Classical lattice vibrations at finite temperature

Mike Hermele

(Dated: September 23, 2012)

I. SETUP

Lattice vibrations have a number of very important measurable effects in solids. In these notes we focus on two – the heat capacity, and the effect of lattice vibrations on scattering experiments. We will treat the lattice vibrations classically, and defer a quantum-mechanical treatment until a little later. Therefore, we are considering only the effects of thermal fluctuations here – there aren't any quantum fluctuations yet.

For concreteness, we always consider a 3d monatomic Bravais lattice. The Hamiltonian is

$$H = \frac{1}{2M}\sum_{\boldsymbol{R}} \boldsymbol{p}_{\boldsymbol{R}}^2 + \frac{1}{2}\sum_{\boldsymbol{R},\boldsymbol{R}'} D^{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}')u^{\mu}(\boldsymbol{R})u^{\nu}(\boldsymbol{R}'). \tag{1}$$

In terms of normal mode coordinates and momenta, the Hamiltonian is written

$$H = \frac{1}{2M}\sideset{}{'}\sum_{\boldsymbol{k}}\sum_{\lambda}\Big([p^R_\lambda(\boldsymbol{k})]^2 + p^I_\lambda(\boldsymbol{k})]^2\Big) + \frac{M}{2}\sideset{}{'}\sum_{\boldsymbol{k}}\sum_{\lambda}[\omega_\lambda(\boldsymbol{k})]^2\Big([u^R_\lambda(\boldsymbol{k})]^2 + u^I_\lambda(\boldsymbol{k})]^2\Big). \tag{2}$$

Here, the sums over $\boldsymbol{k}$ are restricted to the Brillouin zone – the prime over the sums means that in fact the sums are restricted over just half the zone, with $k_x \geq 0$. The normal mode coordinates are defined by writing

$$u^{\mu}(\boldsymbol{R}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} S_{\mu\lambda}(\boldsymbol{k})u_\lambda(\boldsymbol{k}), \tag{3}$$

and $u^R_\lambda(\boldsymbol{k}) = \sqrt{2}\,\mathrm{Re}\,u_\lambda(\boldsymbol{k})$, $u^I_\lambda(\boldsymbol{k}) = \sqrt{2}\,\mathrm{Im}\,u_\lambda(\boldsymbol{k})$. Because $u_\lambda(-\boldsymbol{k}) = u^*_\lambda(\boldsymbol{k})$, $u^R_\lambda(\boldsymbol{k})$ is an even function of $\boldsymbol{k}$, while $u^I_\lambda(\boldsymbol{k})$ is odd. Also, note that $S_{\mu\lambda}(-\boldsymbol{k}) = S_{\mu\lambda}(\boldsymbol{k})$ – this is because S comes from diagonalizing the matrix $D^{\mu\nu}(\boldsymbol{k})$, which is is even in $\boldsymbol{k}$.

To calculate thermal averages, we use the fact that the probability that the system is in a state $\{u,p\}$ is given by the distribution

$$P[\{u,p\}] = \frac{1}{Z}e^{-\beta H[\{u,p\}]}, \tag{4}$$

where $\beta = 1/k_BT$ and Z is the partition function defined by

$$Z = \int d\Gamma e^{-\beta H}. \tag{5}$$

The integration measure is simply a product over all coordinates and momenta:

$$d\Gamma = \sideset{}{'}\prod_{\boldsymbol{k}\neq 0}\prod_{\lambda}\Big[du^R_\lambda(\boldsymbol{k})du^I_\lambda(\boldsymbol{k})dp^R_\lambda(\boldsymbol{k})dp^I_\lambda(\boldsymbol{k})\Big]. \tag{6}$$

The product is over all $\boldsymbol{k}$ in the Brillouin zone with $k_x \geq 0$, and $\boldsymbol{k} \neq 0$. The reason we don't need to integrate over the $\boldsymbol{k} = 0$ coordinates and momenta is that they correspond to the overall position and momentum of the whole crystal. We can fix the crystal at a given position, and fix it to be stationary, without affecting any of the measurable bulk properties we're interested in. Each coordinate and momentum is integrated from $-\infty$ to $+\infty$.

II. HEAT CAPACITY

To calculate the heat capacity, we can simply apply to the equipartition theorem. This says that, for a quadratic Hamiltonian (such as we have here), the internal energy is

$$E = \frac{1}{2}k_BT \times (\text{number of d.o.f.}). \tag{7}$$

For this purpose, the number of degrees of freedom (d.o.f.) is just the total number of coordinates plus momenta that appear quadratically in the Hamiltonian. In our case, there are $3N$ decoupled harmonic oscillator modes, each of which has 2 d.o.f. (1 coordinate and 1 momentum), so there are $6N$ total d.o.f. and $E = 3Nk_BT$. The heat capacity is

$$C_V = \Big(\frac{\partial E}{\partial T}\Big)_V = 3Nk_B. \tag{8}$$

So this treatment predicts that the heat capacity is constant as a function of temperature and, remarkably, only depends on the number of atoms and Boltzmann's constant. Although this value is a decent order of magnitude estimate of the magnitude of heat capacities of solids are relatively high temperature (room temperature and above), it gets the temperature dependence completely wrong. In particular, at low temperature in insulators, $C_V \propto T^3$. In order to obtain this behavior, we will need to treat the lattice vibrations quantum mechanically.

III. EFFECT ON SCATTERING

A. Warm-up

Does the thermal motion of atoms in a crystal destroy Bragg peaks, which we obtained theoretically by assuming a perfect crystal? Obviously not, since Bragg peaks are observed experimentally. So what effect, then, do thermal fluctuations have on the Bragg peaks?

As a warm-up to this question, we will calculate the thermal average $\langle \boldsymbol{u}(\boldsymbol{R})^2\rangle$. This measures the tendency of the atom at $\boldsymbol{R}$ to deviate from its equilibrium position. By discrete translation invariance, this quantity cannot depend on $\boldsymbol{R}$, so we might as well choose $\boldsymbol{R} = 0$. [Also note that $\langle \boldsymbol{u}(\boldsymbol{R})\rangle = 0$, since by definition $\boldsymbol{u}$ is the displacement from the equilibrium position (also, the Hamiltonian has a symmetry $\boldsymbol{u} \to -\boldsymbol{u}$). So to get useful information, the simplest quantity we can look at is $\langle \boldsymbol{u}(0)^2\rangle$.]

To calculate this thermal average, we first calculate the partition function Z. We will need to make use of the important formula

$$\int_{-\infty}^{\infty} dx e^{-ax^2/2} = \sqrt{\frac{2\pi}{a}}. \tag{9}$$

The partition function can be written as:

$$Z = \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \int_{-\infty}^{\infty} du_\lambda^R(\boldsymbol{k}) \exp\Big(-\frac{\beta M[\omega_\lambda(\boldsymbol{k})]^2}{2}[u_\lambda^R(\boldsymbol{k})]^2\Big)\Big] \tag{10}$$

$$\times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \int_{-\infty}^{\infty} du_\lambda^I(\boldsymbol{k}) \exp\Big(-\frac{\beta M[\omega_\lambda(\boldsymbol{k})]^2}{2}[u_\lambda^I(\boldsymbol{k})]^2\Big)\Big] \tag{11}$$

$$\times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \int_{-\infty}^{\infty} dp_\lambda^R(\boldsymbol{k}) \exp\Big(-\frac{\beta}{2M}[p_\lambda^R(\boldsymbol{k})]^2\Big)\Big] \tag{12}$$

$$\times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \int_{-\infty}^{\infty} dp_\lambda^I(\boldsymbol{k}) \exp\Big(-\frac{\beta}{2M}[p_\lambda^I(\boldsymbol{k})]^2\Big)\Big]\Big] \tag{13}$$

$$= \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \sqrt{\frac{2\pi k_BT}{M[\omega_\lambda(\boldsymbol{k})]^2}}\Big] \times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \sqrt{\frac{2\pi k_BT}{M[\omega_\lambda(\boldsymbol{k})]^2}}\Big] \tag{14}$$

$$\times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \sqrt{2\pi k_BTM}\Big] \times \Big[\prod_{\boldsymbol{k}\neq 0}{}' \prod_{\lambda} \sqrt{2\pi k_BTM}\Big]. \tag{15}$$

This expression can be simplified further, but that won't be necessary for obtaining the results below.

Next, we have to evaluate the integral $\int d\Gamma \boldsymbol{u}(0)^2 e^{-\beta H}$. This will be easiest if we first express $\boldsymbol{u}(0)$ in terms of normal mode coordinates. We have

$$u^\mu(0) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}\neq 0} S_{\mu\lambda}(\boldsymbol{k}) u_\lambda(\boldsymbol{k}). \tag{16}$$

We don't sum over the $\boldsymbol{k}=0$ coordinates because we have already fixed them (*e.g.* we fixed $\boldsymbol{u}_\lambda(\boldsymbol{k}=0)\to 0$). Breaking this into real and imaginary parts,

$$u^\mu(0) = \frac{1}{\sqrt{2N}}\sum_{\boldsymbol{k}\neq 0} S_{\mu\lambda}(\boldsymbol{k})[u^R_\lambda(\boldsymbol{k}) + iu^I_\lambda(\boldsymbol{k})] \tag{17}$$

$$= \frac{1}{\sqrt{2N}}\sum_{\boldsymbol{k}\neq 0} S_{\mu\lambda}(\boldsymbol{k})u^R_\lambda(\boldsymbol{k}) \tag{18}$$

$$= \sqrt{\frac{2}{N}}\sum_{\boldsymbol{k}\neq 0}{}^{'} S_{\mu\lambda}(\boldsymbol{k})u^R_\lambda(\boldsymbol{k}). \tag{19}$$

To get the second line we used the fact that $S_{\mu\lambda}(\boldsymbol{k})$ and $u^R_\lambda(\boldsymbol{k})$ are even in $\boldsymbol{k}$, while $u^I_\lambda(\boldsymbol{k})$ is odd in $\boldsymbol{k}$. In the third line we only sum over half the Brillouin zone, and hence gain a factor of 2.

Plugging this into the integral of interest, we have

$$\int d\Gamma \boldsymbol{u}(0)^2 e^{-\beta H} = \frac{2}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'\neq 0}{}^{'}\sum_{\lambda,\lambda'} S_{\mu\lambda}(\boldsymbol{k})S_{\mu\lambda'}(\boldsymbol{k}')\Big[\int d\Gamma u^R_\lambda(\boldsymbol{k})u^R_{\lambda'}(\boldsymbol{k}')e^{-\beta H}\Big] \tag{20}$$

$$= \frac{2}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'\neq 0}{}^{'}\sum_{\lambda,\lambda'} S_{\mu\lambda}(\boldsymbol{k})S_{\mu\lambda'}(\boldsymbol{k}')\Big[\delta_{\lambda\lambda'}\delta_{\boldsymbol{k}\boldsymbol{k}'}\int d\Gamma [u^R_\lambda(\boldsymbol{k})]^2 e^{-\beta H}\Big] \tag{21}$$

$$= \frac{2}{N}\sum_{\boldsymbol{k}\neq 0}{}^{'}\sum_{\lambda} S_{\mu\lambda}(\boldsymbol{k})S_{\mu\lambda}(\boldsymbol{k})\Big[\int d\Gamma [u^R_\lambda(\boldsymbol{k})]^2 e^{-\beta H}\Big]. \tag{22}$$

In the second line, we used the fact that H, for any given $(\boldsymbol{k},\lambda)$, is invariant under $u^R_\lambda(\boldsymbol{k})\to -u^R_\lambda(\boldsymbol{k})$ (while all other coordinates and momenta are unchanged). This means the integral can be nonzero only when $\lambda=\lambda'$ and $\boldsymbol{k}=\boldsymbol{k}'$. We can simplify further, because we have

$$\sum_\mu S_{\mu\lambda}(\boldsymbol{k})S_{\mu\lambda'}(\boldsymbol{k}) = \delta_{\lambda\lambda'}. \tag{23}$$

This is just a rewriting of what it means for S to be an orthogonal matrix (*i.e.* $S^TS=1$). Putting this in, we have

$$\int d\Gamma \boldsymbol{u}(0)^2 e^{-\beta H} = \frac{2}{N}\sum_{\boldsymbol{k}\neq 0}{}^{'}\sum_{\lambda}\Big[\int d\Gamma [u^R_\lambda(\boldsymbol{k})]^2 e^{-\beta H}\Big]. \tag{24}$$

To evaluate the integral, we recall the useful formula

$$\int_{-\infty}^{\infty} dx\, x^2 e^{-ax^2/2} = -2\frac{d}{da}\int_{-\infty}^{\infty} dx e^{-ax^2/2} = -2\frac{d}{da}\sqrt{\frac{2\pi}{a}} = \frac{1}{a}\sqrt{\frac{2\pi}{a}}. \tag{25}$$

Now, in the integral $\int d\Gamma[u^R_\lambda(\boldsymbol{k})]^2 e^{-\beta H}$, all integrals over coordinates and momenta are exactly the same as in Z, except for the integral over $u^R_\lambda(\boldsymbol{k})$. This integral is the same, too, except that the extra $[u^R_\lambda(\boldsymbol{k})]^2$ brings down an extra factor of $1/\beta M[\omega_\lambda(\boldsymbol{k})]^2$ after integration. Therefore,

$$\int d\Gamma [u^R_\lambda(\boldsymbol{k})]^2 e^{-\beta H} = \frac{k_BT}{M[\omega_\lambda(\boldsymbol{k})]^2}Z, \tag{26}$$

and so

$$\int d\Gamma \boldsymbol{u}(0)^2 e^{-\beta H} = \frac{2k_BTZ}{MN}\sum_{\boldsymbol{k}\neq 0}{}^{'}\sum_{\lambda}\frac{1}{\omega_\lambda(\boldsymbol{k})^2} \tag{27}$$

$$= \frac{k_BTZ}{MN}\sum_{\boldsymbol{k}\neq 0}\sum_{\lambda}\frac{1}{\omega_\lambda(\boldsymbol{k})^2}. \tag{28}$$

So, finally, we have

$$\langle \boldsymbol{u}(0)^2 \rangle = \frac{k_B T}{MN} \sum_{\boldsymbol{k} \neq 0} \sum_{\lambda} \frac{1}{\omega_\lambda(\boldsymbol{k})^2} \tag{29}$$

$$= \frac{k_B T a^3}{M} \sum_{\lambda} \int_{\boldsymbol{k} \in \text{B.Z.}} \frac{d^3\boldsymbol{k}}{(2\pi)^3} \frac{1}{\omega_\lambda(\boldsymbol{k})^2}. \tag{30}$$

In the last line, we converted the sum to an integral using $\sum_{\boldsymbol{k}} = V \int d^3\boldsymbol{k}/(2\pi)^3$ and $V = Na^3$.

The integral is dominated by $\boldsymbol{k} \to 0$, where $\omega_\lambda(\boldsymbol{k}) \propto |\boldsymbol{k}|$. Going to spherical coordinates, the integral there looks like $\int dk\, k^2/k^2$, which is finite at $k = 0$. So we have found that $\langle \boldsymbol{u}(0)^2 \rangle$ is a finite constant. This means that thermal fluctuations are not expected to destroy crystalline order.

However, if we repeat this analysis in 2d or 1d, we quickly see that the same integral diverges at $k = 0$, and $\langle \boldsymbol{u}(0)^2 \rangle$ is divergent. This means we should not expect to have true crystalline order in 2d or 1d systems. However, note that this divergence comes from small k. In reality, if we go back to the sum rather than doing the integral, we see that the integral gets cut off for a minimum k on the order of $k \sim 2\pi/L$, where L is a linear dimension of the system. In 2d we find a divergence like $\log(L)$, and in 1d we find a divergence proportional to L. So for small enough samples, the fluctuations that tend to destroy crystalline order are not expected to be detectable. Even in much larger samples, to see the effects of these fluctuations we need to probe crystalline order on (possibly) very long length scales, which may be difficult.

B. Modification of Bragg peaks

Earlier in the course, we showed that the scattering cross section for momentum transfer $\boldsymbol{q}$ is proportional to

$$|M(\boldsymbol{q})|^2 = |U_1(\boldsymbol{q})|^2 \sum_{\boldsymbol{R},\boldsymbol{R}'} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})}. \tag{31}$$

Here we assume for simplicity that the crystal is a monatomic Bravais lattice, with atomic form factor $U_1(\boldsymbol{q})$. Before we evaluated this expression assuming that the atomic positions were exactly at the Bravais lattice points (a perfect crystal), and found Bragg peaks at reciprocal lattice vectors $\boldsymbol{Q}$:

$$|M(\boldsymbol{q})|^2 = N^2 |U_1(\boldsymbol{q})|^2 \sum_{\boldsymbol{Q}} \delta_{\boldsymbol{q},\boldsymbol{Q}}. \tag{32}$$

To do better, we should recognize that in reality the scattering cross section should be given by a thermal average of the above quantity:

$$\langle |M(\boldsymbol{q})|^2 \rangle = |U_1(\boldsymbol{q})|^2 \sum_{\boldsymbol{R},\boldsymbol{R}'} \langle e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \rangle. \tag{33}$$

By writing this down, we are assuming that the scattering particle has some chance (given by the thermal distribution) of seeing any given configuration of the atoms and scattering off of it. We are still not allowing for the possibility that the scattering particle deposits energy in the crystal – this will obviously have to be corrected in a more careful treatment.

Let's evaluate the above average, by putting $\boldsymbol{R} \to \boldsymbol{R} + \boldsymbol{u}(\boldsymbol{R})$:

$$\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \rangle = e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \langle e^{i\boldsymbol{q}\cdot(\boldsymbol{u}(\boldsymbol{R}')-\boldsymbol{u}(\boldsymbol{R}))} \rangle \tag{34}$$

$$= e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \exp\Big(-\frac{1}{2} \big\langle [\boldsymbol{q}\cdot(\boldsymbol{u}(\boldsymbol{R}') - \boldsymbol{u}(\boldsymbol{R}))]^2 \big\rangle \Big). \tag{35}$$

In the second line we used a result (proved in Appendix A) that says the following: if H is a quadratic Hamiltonian, and A is any linear combination of coordinates and momenta, then $\langle e^A \rangle = \exp[(1/2)\langle A^2 \rangle]$.

Simplifying further, we have

$$\exp\Big(-\frac{1}{2} \big\langle [\boldsymbol{q}\cdot(\boldsymbol{u}(\boldsymbol{R}') - \boldsymbol{u}(\boldsymbol{R}))]^2 \big\rangle \Big) = \exp\Big(-\frac{1}{2} \big\langle [\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R}')]^2 \big\rangle - \frac{1}{2} \big\langle [\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R})]^2 \big\rangle + \big\langle [\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R})][\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R}')] \big\rangle \Big) \tag{36}$$

$$= \exp\Big(-\big\langle [\boldsymbol{q}\cdot\boldsymbol{u}(0)]^2 \big\rangle \Big) \exp\Big(\big\langle [\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R})][\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R}')] \big\rangle \Big), \tag{37}$$

where in the second line we used translation invariance. It is conventional to define

$$e^{-2W} = \exp\Big(- \big\langle [\boldsymbol{q}\cdot \boldsymbol{u}(0)]^2 \big\rangle \Big), \tag{38}$$

and to call e^{-2W} the Debye-Waller factor. Note that W depends on $\boldsymbol{q}$, although this dependence is often not written explicitly.

Putting all of this together, we have

$$\langle |M(\boldsymbol{q})|^2\rangle = |U_1(\boldsymbol{q})|^2 e^{-2W} \sum_{\boldsymbol{R},\boldsymbol{R}'} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \exp\Big(\big\langle [\boldsymbol{q}\cdot \boldsymbol{u}(\boldsymbol{R})][\boldsymbol{q}\cdot \boldsymbol{u}(\boldsymbol{R}')] \big\rangle \Big). \tag{39}$$

In general, this sum is essentially impossible to evaluate. Fortunately, we can Taylor expand the exponential inside the sum, which gives a series of *additive* contributions to the scattering cross-section. To properly understand the meaning and effect of the terms in this expansion beyond zeroth-order, we will need to go to a quantum mechanical treatment of the lattice vibrations. However, just looking for now at the zeroth-order term, we have

$$\langle |M^0(\boldsymbol{q})|^2\rangle = |U_1(\boldsymbol{q})|^2 e^{-2W} \sum_{\boldsymbol{R},\boldsymbol{R}'} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'-\boldsymbol{R})} = N^2 |U_1(\boldsymbol{q})|^2 e^{-2W} \sum_{\boldsymbol{Q}} \delta_{\boldsymbol{q},\boldsymbol{Q}}. \tag{40}$$

Remarkably, the only effect of thermal fluctuations is to multiply the Bragg peaks by the Debye-Waller factor. In particular, the peaks do not get broadened by thermal fluctuations!

It just remains to calculate W, which is almost the same as $\langle \boldsymbol{u}(0)^2\rangle$ that we already calculated. Following the same manipulations we used to do that calculation, we have

$$\begin{aligned}
W &= \frac{1}{2} q^\mu q^\nu \langle u^\mu(0) u^\nu(0)\rangle && (41)\\
&= \frac{1}{2} q^\mu q^\nu \frac{2}{N} {\sum_{\boldsymbol{k}\neq 0}}' \sum_\lambda S_{\mu\lambda}(\boldsymbol{k}) S_{\nu\lambda}(\boldsymbol{k}) \langle [u^R_\lambda(\boldsymbol{k})]^2\rangle && (42)\\
&= q^\mu q^\nu \frac{k_B T}{MN} {\sum_{\boldsymbol{k}\neq 0}}' \sum_\lambda \frac{S_{\mu\lambda}(\boldsymbol{k}) S_{\nu\lambda}(\boldsymbol{k})}{\omega_\lambda(\boldsymbol{k})^2} && (43)\\
&= q^\mu q^\nu \frac{k_B T}{2MN} \sum_{\boldsymbol{k}\neq 0} \sum_\lambda \frac{S_{\mu\lambda}(\boldsymbol{k}) S_{\nu\lambda}(\boldsymbol{k})}{\omega_\lambda(\boldsymbol{k})^2} && (44)\\
&= q^\mu q^\nu \frac{k_B T a^3}{2M} \sum_\lambda \int_{\boldsymbol{k}\in \text{B.Z.}} \frac{d^3\boldsymbol{k}}{(2\pi)^3} \frac{S_{\mu\lambda}(\boldsymbol{k}) S_{\nu\lambda}(\boldsymbol{k})}{\omega_\lambda(\boldsymbol{k})^2}. && (45)
\end{aligned}$$

Again, this is constant in 3d, and is expected to diverge in 1d or 2d. If W diverges, it means that the Debye-Waller factor vanishes, which eliminates the Bragg peaks. So thermal fluctuations destroy Bragg peaks for 1d or 2d crystals, but not in 3d. The presence of Bragg peaks is essentially what it means to have a crystal, so this means that, strictly speaking, it is impossible to have a true crystal in one or two dimensions.

Appendix A: Thermal averages of exponentials

To be general, let's suppose we have N coordinates and momenta labeled by x_i, where $i = 1, \ldots, N$. We will represent these by an N-dimensional vector x. Let's suppose that our Hamiltonian has the form

$$H = \frac{1}{2} x^T M x, \tag{A1}$$

where M is a real, symmetric matrix. So that the Hamiltonian is not unstable, we also assume that M is positive definite (*i.e.* all its eigenvalues are positive). The partition function is

$$Z = \prod_{i=1}^{N} \int_{-\infty}^{\infty} dx_i e^{-\beta H} \equiv \int d\Gamma e^{-\beta H}. \tag{A2}$$

We want to compute the thermal average $\langle e^{a^T x}\rangle$, where a is some constant N-dimensional vector. In particular, we would like to show that

$$\langle e^{a^T x}\rangle = \exp\Big(\frac{1}{2}\big\langle (a^T x)^2\big\rangle\Big). \tag{A3}$$

The strategy will be to directly calculate the expectation values on the right-hand and left-hand sides, and show they are the same.

First, we calculate $\langle e^{a^T x}\rangle$. We have

$$\langle e^{a^T x}\rangle = \frac{1}{Z}\int d\Gamma \exp\Big(-\frac{1}{2}x^T(\beta M)x + a^T x\Big). \tag{A4}$$

Since M (and hence βM) is invertible, we can make the change of variables $x \to x + (\beta M)^{-1}a$ in the above integral. Because this change of variables is just a constant shift of x, it doesn't affect the integration measure. Working through the algebra we find

$$\langle e^{a^T x}\rangle = \frac{1}{Z}\exp\Big(\frac{1}{2}a^T(\beta M)^{-1}a\Big)\int d\Gamma \exp\Big(-\frac{1}{2}x^T(\beta M)x\Big) \tag{A5}$$

$$= \exp\Big(\frac{1}{2}a^T(\beta M)^{-1}a\Big). \tag{A6}$$

Let's now consider the thermal average $\langle (a^T x)^2\rangle = a_i a_j \langle x_i x_j\rangle$. Let's calculate $\langle x_i x_j\rangle$, using a trick. Looking at Eq. (A4), we can see that the following relation is true:

$$\langle x_i x_j\rangle = \frac{\partial^2 \langle e^{a^T x}\rangle}{\partial a_i \partial a_j}\Big|_{a=0}. \tag{A7}$$

We can evaluate this derivative using the result of Eq. (A6), and we find

$$\langle x_i x_j\rangle = (\beta M)^{-1}_{ij}. \tag{A8}$$

It should be noted here that, since M is a symmetric matrix, so is M^{-1}. Therefore

$$\langle (a^T x)^2\rangle = a_i a_j \langle x_i x_j\rangle = a^T(\beta M)^{-1}a. \tag{A9}$$

With this result, combined with Eq. (A6), we have proved Eq. (A3), as desired.