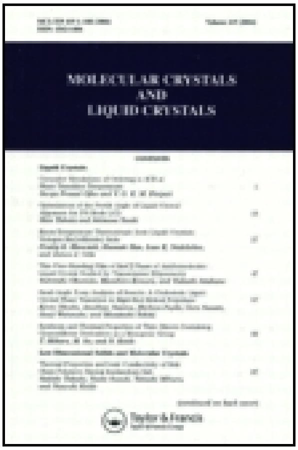

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ice-Like Melting of Flexible Line Crystals

David R. Nelson [a]
[a] Lyman Laboratory of Physics, Harvard University, Cambridge, MA, 02138, USA

To cite this article: David R. Nelson (1996): Ice-Like Melting of Flexible Line Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 1-6

To link to this article: http://dx.doi.org/10.1080/10587259608034578

Mol. Cryst. Liq. Cryst., 1996, Vol. 288, pp. 1–6
Reprints available directly from the publisher
Photocopying permitted by license only

ICE-LIKE MELTING OF FLEXIBLE LINE CRYSTALS

DAVID R. NELSON
Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA

Abstract A small number of crystalline materials composed of point-like atoms or molecules are known to contract upon melting into the liquid state. The most famous example is ice, which melts into a liquid which is **denser** than the coexisting solid phase. We discuss the conditions under which this unusual melting may be expected for collections of flexible directed **lines** with repulsive pairwise interactions arrayed in, say, a triangular lattice. Ice-like melting should occur generically for flexible lines with sufficiently long-range interactions.

The unusual behavior of ice, which transforms into a **denser** liquid (4% denser than the coexisting crystal) upon melting at atmospheric pressure is well known, as is the connection of this phenomenon with the negative slope of the melting curve in the temperature-pressure phase plane. Indeed, the Clausius-Clapeyron equation predicts that the slope of the melting curve $p_\sigma(T)$ is given by

$$\frac{dp_\sigma(T)}{dT} = \frac{\Delta s}{\Delta v} \tag{1}$$

where $\Delta s = s_\ell - s_\times$ and $\Delta v = v_\ell - v_\times$ are respectively the entropy and volume differences per particle from liquid (l) to solid ($\times$) across the first-order phase boundary. The reasonable assumption that the entropy of the crystal phase is lower than that of the liquid then implies immediately that the liquid is denser if dp_σ/dT is negative. Contraction upon melting arises as well in gallium (1% contraction), silicon (10%) and germanium (5%). The physical mechanism for this phenomenon in tetrahedrally coordinated crystals such as in H_2O, Si and Ge is the relatively open diamond lattice structure—the molecules or atoms then pack more efficiently when jumbled together in the coexisting liquid state.

A negative dp_σ/dT implies that these crystals melt upon the application of pressure. From this point of view, the famous Wigner crystal [2] of quantum mechanical electrons at $T = 0$ behaves in a similar fashion: it too melts when squeezed. The physical explanation in this case is that electrons form a crystal only when they are far apart and their long-range electrostatic potential energy

($\sim e^2/a_0$, where a_0 is the lattice constant) dominates in determining the ground state. When the electrons are forced closer together, their quantum zero motion energy of confinement in a Wigner-Seitz cell ($\sim \hbar^2/ma_0^2$) eventually dominates and forces melting into a Fermi liquid of delocalized electrons.

In this note we point out that crystals of long flexible lines (e.g., solutions of semiflexible polymers arranged in a hexagonal columnar phase with the polymers directed on average along the z axis) may also be expected to exhibit ice-like melting when squeezed by application of, say, an osmotic pressure. We assume a purely repulsive pair potential and argue that anomalous melting occurs provided the lines are flexible and interact via relatively long-range forces. See Ref. 3 for a review of such line crystals. Although the system is entirely classical, we shall see that the physics is closer to the melting of a quantum Wigner crystal than it is to real ice. The entropic penalty for confining these flexible lines in a cage of nearest neighbors plays the role of "zero-point motion" in the Wigner crystal. Provided the pair potential falls off slowly enough with distance, entropy eventually forces a transition at high densities into an entangled liquid-like phase such as a polymer nematic. The coexisting liquid is denser because the directed lines can then entangle more intimately and acquire more entropy. This "braiding entropy" compensates for the potential energy cost required to bring the polymers closer together.

In this note, we determine the conditions under which long flexible lines melt like ice, using a simple Einstein model of a flexible directed string confined to a cage [4]. See Ref. 5 for a more extensive discussion, including numerical and analytic evaluations of path integrals and a more exact Debye treatment of the phonon fluctuations.

Consider one representative trajectory $\vec{r} \equiv [x(z), y(z)]$ for a polymer in the confining potential "cage" provided by its surrounding polymers in a triangular crystal with lattice constant a_0. The free energy of this single strand may be written

$$F_1 = \frac{1}{2}\kappa \int_0^L \left(\frac{d^2\vec{r}}{dz^2}\right)^2 dz + \int_0^L V_1[\vec{r}(z)]\, dz, \tag{1}$$

where κ is the polymer bending rigidity and $V_1[\vec{r}]$ is chosen to mimic the pair potential per unit length. We now expand $V_1(\vec{r})$ about its minimum at $\vec{r} = 0$ to find

$$F_1 = \frac{1}{2}\kappa \int_0^L \left(\frac{d^2\vec{r}}{dz^2}\right)^2 dz + \frac{1}{2}k \int_0^L r^2(z)\, dz. \tag{2}$$

Up to constants of order unity, k can be estimated from a pair potential $V(r)$ which acts between two approximately parallel polymers with separation r in planes perpendicular to the z axis. Assuming for concreteness a power-law pair potential energy per unit length of the form $V(r) = \epsilon_0(\lambda/r)^n$, we have

$$\begin{aligned} k &\approx V''(r = a_0) \\ &\approx \epsilon_0(\lambda/a_0)^n/a_0^2. \end{aligned} \tag{3}$$

Charged flexible rods in solution are described by a potential $V(r) = \epsilon_0 K_0(r/\lambda)$, where ϵ_0 is the interaction energy per unit length, $K_0(x)$ is the MacDonald function, and λ is the Debye screening length [3]. The interaction is logarithmic in the regime $a_0 \gtrsim \lambda$, corresponding to $n = 0$ in Eq. (3). More generally, k should be of order of the crystalline in-plane shear modulus.

Let us assume that, under the influence of thermal fluctuations, a typical polymer wanders a perpendicular distance r as it wanders from one side of the parabolic confining potential to the other, and that it takes a "time" ℓ along the z axis to do this. The free energy of a segment of length ℓ arising from Eq. (2) is then approximately

$$F_1 \approx \frac{\kappa r^2}{\ell^3} + kr^2\ell. \tag{4}$$

Upon optimizing ℓ, we find that the preferred segment length is

$$\ell^* = (\kappa/k)^{1/4}, \tag{5}$$

while the corresponding free energy of the segment is

$$f_1^* = \kappa^{1/4}k^{3/4}r^2. \tag{6}$$

We now assume that successive segments of length ℓ^* along the polymer fluctuate independently, and apply the equipartition theorem to obtain

$$\langle r^2\rangle \approx k_BT/\kappa^{1/4}k^{3/4}. \tag{7}$$

According to the Lindemann criterion, melting occurs when $\langle r^2\rangle = c_L^2 a_0^2$, where the Lindemann constant is expected to be in the range $c_L \approx 0.10 - 0.20$. We then find that the melting point is given by

$$k_BT_m \approx c_L^2\kappa^{1/4}k^{3/4}a_0^2. \tag{8}$$

Upon using Eq. (3), we see that the Lindemann *ratio* is

$$\frac{\langle r^2\rangle}{a_0^2} = \frac{k_BT}{\kappa^{1/4}\epsilon_0^{3/4}}\left(\frac{a_0}{\lambda}\right)^{3n/4}\frac{1}{a_0^{1/2}}. \tag{9}$$

Provided the polymer bending rigidity κ and the interaction parameter ϵ_0 are approximately independent of the polymer spacing a_0, the Lindemann ratio ***increases*** with decreasing a_0 for power-law potentials whenever

$$n < \frac{2}{3}. \tag{10}$$

This is the condition for ice-like melting of a polymer crystal in solution when subjected to, say, an osmotic pressure. Ice-like melting should arise, in particular, for $n = 0$, corresponding to parallel charge rods interacting logarithmically when the lattice constant a_0 is less than the Debye screening length.

Equation (5) generalizes the concept of the Odijk "deflection length" [6] to directed polymers with interactions not limited to a simple hard core repulsion. A similar free energy with a tilt modulus term proportional to $\int_0^L \left(\frac{d\vec{r}}{dz}\right)^2 dz$ replacing the bending rigidity term in Eq. (1) has been proposed for polymers by Podgornik and Parsegian in Ref. 7. This later model would be appropriate for directed polymer crystals subjected to a strong external magnetic field $\vec{H}||\hat{z}$. Equation (1) must then be replaced by

$$F_1 = \frac{1}{2} g \int_0^L \left(\frac{d\vec{r}}{dz}\right)^2 dz + \int_0^L V_1[\vec{r}(z)]\, dz, \tag{11}$$

where $g \approx H^2 \chi_a a_0^2$, with χ_a the anisotropic part of the bulk magnetic susceptibility. We expect that, similar to the bending rigidity, g is a ***single*** polymer property and is approximately independent of a_0. As for semiflexible polymers controlled by a bending rigidity, we assume a power-law potential and expand the potential $V_1(r)$ about its minimum at $r = 0$,

$$F_1 = \frac{1}{2} g \int_0^L \left(\frac{d\vec{r}}{dz}\right)^2 dz + \frac{1}{2} k \int_0^L r^2(z)\, dz, \tag{12}$$

where k for power-law potentials is given by Eq. (3). The statistical mechanics associated with Eq. (12) can be analyzed via an analogy with a two-dimensional quantum harmonic oscillator [7]. Alternatively, we can assume as above that a typical vortex trajectory wanders a perpendicular distance r, from one side of the parabolic confining potential to the other, and that it takes a "time" ℓ along the z axis to do this. The free energy of the segment length ℓ is now approximately

$$F_1 \approx \frac{g r^2}{\ell} + k r^2 \ell. \tag{13}$$

Upon optimizing ℓ, we find that the preferred segment length is

$$\ell^* \approx \sqrt{g/k} \tag{14}$$

while the corresponding free energy of the segment is

$$F_1^* \approx \sqrt{gk}\, r^2. \tag{15}$$

We again assume that successive segments of length ℓ along the vortex fluctuate independently, and apply the equipartition theorem to one such segment to obtain

$$\langle r^2 \rangle \approx \frac{k_B T}{\sqrt{gk}}. \tag{16}$$

The melting temperature is now

$$k_B T_m = c_L^2 \sqrt{gk} a_0^2, \tag{17}$$

and the Lindemann ratio with pair potential per unit length $V(r) = \epsilon_0(\lambda/r)^n$ is

$$\frac{\langle r^2 \rangle}{a_0^2} \approx \frac{k_B T}{\sqrt{g\epsilon_0}} \left(\frac{a_0}{\lambda}\right)^{n/2} \frac{1}{a_0}. \tag{18}$$

We conclude that $\langle r^2 \rangle / a_0^2$ increases with decreasing a_0 and that ice-like melting will be possible upon application of osmotic pressure whenever

$$n < 2. \tag{19}$$

This simple model of melting (with $n = 0$) is also applicable to melting of the Abrikosov flux lattice in superconductors in strong magnetic fields [8]. Vortex crystals coexisting at a first-order transition with denser flux liquids have recently been observed in one of the high-T$_c$ superconductors [9].

We should emphasize that, even within the crude "Einstein oscillator within a cage" model used here, we have been approximating some rather subtle functional integrals. For example, the partition function associated with Eq. (2) is

$$Z_1 = \int \mathcal{D}r(z) \exp\left[-\frac{\kappa}{2k_B T}\int_0^L \left(\frac{d^2 r}{dz^2}\right)^2 - \frac{1}{2}\frac{k}{k_B T}\int_0^L r^2(z)\, dz\right] \tag{20}$$

For an explicit numerical and analytic evaluation of functional integrals of this kind, see Ref. 5.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge helpful conversations with S. Jain. This research was supported by the National Science Foundation, in part by the MRSEC Program through Grant DMR–9400396 and through Grant DMR–9417047.

REFERENCES

1. A.B. Pippard, The Elements of Classical Thermodynamics (Cambridge University Press, Cambridge 1974).
2. E. Wigner, Phys. Rev., 46, 1002 (1934).
3. D.R. Nelson, in Observation, Prediction and Simulation of Phase Transitions in Complete Fluids (Kluwer, The Netherlands, 1995).
4. We follow the presentation in Ref. 3. See Ref. 6 and 7 for related models of confined directed polymers.
5. S. Jain and D.R. Nelson, to be published.
6. T. Odijk, Macromolecules, 17, 2313 (1986).
7. R. Podgornik, D.C.Rau and V.A. Paregian, Macromolecules, 22, 1780 (1989). R. Podgornik and V.A. Paregian, Macromolecules, 22, 2266 (1990).
8. D.R. Nelson, in The Vortex State, edited by N.Bontemps et al. (Kluwer, The Netherlands, 1994).
9. E.Zeldov et al., Nature, 375, 373 (1995).