

**On the low-dimensional solids and their melting**

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**Abstract**

It is shown that the one- and two-dimensional solids may exist and melt.

Suppose that we have  $N$  identical atoms, of mass  $M$  each, arranged along a rectilinear chain; suppose that the atoms interact through a nearest-neighbours potential, and we are interested in small atomic displacements  $u_i$ ,  $i = 1, 2, \dots, N$ , of immaterial polarization, around equidistant equilibrium positions  $x_i = i \cdot a$ , where  $a$  is the lattice constant. Within the harmonic approximation with the elastic force constant  $K$  this motion is described by the hamiltonian

$$H = \sum_i \frac{1}{2M} p_i^2 + \frac{1}{2} K \sum_{\langle ij \rangle} (u_i - u_j)^2 \quad , \quad (1)$$

where  $p_i$  is the conjugate momentum,  $[p_i, u_j] = -i\hbar\delta_{ij}$ . With cyclic boundary conditions we have

$$u_i = \frac{1}{\sqrt{N}} \sum_k u_k e^{ikx_i} \quad , \quad (2)$$

$k = (2\pi/Na) \cdot \text{integer}$ ,  $-\pi/a < k < \pi/a$ ,  $u_k^\dagger = u_{-k}$ ,

$$p_i = M \dot{u}_i = \frac{1}{\sqrt{N}} \sum_k p_k e^{-ikx_i} \quad , \quad (3)$$

$p_k = M \dot{u}_{-k}$ ,  $[p_k, u_{k'}] = -i\hbar\delta_{kk'}$ , and the hamiltonian (1) becomes

$$H = \sum_k \left( \frac{1}{2M} p_k^\dagger p_k + \frac{1}{2} M \omega_k^2 u_k^\dagger u_k \right) \quad , \quad (4)$$

where

$$\omega_k^2 = \frac{4K}{M} (1 - \cos ka) \quad ; \quad (5)$$

it is brought into the diagonal form

$$H = \sum_k \hbar \omega_k (n_k + 1/2) \quad , \quad (6)$$

where  $n_k = a_k^\dagger a_k$ , by introducing the phonon operators  $a_k$ ,

$$u_k = \sqrt{\frac{\hbar}{2M\omega_k}} (a_k + a_{-k}^\dagger) \quad , \quad p_k = i\sqrt{\frac{\hbar M \omega_k}{2}} (a_k^\dagger - a_{-k}) \quad . \quad (7)$$

The mean square deviation of the atomic displacements in the phonon vacuum

$$\overline{u_i^2} = \frac{1}{N} \sum_k \overline{u_k^\dagger u_k} = \frac{1}{N} \sum_k \frac{\hbar}{2M\omega_k} (2\bar{n}_k + 1) = \frac{a}{2\pi} \int_0^{\pi/a} dk \cdot \frac{\hbar}{M\omega_k} \quad (8)$$

diverges logarithmically at  $k = 0$ . This infrared divergence, in various contexts, is currently invoked to rule out the existence of the one-dimensional solid.[1]·[2]

However, the mean square deviation of the lattice constant

$$\begin{aligned} \overline{[x_i - x_j - \overline{(x_i - x_j)}]^2} &= \overline{(u_i - u_j)^2} = \frac{1}{N} \sum_k \overline{u_k^\dagger u_k} \cdot 2(1 - \cos ka) = \\ &= \frac{1}{N} \sum_k \frac{\hbar}{M\omega_k} (1 - \cos ka) (2\bar{n}_k + 1) = \frac{a}{\pi} \int_0^{\pi/a} dk \cdot \frac{\hbar}{M\omega_k} (1 - \cos ka) \end{aligned} \quad (9)$$

is finite, which indicates that the solid exists, only its center of mass fluctuates immeasurably. Obviously, the thermodynamics is meaningless in this case.

The question one should ask is whether the phonons do exist in the one-dimensional solid subjected to the actual experimental conditions. These always imply an uncertainty  $u$  in the localization of the center of mass of the rigid lattice, and the constraint under which we should look for phonons reads

$$\sum_i \overline{u_i^2} = Nu^2 \quad . \quad (10)$$

The magnitude of  $u$  can not be smaller than  $a/2$ , unless the crystal is destroyed, but usually it is much larger than the lattice constant  $a$ .

Introducing the Lagrange multiplier  $\omega_0^2$  and setting

$$\mathcal{H} = H - \frac{1}{2} M \omega_0^2 \sum_i (u^2 - u_i^2) \quad (11)$$

we get straightforwardly

$$\mathcal{H} = \sum_k \left( \frac{1}{2M} p_k^\dagger p_k + \frac{1}{2} M \Omega_k^2 u_k^\dagger u_k \right) - \frac{1}{2} M \omega_0^2 N u^2 \quad , \quad (12)$$

where

$$\Omega_k^2 = \omega_0^2 + \omega_k^2 \quad , \quad (13)$$

*i.e.* the phonon spectrum acquires a threshold frequency  $\omega_0$  which acts as an infrared cut-off. In addition, the ground-state energy

$$E_0 = \overline{\mathcal{H}} = \sum_k \frac{1}{2} \hbar \Omega_k - \frac{1}{2} M \omega_0^2 N u^2 \quad (14)$$

has a minimum with respect to  $\omega_0^2$ ,

$$\frac{\partial E_0}{\partial \omega_0^2} = \sum_k \frac{\hbar}{4\Omega_k} - \frac{1}{2} M N u^2 \quad , \quad (15)$$

which is exactly the constraint (10); indeed,

$$\sum_i \overline{u_i^2} = \sum_k \overline{u_k^\dagger u_k} = \sum_k \frac{\hbar}{2M\Omega_k} = Nu^2 \quad (16)$$

coincides with (15). Assuming a Debye spectrum  $\omega_k = ck$ , where  $c = a(2K/M)^{\frac{1}{2}}$  is the sound velocity, and introducing the Debye wavevector  $k_D = \pi/a$  and the Debye frequency  $\omega_D = ck_D$ , we get from (16)

$$\int_0^{\omega_D/\omega_0} dx \cdot \frac{1}{\sqrt{1+x^2}} = \frac{2M\omega_D}{\hbar} u^2 . \quad (17)$$

The right-hand side of (17) is, typically, very large, so that we get the threshold frequency

$$\omega_0 \cong 2\omega_D \cdot e^{-\frac{2M\omega_D}{\hbar} \cdot u^2} \quad (18)$$

which is extremely small.

The phonon partition function for  $\mathcal{H}$  given by (12) reads

$$Z = \prod_k \frac{e^{-\hbar\Omega_k/2T}}{1 - e^{-\hbar\Omega_k/T}} = e^{-(F + \frac{1}{2}M\omega_0^2 Nu^2)/T} , \quad (19)$$

where  $F$  is the free energy; its minimum  $\partial F/\partial\omega_0^2 = 0$  gives

$$\sum_k \frac{\hbar}{2M\Omega_k} (2\bar{n}_k + 1) = Nu^2 , \quad (20)$$

*i.e.* again the constraint (10), at finite temperatures. Equation (20) reads

$$\int_0^{\omega_D/\omega_0} dx \cdot \frac{1}{\sqrt{1+x^2}} \cdot \coth\left(\frac{\hbar\omega_0}{2T} \sqrt{1+x^2}\right) = \frac{2M\omega_D}{\hbar} \cdot u^2 , \quad (21)$$

whose solution for  $T \rightarrow 0$  is (18) and

$$\omega_0 \cong \frac{\pi}{2M\omega_D u^2} \cdot T \quad (22)$$

for  $T \rightarrow \infty$ ; this is again an extremely small frequency for any normal temperature, and (22) may be used satisfactorily for any finite temperature. The constraint (10) introduces therefore an extremely small infrared cut-off  $\omega_0$  in the phonon spectrum, according to (13), slightly depending on temperature, whose effect is practically unobservable. We remark that the mean square deviation of the distance between any pair of atoms

$$\overline{(u_i - u_j)^2} = \frac{1}{N} \sum_k \frac{\hbar}{2M\Omega_k} \cdot 2 \{1 - \cos[ka(i-j)]\} \cdot (2\bar{n}_k + 1) \quad (23)$$

is always smaller than  $4u^2$ , according to (20), so that the (on-diagonal) crystalline long-range order does exist in one dimension.

In this connection the question of melting of the one-dimensional solid is meaningful. The elastic force constant  $K$  in (1) is a function of  $a$ ; actually it is a function of the nearest-neighbours distance  $a + u_i - u_j$ ; more than this, it is a periodic function with the period  $a$ , whose integral extended to the whole crystal vanishes. Consequently, it may be expanded as a Fourier series of the reciprocal vectors of the lattice, and we may write it as

$$K(a + u_i - u_j) = K \cos[G(u_i - u_j)] + \dots , \quad (24)$$

where  $G = 2\pi/a$ . Assuming vanishing fluctuations we may approximate the cosine in (24) by its average

$$\overline{\cos[G(u_i - u_j)]} = e^{-\frac{1}{2}\delta^2} , \quad (25)$$

where  $\delta^2 = \overline{[G(u_i - u_j)]^2}$ , and keep the first  $G$ -term in (24). The sound velocity changes, therefore, from  $c$  to  $c \cdot \exp(-\delta^2/4)$ , and we get a mean-field theory known as the self-consistent harmonic approximation. Remark that it is  $\overline{(u_i - u_j)^2}$  which enters the theory, not  $\overline{u_i^2}$ . [3] On the other hand

$$\delta^2 = G^2 \overline{(u_i - u_j)^2} = \frac{G^2}{N} \sum_k \frac{\hbar}{M\Omega_k} (1 - \cos ka) \cdot (2\bar{n}_k + 1) \quad , \quad (26)$$

and we may neglect  $\omega_0$  here and approximate  $1 - \cos ka$  by  $(ka)^2/2$  over the whole integration range. With the Debye spectrum (26) becomes

$$\delta^2 = \frac{2\pi^2 G^2}{\hbar M \omega_D^3} \cdot T^2 \cdot e^{\frac{3}{4}\delta^2} \cdot \int_0^{\frac{\hbar\omega_D}{2T}} e^{-\delta^2/4} dx \cdot x \coth x \quad . \quad (27)$$

There is a critical temperature beyond which this equation has no solution anymore; it is given by the tangent point of the curves described by the two sides of (27), which may be approximated by

$$1 \cong \frac{2\pi^2 G^2}{\hbar M \omega_D^3} \cdot T^2 \cdot \frac{3}{4} e^{\frac{3}{4}\delta^2} \cdot \int_0^{\frac{\hbar\omega_D}{2T}} e^{-\delta^2/4} dx \cdot x \coth x \quad , \quad (28)$$

whence, together with (27), yields

$$\delta^2 \cong \frac{4}{3} \quad . \quad (29)$$

The high-temperature limit of (27) reads now

$$\delta^2 = \frac{\pi^2 G^2}{M \omega_D^2} \cdot T \cdot e^{\frac{1}{2}\delta^2} \quad , \quad (30)$$

whence we get the melting temperature (not to be mistaken for the freezing temperature[4])

$$T_m = \frac{4M\omega_D^2}{3\pi^2 G^2 e^{2/3}} = \frac{1}{3\pi^2 e^{2/3}} \cdot M c^2 \cong 0.017 \cdot M c^2 \quad . \quad (31)$$

It is interesting to compare  $\overline{(u_i - u_j)^2} = a^2/3\pi^2$  at the melting point given by (29) with the square of the lattice constant  $a^2$ . The melting temperature given by (31) indicates a sharp transition where the crystal gets soft and can no longer bear phonons. The investigation of the validity of this mean-field theory may indicate, in general, a continuous transition, with a variable range of crystallinity, both in magnitude and orientation.[5]

The constraint (10) applies to all the atoms in the lattice, as, for example, to a lattice with a basis in the unit cell. However, the optical phonons do not contribute practically to the translational displacement of the lattice, so that the threshold frequency  $\omega_0$  (appearing now in the whole phonon spectrum) is practically unchanged. The constraint (10) applies also to solids of any dimensionality, and we shall discuss now, for the sake of reference, the case of a cubic three-dimensional Bravais lattice. The hamiltonian of the atomic vibrations can be written as

$$H = \sum_{\alpha i} \frac{1}{2M} p_{\alpha i}^2 + \frac{1}{2} \sum_{\alpha\beta\langle ij \rangle} G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) u_{\alpha i} u_{\beta j} \quad , \quad (32)$$

where  $\alpha, \beta$  are the cartesian labels of the components of the displacement vector  $\mathbf{u}_i$ ,  $\mathbf{r}_i$  are the equilibrium positions, and  $G_{\alpha\beta}$  is the matrix of the elastic force constants. A Fourier expansion brings  $H$  into

$$H = \sum_{\alpha\mathbf{k}} \frac{1}{2M} \cdot p_{\alpha\mathbf{k}}^\dagger p_{\alpha\mathbf{k}} + \frac{1}{2} \sum_{\alpha\beta\mathbf{k}} G_{\alpha\beta}(\mathbf{k}) \cdot u_{\alpha\mathbf{k}}^\dagger u_{\beta\mathbf{k}} \quad , \quad (33)$$

where

$$G_{\alpha\beta}(\mathbf{k}) = \sum_j G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) \cdot e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \quad , \quad (34)$$

$j$ 's being the nearest neighbours of  $i$ . A canonical transform diagonalizes  $G_{\alpha\beta}(\mathbf{k})$  into  $G_\alpha(\mathbf{k})$ , where we use the same label  $\alpha$  for polarizations. In addition, we assume a Debye, isotropic, identical spectrum for all the polarizations,

$$G_\alpha(\mathbf{k}) = M\omega_k^2 = Mc^2k^2 \quad . \quad (35)$$

We remark that the constraint (10), which now reads

$$\sum_i \overline{\mathbf{u}_i^2} = Nu^2 \quad (36)$$

is left unchanged under the canonical transform. Under these conditions we get the spectrum  $\Omega_k^2 = \omega_0^2 + \omega_k^2$  and (36) gives

$$\sum_{\alpha\mathbf{k}} \frac{\hbar}{2M\Omega_k} \cdot \coth\left(\frac{\hbar\Omega_k}{2T}\right) = Nu^2 \quad . \quad (37)$$

Making use of the Debye wavevector  $k_D = (6\pi^2)^{1/3}/a$ , and the Debye frequency  $\omega_D = ck_D$ , (37) becomes

$$\frac{3\hbar\omega_0^2}{2M\omega_D^3} \cdot \int_0^{\omega_D/\omega_0} dx \cdot \frac{x^2}{\sqrt{1+x^2}} \cdot \coth\left(\frac{\hbar\omega_0}{2T}\sqrt{1+x^2}\right) = \frac{u^2}{3} \quad . \quad (38)$$

For  $T \rightarrow 0$  the only solution of (38) is  $\omega_0 = 0$  and the zero-point fluctuations  $u_0^2 = 9\hbar/4M\omega_D$  ( $\ll a^2$ ); for  $T \rightarrow \infty$  we find  $\omega_0 = 0$  again, and  $u^2 = 9T/M\omega_D^2$ , which varies extremely slowly with the temperature, and may be used for any normal range of temperatures. Therefore, there is no frequency cut-off on the phonon spectrum in three dimensions, and the lattice develops its own fluctuations.

In order to compute the melting temperature we use again the self-consistent harmonic approximation, according to which

$$G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) \implies G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{u}_i - \mathbf{u}_j) = \sum_{\mathbf{G}} G_{\alpha\beta}(\mathbf{G}) \cos[\mathbf{G}(\mathbf{u}_i - \mathbf{u}_j)] \implies \sum_{\mathbf{G}} G_{\alpha\beta}(\mathbf{G}) e^{-\frac{1}{2}[\mathbf{G}(\mathbf{u}_i - \mathbf{u}_j)]^2} \quad . \quad (39)$$

On the other hand

$$\begin{aligned} \mathbf{G}(\mathbf{u}_i - \mathbf{u}_j) &= \sum_{\alpha} G_{\alpha}(u_{\alpha i} - u_{\alpha j}) = \\ &= \frac{1}{\sqrt{N}} \sum_{\alpha\mathbf{k}} G_{\alpha} u_{\alpha\mathbf{k}} \left[1 - e^{i\mathbf{k}(\mathbf{r}_j - \mathbf{r}_i)}\right] e^{i\mathbf{k}\mathbf{r}_i} \end{aligned} \quad (40)$$

and

$$[\mathbf{G}(\mathbf{u}_i - \mathbf{u}_j)]^2 = \frac{1}{N} \sum_{\alpha\mathbf{k}} G_{\alpha}^2 \cdot \overline{u_{\alpha\mathbf{k}}^\dagger u_{\alpha\mathbf{k}}} \cdot 2 \{1 - \cos[\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)]\} \quad . \quad (41)$$

For a cubic lattice the sum in (41) does not depend on  $\langle ij \rangle$  and it may be approximated by

$$[\mathbf{G}(\mathbf{u}_i - \mathbf{u}_j)]^2 \cong \frac{G^2 a^2}{N} \sum_{\mathbf{k}} \frac{\hbar}{2M\omega_k} \cdot k_x^2 \cdot (2\bar{n}_k + 1) \quad , \quad (42)$$

or

$$[\mathbf{G}(\mathbf{u}_i - \mathbf{u}_j)]^2 = G^2 \frac{8(6\pi^2)^{2/3}}{\hbar^3 M\omega_D^5} \cdot T^4 \int_0^{\hbar\omega_D/2T} dx \cdot x^3 \coth x \quad . \quad (43)$$

We may therefore keep the first  $\mathbf{G}'$ s in (39) and, denoting the corresponding (43) by  $\delta^2$ , we have

$$G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) \implies G_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) \cdot e^{-\frac{1}{2}\delta^2} \quad , \quad (44)$$

$$c \implies c \cdot e^{-\frac{1}{4}\delta^2} , \quad (45)$$

and a similar relation for  $\omega_D$  . Equation (43) becomes

$$\delta^2 = G^2 \frac{8(6\pi^2)^{2/3}}{\hbar^3 M \omega_D^5} \cdot T^4 \cdot e^{\frac{5}{4}\delta^2} \cdot \int_0^{\frac{\hbar\omega_D}{2T}} e^{-\frac{1}{4}\delta^2} dx \cdot x^3 \coth x , \quad (46)$$

whose critical solutions are given by

$$\delta^2 \cong 4/5 . \quad (47)$$

The finite-temperature estimation of (46) is

$$\delta^2 = \frac{G^2 a^2}{3Mc^2} \cdot T \cdot e^{\frac{1}{2}\delta^2} , \quad (48)$$

whence the melting temperature

$$T_m = \frac{3}{5\pi^2 e^{2/3}} \cdot Mc^2 \cong 0.04 \cdot Mc^2 ; \quad (49)$$

this is the Lindemann's law of melting.[6] At the melting temperature the fluctuations in the atomic positions are

$$u_m^2 = \frac{9}{M\omega_D^2} \cdot T_m \cong 0.025a^2 , \quad (50)$$

according to (38) , and we may see that their ratio to the zero-point fluctuations is given by

$$u_m^2/u_0^2 = 4T_m/\hbar\omega_D \cong 0.04 \cdot \frac{Mca}{\hbar} . \quad (51)$$

We shall discuss now briefly the two-dimensional case. Under the same assumptions as those employed for the three-dimensional solid the constraint equation (38) becomes

$$\frac{\hbar\omega_0}{M\omega_D^2} \int_0^{\omega_D/\omega_0} dx \cdot \frac{x}{\sqrt{1+x^2}} \cdot \coth \left( \frac{\hbar\omega_0}{2T} \sqrt{1+x^2} \right) = \frac{u^2}{2} , \quad (52)$$

where  $\omega_D = ck_D$ ,  $k_D = 2\sqrt{\pi}/a$  . For  $T \rightarrow 0$  this equation has the solution  $\omega_0 = 0$  and the zero-point fluctuations  $u_0^2 = 2\hbar/M\omega_D$ . For  $T \rightarrow \infty$  we get

$$\omega_0 \cong \omega_D \cdot e^{-\frac{M\omega_D^2}{4T} \cdot u^2} , \quad (53)$$

*i.e.* the two-dimensional solid may exist at finite temperatures,[7] under the constraint (10). The cut-off frequency given by (53) is extremely small and varies very slowly with the temperature; it may be used for any finite temperature range (remark that it vanishes for  $T \rightarrow 0$  ), and its effects are practically unnoticeable. The melting may be treated similarly with the three-dimensional case. Instead of (46) we get now

$$\delta^2 = G^2 \frac{16\pi}{\hbar^2 M \omega_D^4} \cdot T^3 \cdot e^{\delta^2} \int_0^{\frac{\hbar\omega_D}{2T}} e^{-\frac{1}{4}\delta^2} dx \cdot x^2 \cdot \coth x , \quad (54)$$

whose critical solution is given by

$$\delta^2 \cong 1 . \quad (55)$$

The finite-temperature integral in (54) gives

$$\delta^2 = \frac{2\pi^2}{Mc^2} \cdot T \cdot e^{\frac{1}{2}\delta^2} , \quad (56)$$

whence the melting temperature

$$T_m = \frac{1}{2\pi^2 e^{1/2}} \cdot Mc^2 \cong 0.03 \cdot Mc^2 . \quad (57)$$

We stress again the possibility of a continuous transition,[8] including various structural phases.

Similar considerations as those presented here apply for highly anisotropic solids. A natural question arises of what happens for quasi-low dimensional solids, as for a slab or a rod of thickness  $d$  . The qualitative picture given here remains unchanged, but, of course, the quantitative results are altered. The main feature is the occurrence of a cross-over temperature toward a three-dimensional behaviour, of the order of  $\hbar c/d$  ; for  $d = N_t a$  this temperature is about  $10^2/N_t$  Kelvins, for a typical sound velocity  $c \sim 10^3$  m/s .

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