar to the data in [3], e.g., $\Delta = 250$ μm and $\kappa = 4.8$. We also take $a = 3.5$ μm for the radius of the particles and 1.57 g/cm^3 (Melamine $C_3H_6N_6$) for the density giving $m = 2.83 \times 10^{-10}$ g [12]. At $T = 300$ K, the viscosity coefficient of air is $\eta = 18.6 \times 10^{-6}$ N s/m^2, which leads through Stokes' formula to $\beta = 6\pi\eta a/m = 4.26 \times 10^3$ s^{-1}. It can be seen from Eqs. (3) and (4) that if we scale t to keep βt constant, then any change in η and hence β (if the change is not extreme) will have no effect, apart from the rate to reach equilibrium. Indeed β^{-1} is known as the relaxation time and is meant to scale the time [9]. The change in η is indeed modest for a range of gases, including Ar, N_2, etc. [12], so that our simulation is quite general. It is worth noting that, according to the classic view of the kinetic theory, the viscosity coefficient of a gas is almost independent of gas pressure, unless the mean free path of gas molecules ($\sim$70 μm at 2 mbar) is comparable with the size of the container [13]. Initially the particles are placed randomly and subsequently move on a 128×128 square grid, with a step size $\Delta/6$. While direct error analysis justifies this choice, we also tried different step sizes, as well as an off-grid simulation ($\mathbf{F}$ calculated exactly for each fresh arrangement of the particles), and the results were virtually the same. The reason appears to lie in the nature of the many-body problem, where the physical movements and numerical errors can be similar statistically. If the errors are Gaussian (or Maxwellian, a reasonable assumption), then they can be seen as a small temperature perturbation for the Brownian motion. The magnitude of the errors is not very important, so long as they do not accumulate. In our system the particle energy is heavily damped, so that errors inherited by the initial velocity $\mathbf{v}_0$ from previous steps of the difference scheme will disappear after a few iterations [see Eq. (3) where $\mathbf{v}_0$ is paired with a factor $\exp(-\beta t)$]. This also ensures the accuracy of $\mathbf{r}$ in Eq. (4), which is a simple integration of Eq. (3). Once the temperature is settled through the parameters of Brownian motion, the program does not need adjustment when it runs, in contrast to vacuum systems [6].

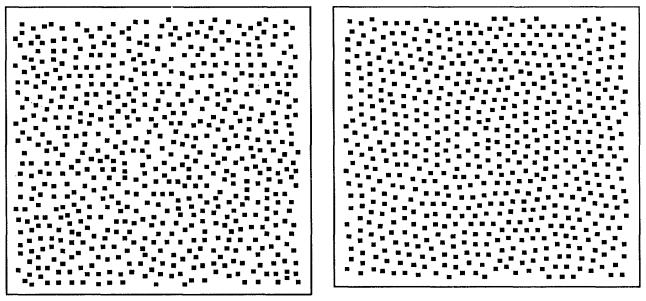

FIG. 1. Examples of the particle assembly at equilibrium for $\Gamma = 10^2$ (left) and $\Gamma = 10^4$ (right).

It was found that the numerical system takes some time to reach equilibrium, equivalent to a few seconds or more in real time. Typical snapshots of the system at equilibrium are shown in Fig. 1. Apparently the particles become ordered for $\Gamma \sim 10^4$ but never for $\Gamma = 10^2$. More subtle difference, however, require quantitative measurements. Figure 2 shows the Voronoi diagrams of the particle arrays, and Table I lists some statistics. We see that the percentage of cells with six neighbors increases from 52.3 to 88.6, as Γ increases from 10^2 to 10^5. This suggests a continuous increase of order, because in two dimensions cells with other than six neighbors represent defects. Figure 3 shows that the pair correlation function $g(r)$, which is the density of particles at distance r from a center, changes systematically as Γ increases. At first $g(r)$ is almost featureless, apart from the low r exclusion region, which reflects the fact that the particles are always

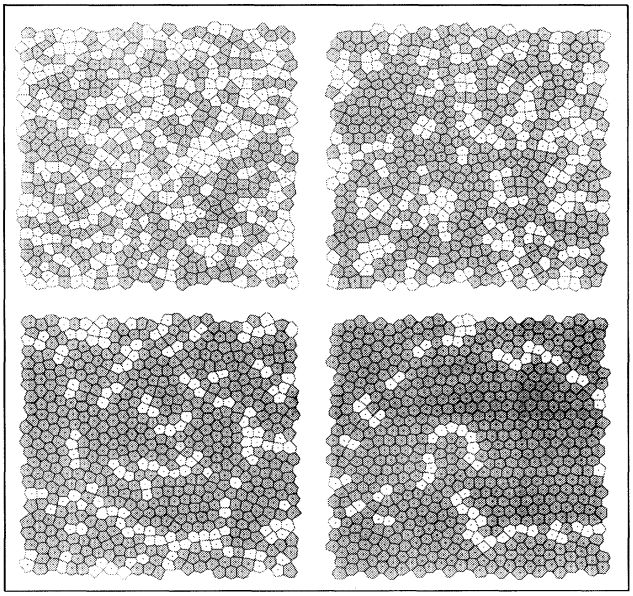

FIG. 2. Voronoi diagrams of the equilibrated system for $\Gamma = 10^2$ (upper left), $\Gamma = 10^3$ (upper right), $\Gamma = 10^4$ (lower left), and $\Gamma = 10^5$ (lower right). Cells with six neighbors are shaded.

kept apart at a fairly stable distance by the Coulomb force, which in tern is also fairly stable. This confirms the inability of Brownian motion to pack particles close together, as noted above. When the value of Γ increases a nearest-neighbor peak emerges, which grows in intensity as further oscillations appear, indicating the growth of longer range order in the system. As far as we are entitled to judge from simulations on this scale, it seems clear that $\Gamma \sim 10^4$ marks some sort of threshold for order to take place in the system. This threshold is related to the mass of particles. It is clear from Eqs. (3) and (4) that when we use $m^{1/2}\mathbf{v}$ and $m^{1/2}\mathbf{r}$ as the normalized values of $\mathbf{v}$ and $\mathbf{r}$, all the effects of m in these two equations are reduced to a ratio $\mathbf{F}/m^{1/2}$. Since the Coulomb interaction is characterized by Γ, after proper normalization, $\mathbf{F}/m^{1/2}$ is found to be proportional to $\Gamma/m^{1/2}$. Therefore, in order to let the system condense, we must, say double Γ if m is increased by four times. Effort was made to ensure our results represent genuine phase transitions. For example, in addition to letting the program run for up to a week (including hundreds of thousands of time steps), we reduced the value of Γ of the ordered system slowly. We found the system always melts below $\Gamma \sim 10^4$. Therefore the system cannot be in a metastable glassy state, which can only be reached by quenching from a liquid state. To compare with previous simulations, which are often in 3D, we turned off the Brownian acceleration by letting $\beta \rightarrow 0$ in Eqs. (3) and (4) and simulated the vacuum system in 2D. The system is no longer damped, so that the velocity of particles has to be normalized frequently [6]. We found condensation requires $\Gamma \sim 50$ when $\kappa = 0$ and $\Gamma \sim 600$ when $\kappa = 4.8$, which are comparable with the 3D results of Stevens and Robbins [6]. Thus dimensional change does not make much difference in Γ, Brownian motion does.

It was reported that the plasma-dust system became ordered when Γ was between 2.1×10^4 and 1.6×10^5 and κ between 0.6 and 4.8 [3]. In another report Γ and κ were 10^6 and 9.8, respectively [4]. We believe these results are supported by our simulations which, for the first time, provide an understanding of the apparently excessive values of Γ required for crystallization to occur. Differences remain; for example, Voronoi cells with other than six neighbors (i.e., defects) are more numerous experimentally [3] than in our simulationsfor $\Gamma = 10^4$. Probably it is easier to reduce defects in a small numerical system. Furthermore, the numerical system is free from any disturbance other than Brownian motion. But, according to Ref. [3], the rf electromagnetic field may disturb the experimental system: When the rf power was raised, particles moved more violently, and many appeared to have no equilibrium positions. Perhaps $\mathbf{F}$ in Eqs. (3) and (4) should be modified to simulate the rf field. In addition to the plasma-dust system, other macroscopic systems have been used to simulate phase transitions [1]; here thermal agitation is also replaced by Brownian motion, which may have important effects in both theory and experiment. Further work in this direction appears to be justified.

TABLE I. Distribution of different Voronoi cells (%).

Sides	4	5	6	7	8	9
$\Gamma = 10^2$	1.9	23.7	52.3	19.8	2.1	0.2
$\Gamma = 10^3$	0.0	16.5	69.1	14.4	0.0	0.0
$\Gamma = 10^4$	0.0	12.8	77.0	10.2	0.0	0.0
$\Gamma = 10^5$	0.2	5.9	88.6	5.3	0.0	0.0

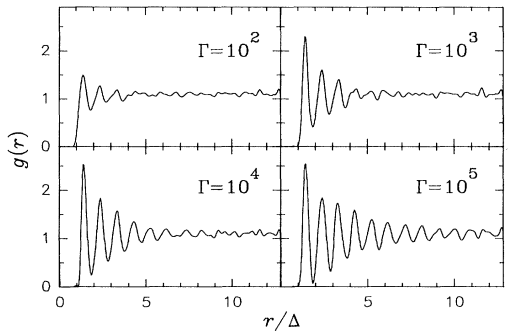

FIG. 3. Pair correlation functions of the numerical system for various Γ values, where r is normalized by Δ.

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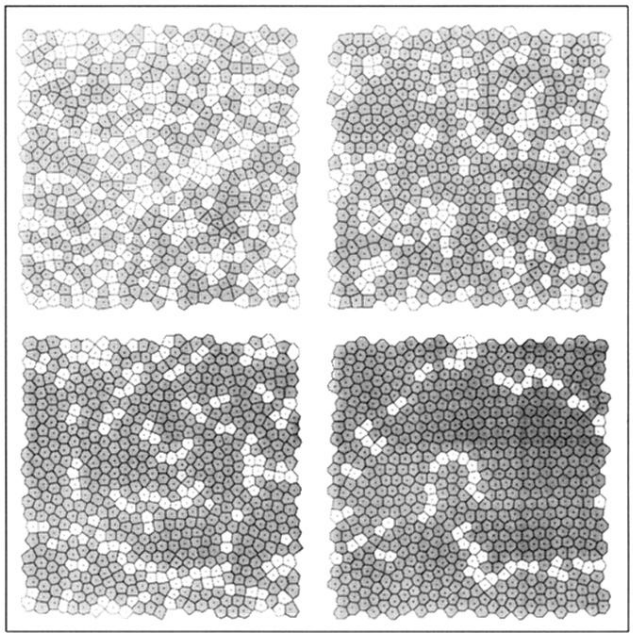

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