

Melting-freezing cycles in a relatively sheared pair of crystalline monolayers

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Abstract. – The nonequilibrium dynamical behaviour that arises when two ordered two-dimensional monolayers of particles are sheared over each other is studied in Brownian dynamics simulations. A curious sequence of nonequilibrium states is observed as the driving rate is increased, the most striking of which is a sliding state with irregular alternation between disordered and ordered states. We comment on possible mechanisms underlying these cycles, and experiments that could observe them.

Solid friction [1,2,3] and related problems involve the flow of ordered, deformable structures over or through an inhomogeneous medium [4] which may itself be either ordered or disordered. These physical systems are frequently modelled theoretically in one of two ways: (i) a driven Frenkel-Kontorova (FK) model [1, 5], where a density wave, in the form of a ball-and-spring array, is driven by a constant force over a substrate modelled by a periodic pinning potential, or (ii) molecular [6] or Brownian [8] dynamics studies of particles interacting with each other and the substrate via pair potentials. Among the most interesting phenomena seen in these systems are stick-slip [7, 6] and shear-induced melting [9, 10, 12, 11, 13]. It is clearly of great interest to find the minimal model system capable of showing phenomena such as these. In particular: (a) does stick-slip involve crucially the influence of the periodic potential of the crystalline confining walls on the film of confined fluid? (b) Is inertia essential? (c) Is a three-dimensional model necessary? In addition, the dynamics of ordered monolayers of surfactant or copolymer adsorbed onto two solid surfaces sheared past each other [14, 15] cannot adequately be described by approaches so far discussed in the literature. Accordingly, we report in this Letter a Brownian dynamics study of a model with two species of particles, 1 and 2, moving in two dimensions. The 11 and 22 interactions are identical, while the 12 interaction has the same form but is smaller by a factor ϵ . The 1 and 2 particles are driven in the $+x$ and $-x$ directions respectively under the action of a constant force of magnitude F , as in Fig.1. The

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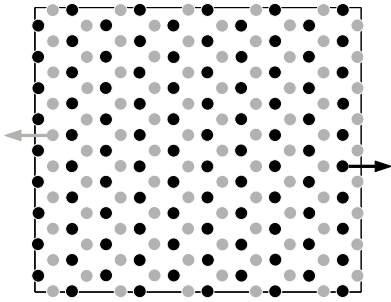


Fig. 1

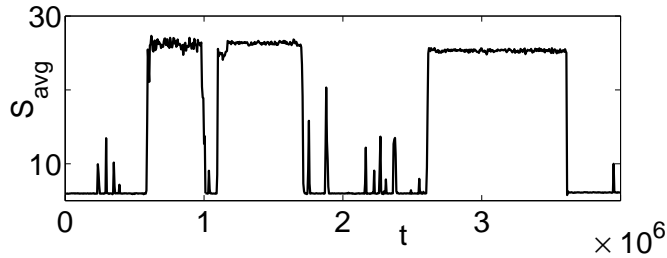


Fig. 2

Fig. 1 – Schematic diagram of the model.

Fig. 2 – The structure factor height (averaged over 1st ring of maxima) as a function of time in the melt-freeze cycle state, for $\epsilon = 0.05$.

physics of the third direction enters phenomenologically via ϵ , the relative strength of the 12 interaction: as the two planes of particles are pushed together with increasing normal pressure, their in-plane repulsion and hence ϵ will increase. While preparing this paper for publication we noted Ref. [16], which studies lane formation in inter-driven interacting Brownian particles. That work uses a model similar to ours, but well away from the regime where either species can crystallise.

Our main results are as follows: keeping interaction strengths and temperature fixed, the driving force F displays three threshold values F_i , $i = 1, 2, 3$. Our most striking observations are the melt-freeze cycles (Fig.2), to which we shall return. In sequence, however: For $F < F_1$, the drift speed v_d is effectively pinned at zero. In this regime, an initial poorly ordered configuration displays transient motion while settling down into a macroscopically ordered state, and then ceases to drift. For all $F > F_1$, $v_d > 0$, with a smooth onset (Fig.3) and enhanced velocity fluctuations (Fig.4) at F_1 . For $F_1 < F < F_2$ as well as for $F > F_3$, both 1 and 2 components are well-ordered, sliding crystals. For $F_2 < F < F_3$ we find striking cycles of melting and freezing, as signalled by the alternating growth and decay of the peaks in the structure factors or pair correlation functions for either species (Fig.2). In the course of these irregular cycles the observed structures range from highly crystalline to (anisotropic) liquid-like or perhaps smectic-like, and onsets of the change between these two states are not necessarily simultaneous for 1 and 2. Unlike in [6], it can be seen from the figure that the system spends *comparable* amounts of time in the ordered and disordered states. With time, columns of particles aligned normal to the mean drift start to undulate and, when this undulation builds up sufficiently, the whole system disorders abruptly. The thresholds F_i depend, of course, on the pair interactions. We are unaware of any other driven systems with *neither inertia nor a lubricating fluid film* which display such alternating *cycles of order and disorder as the persistent long-time state*. We defer to the end of this paper our qualitative explanation of the melt-freeze cycles, as well as an outline of possible experimental tests. Let us now present our study and its results in more detail.

The positions $\{\mathbf{R}^i(t)\}$, where the superscript $i = 1, \dots, N$ labels the particle, evolve according to overdamped Langevin equations, with independent Gaussian, zero-mean, thermal white noise sources \mathbf{h}^i , interparticle forces \mathbf{f}^i from the pair potentials, and equal and opposite constant external forces $\pm F\hat{\mathbf{x}}$ on the 1 and 2 species respectively. Let us nondimensionalise our variables as follows: scale all lengths by $\ell = (2\sqrt{3}n_0)^{-1/2}$, where n_0 is the mean number

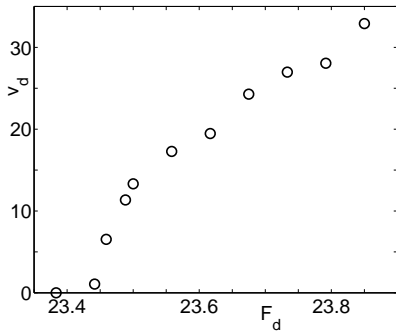


Fig. 3

Fig. 3 – Mean drift velocity at onset of smooth sliding regime.

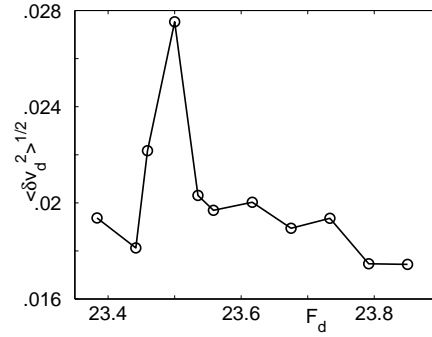


Fig. 4

Fig. 4 – RMS velocity fluctuations at onset of smooth sliding regime; $\epsilon = 0.02$.

density of either species, energy by Boltzmann’s constant k_B times temperature T (and hence force by $k_B T/\ell$), and time by $\tau \equiv \ell^2/D$, where D is the Brownian diffusivity. Then our nondimensional discretised Langevin equations are

$$\mathbf{R}^i(t + \delta t) = \mathbf{R}^i(t) + \delta t[\mathbf{F}^i + \mathbf{f}^i(\mathbf{R}(t)) + \mathbf{h}^i(t)] \quad (1)$$

where $\mathbf{F}^i = (-1)^{\alpha_i} F \hat{\mathbf{x}}$ is the external driving force on the i th particle of type α_i ($= 1$ or 2), $\mathbf{f}^i(\mathbf{R}^i) = -\sum_{j \neq i} \nabla_{\alpha_i \alpha_j} V_{\alpha_i \alpha_j}(\mathbf{R}^i - \mathbf{R}^j)$, and $\langle \mathbf{h}^i(0) \mathbf{h}^j(t) \rangle = 2\mathbf{l} \delta^{ij} \delta(t)$, \mathbf{l} being the unit tensor⁽¹⁾. The dimensionless pair potentials have the screened Coulomb form $V_{11}(r) = V_{22}(r) = \epsilon^{-1} V_{12}(r) = (U/r) \exp(-\kappa r)$ at interparticle separation $\mathbf{r} = (x, y)$, where the subscripts indicate which types of particles are interacting. The dimensions $L = (\sqrt{3}/2) \times 20$ and $W = 20$ of our rectangular box are such that for $\epsilon = 0$ a triangular lattice of each species fits in the box, and $U = 1.75 \times 10^4$ and $\kappa \ell = 0.5$ are chosen so that the equilibrium phase for $\epsilon = 0$ is such a triangular lattice⁽²⁾. We first discuss results for a system with $N = 200$ particles, i.e., 100 of each species, with $\epsilon = 0.02$. Later in the paper we shall mention observations for other system sizes and values of interspecies interaction wherever relevant.

The dimensionless time-step $\delta t = 6.5 \times 10^{-6}$, and the results we report are mainly for runs of 10^6 such steps. Over this time, the 1 and 2 lattices sweep through each other a few to several hundred times depending upon the drive. In order to drift under the action of the driving force F the particles have to overcome a barrier of order $V_{12}(\ell)$ over a distance of order ℓ . Thus, although F is itself dimensionless, we state our results in terms of the physically relevant dimensionless combination $F_d \equiv F \ell / V_{12}(\ell)$. We monitor the structure and dynamics of the system through snapshots of configurations, drift velocities v_d , particle-averaged local velocity variances $\langle (\delta v)^2 \rangle$, pair correlation functions $g_{\alpha\beta}(\mathbf{r})$ as functions of separation \mathbf{r} , and static structure factors $S_{\alpha\beta}(\mathbf{q})$ as functions of wavevector \mathbf{q} , where α and β range over 1, 2. Let us discuss the “phases” seen as F_d is increased, keeping other parameters fixed at values $\epsilon = 0.02$ and $\kappa \ell = 0.5$. The typical initial state of the system at $F_d = 0$ is an imperfectly ordered crystal. The application of a small nonzero F_d , well below that required

⁽¹⁾The dynamics will in general generate *nonthermal* noise which will emerge upon coarse-graining, and does not need to be included by hand in our microscopic description. This renormalised noise will have anisotropic correlations with a strength determined by a combination of the driving force and $k_B T$.

⁽²⁾If the two species differed in such a way as to form lattices which were mutually incommensurate, very different physics could be expected, which we do not discuss here.

for macroscopic relative motion of species 1 and 2, is seen to produce movement in regions where particles were initially in unfavourable positions. After these transient motions the system settles down into a highly annealed structure with both 1 and 2 components showing near-perfect long-range crystalline order, with no further relative drift of 1 and 2 except presumably an activated creep which we cannot detect. This “phase” does not seem to have any striking properties so we shall not discuss it further. The first nonequilibrium steady state of interest is seen when F_d crosses the first threshold F_1 , whereupon the 1 and 2 components acquire a macroscopic relative drift velocity v_d as shown in Fig.3. The two components slide smoothly past each other in lanes of width equal to the interparticle distance, with negligible distortion or disorder. A large but finite enhancement in $\langle(\delta v)^2\rangle$ is clearly seen (Fig.4) at the onset of this smooth sliding state, indicating large-scale inhomogeneous depinning. This does not tell us in detail about the character of the depinning transition since $\langle(\delta v)^2\rangle$ can be finite even if the small-wavevector velocity variance (which we have not measured) diverges. Detailed measurements of the spatial and temporal correlations of the velocity are required before we can say more about the nature of this depinning ⁽³⁾ [17].

Upon further increasing F_d the melt-freeze cycles mentioned above appear. These cycles are our most important observation, so let us present their features in some detail. They are seen most strikingly in the time-dependence of the peak height of the (short-time averaged) static structure factor $S(\mathbf{k})$ as shown in Fig.2, which alternates between long stretches of crystal-like and comparably long stretches of liquid-like values as the simulation progresses. This is in contrast with the behaviour seen in [6], where the time spent in the disordered state is much smaller, as though the system preferred order to disorder. The structure factor height in the ordered part of the cycle is proportional to the number of particles, so that we are justified in terming this regime crystalline. The cycle persists without limit in time, so far as we can tell. For $\epsilon = 0.02$ the threshold $F_d = F_2 = 40.54$. For slightly *higher* values of ϵ , say 0.03, 0.04, 0.05 we find the stretches of ordered and disordered behaviour are better defined than for 0.02. In addition, increasing ϵ slows down the onset of order during the cycle. The drift velocity correspondingly is large in the disordered and small in the ordered part of the cycle. As can be inferred from Fig.2, this is not at all like the sawtooth stick-slip seen, e.g., in [6]. Both velocities and order parameters grow and decline abruptly. There is a curious metastability associated with the cycles: if the initial state is chosen to be a *perfectly ordered lattice* as in Fig.1, a disordered configuration fails to nucleate over the largest time we are able to simulate. Both the cycles and the ordered sliding states thus seem to be locally stable. But if we disturb this initial perfectly ordered lattice by moving a single particle by, say, one lattice spacing, the melt-freeze cycles resume. In the ordered part of the cycle the smooth relative motion of the 1 and 2 lattices is disturbed now and then by kinks, i.e., a row moving out of step with adjacent rows, as seen in Fig.5a. The positional variance along x increases (Figs.5b and c) and, when it gets large enough, the system abruptly transits to a disordered state (Fig.5d). This state persists for a long time, before order once again sets in. The cycles are seen clearly in the time evolution of the pair distribution functions for separations along and transverse to the direction of the drive (Figs.6 and 7). Note that the order along y is never totally destroyed; larger simulations are required to establish its character over the course of the cycles. Fig.5 suggests that the disordering mechanism can also be regarded as excess fluctuations, with wavevector along y , in the phase of the density-wave component with wavevector along x . The cycles are asymmetrical: the order grows appreciably faster than it decays but both growth and decay are over timescales much shorter than the ordered or disordered stretches. The melt-freeze cycles for the two species are not necessarily simultaneous. Typically one

⁽³⁾which should be a strong crossover rather than a true transition.

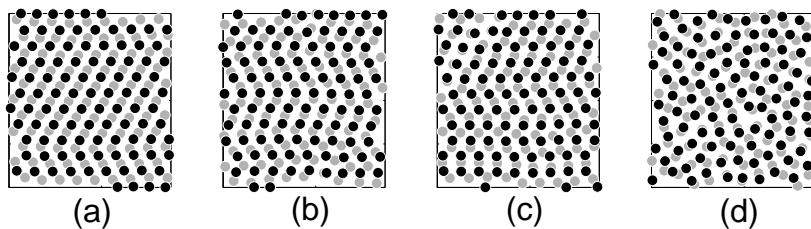


Fig. 5 – From order with kinks (a) to disorder (d) over a short time in the Melt-Freeze cycle. Black and grey particles move to the right and the left respectively; $\epsilon = 0.02$, $F_d = 40.83$.

species begins to order while the other is still disordered.

Let us consider briefly the effect of finite size. Inspection of Fig.5d (an image from the disordered part of the cycle) shows strong residual correlations, most easily seen by looking along a grazing angle. This is consistent as well with the form of $g(y)$ in Fig.7a and c. This indicates that the correlation length does not drop below about 4 interparticle spacings, so that the difference between ordered and disordered states will be hard to detect for small system sizes. Indeed, we are unable to see ‘cycles’ for $N \leq 64 \times 2$. Simulations of larger systems, $N = 144 \times 2$, 169×2 and 256×2 show the same qualitative behaviour as for $N = 100 \times 2$ particles, with less than a 1 percent change in the range of values of F for which the “cycles” are seen.

We also observe that an increase in the relative strength ϵ of the 1–2 interaction slows down the onset of order substantially. For $\epsilon = 0.05$, starting from a random initial configuration, we observed only a few cycles over the simulation run, and none for $\epsilon = 0.10$. Fig.8 shows the amplitude A of the cycle (an “order parameter” for this behaviour), defined as the difference in the value of S in the ‘ordered’ and ‘disordered’ regimes, averaged over the duration of the cycle, as a function of F_d for fixed values of the other parameters.

Remarkably, the cycles are seen only in a limited range of F_d , disappearing again when F_d crosses another threshold F_3 . Beyond F_3 , the structure again consists of ordered relatively sliding 1 and 2 lattices. This phase appears to be of the same nature as that below $F_d = F_2$. If we lower F_d below F_2 after the system has settled into a steady state, we find, as we remarked above, that the melt-freeze cycles do not appear unless at least one particle is displaced sufficiently from its ideal ordered location. Thus, the transition into the melt-freeze cycle phase is characterised by metastability and hysteresis.

We note here that the re-appearance of a smooth sliding state resembles the re-entrant ordered state seen in [11, 12]. Possibly, therefore, the melting-freezing cycles are the analogue, in our system, of the phenomenon of shear-induced melting [9, 10, 11, 12, 13].

Having established the reality of the melt-freeze cycles as a distinct, reproducible type of behaviour in relatively driven lattices, let us try to explain why they occur. When the two arrays of particles are pushed through each other, there is a competition between two timescales. The arrays traverse one lattice spacing a in a time τ_1 given by a/v_d . The slowest local relaxation will be that of species-1 particles in the potential well provided by their species-2 neighbours (and vice versa). The timescale τ_2 for this will be of order the friction coefficient divided by the curvature of the local 1-2 potential. If $\tau_1 \gg \tau_2$, the lattices of the two species have plenty of time to relax as they interpenetrate, so that we find smooth, orderly sliding. If instead $\tau_1 \ll \tau_2$, each species averages over the periodic potential of the lattice of the other species, so that again we expect smooth sliding. The maximum mutual disruption of the two lattices is expected only in a window of parameter values where the two times are

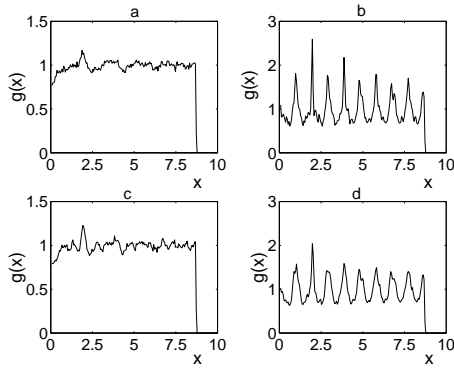


Fig. 6

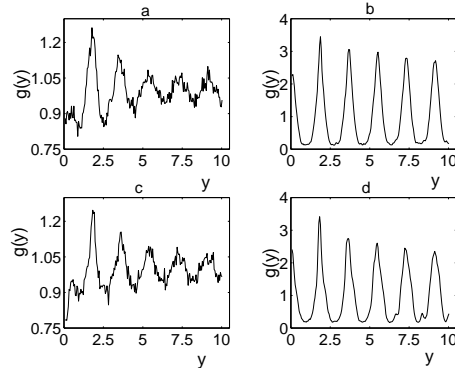


Fig. 7

Fig. 6 – Time evolution of $g(x)$ for species 1. Each figure is an average over 100 configurations evenly spaced in time over a span of 5000 time steps, for $\epsilon = 0.02$, $F_d = 40.83$. The final times for (a), (b), (c) and (d) correspond respectively to 9.5×10^4 , 8.65×10^5 , 1.01×10^6 and 1.39×10^6 timesteps.

Fig. 7 – Time evolution of $g(y)$ for species 1; times, parameter values and averaging as in Fig. 6.

comparable. When this condition is met, a species-2 unit cell, say, is distorted by successive passages of species-1 particles, resulting in total disruption of the density-wave components with wavevector along x . The resulting structure probably retains some order along y (see Fig.7), so that each species perhaps provides a weak periodic potential along y for the other species. Through a mechanism similar to that in [18], this can once again induce order along x as well. Once this happens the movement of the lattices will again cause disruptions, and the cycle then continues. For our parameter values, $\tau_1 \simeq 0.00022$ in the regime $F_2 < F < F_3$, and $\tau_2 \simeq 0.00019$ for $\epsilon = 0.05$, which suggests the two scales should be in competition in the melt-freeze regime, consistent with our arguments above. This reasoning is of course simplistic, since the ordered or disordered nature of a state is determined only in the limit of infinite size, where long-wavelength collective modes will play an important role. It is nonetheless reassuring that our crude estimates above are consistent with our observations.

Let us take these arguments further: In the presence of the constant mutual driving force the system alternates in time between a situation where interpenetrating triangular lattices are favoured and one where such a state is hard to accommodate. This suggests a possible

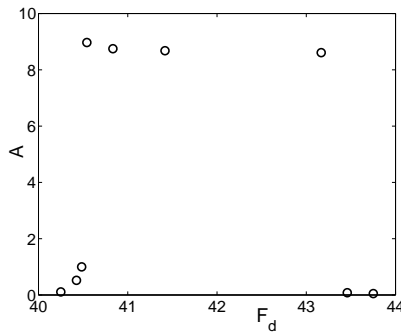


Fig. 8 – Amplitude of the melting freezing cycle as a function of driving force F_d , for $\epsilon = 0.02$.

relation to stochastic resonance [19], and indeed Fig.2 is strongly reminiscent of the time-series of a particle in a periodically modulated bistable potential. Further work is in progress to make this connection more precise.

In conclusion, we have studied a rather special nonequilibrium binary system in which the two species, separately in crystalline arrays, are driven through each other in opposite directions. We predict a rich range of nonequilibrium effects, the most striking of which are irregular cycles of melting and freezing. Such systems can be experimentally realised, generalising the ideas of [16], by starting with a compound colloidal crystal made of two species of differently charged colloidal particles and applying a constant external electric field. Measurements made in the centre-of-mass frame would mimic two species being driven in opposite directions. Another possibility would be to shear past each other two dissimilar solid surfaces patterned with ordered copolymer structures [15] or colloidal particles. The copolymer or colloids would have to be of two kinds, one of which adsorbed preferentially onto each of the two surfaces. We expect that similar effects should arise in sheared colloidal crystals as well, where adjacent crystal planes play the role of the two crystalline layers. Lastly, although the basic ideas and observations presented here could conceivably play some role in solid friction as well, the driving speeds required might be proportional to elastic wave speeds, making the effects inaccessible to experiment.

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