Physics 7450: Solid State Physics 2

Lecture 2: Elasticity and phonons

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(Dated: 12 January, 2015)

Abstract

In these lecture notes, starting with semi-microscopic model of a crystal we will develop a generic discrete model of crystalline elasticity. We will study quantum and thermal fluctuations governed by this elastic Hamiltonian within the discrete and continuum elastic limits. We will conclude with the study of effects of elastic nonlinearities.

I. CRYSTAL LATTICE IN HARMONIC APPROXIMATION

A. General discrete formulation

As discussed in lecture 1, interacting ions forms a lattice, characterized by (in general) quantum coordinates $\mathbf{R}_i$ with a Hamiltonian

$$H_{ion} = \sum_i^N \frac{\mathbf{P}_i^2}{2M_i} + \frac{1}{2}\sum_{i,j}^N U_{pair}(|\mathbf{R}_i - \mathbf{R}_j|), \tag{1}$$

where $U_{pair}(R)$ is the inter-ionic pair potential that we have approximated to be of central force type, depending only on the inter-atomic distance R and not on the bond angles. Although microscopically it is simply the Coulomb potential, because of the screening effects by the electrons we have taken it to be a generic function with a minimum that by construction gives a particular equilibrium crystal structure, $\mathbf{R}_i = \mathbf{R}_{n,s}$ (recall that $n = (n_1, n_2, n_3)$ labels Bravais lattice sites and s p-atom basis within the unit cell). The calculation of the latter requires quite involved first-principles numerical analysis that we will avoid here and package that information into U_{pair}.

The full quantum description of the crystal structure is then formulated in terms of deviations $\mathbf{u}^s(n) \equiv \mathbf{u}(\mathbf{R}_{n,s}) \equiv \mathbf{u}_\mathbf{R}$ from this perfect crystalline structure

$$\mathbf{R}_i = \mathbf{R}_{n,s} + \mathbf{u}(\mathbf{R}_{n,s}). \tag{2}$$

For small fluctuations, we can employ the harmonic approximation, Taylor-expanding a generic ionic potential energy

$$\begin{aligned} U(\{\mathbf{R}_i\}) &= U_0 + \frac{1}{2}\sum_{m,n;s,t;\alpha,\beta} U^{s,t}_{\alpha,\beta}(m,n)u^s_\alpha(m)u^t_\beta(n), &(3)\\ &= U_0 - \frac{1}{4}\sum_{m,n;s,t;\alpha,\beta} U^{s,t}_{\alpha,\beta}(m-n)(u^s_\alpha(m) - u^t_\alpha(n))(u^s_\alpha(m) - u^t_\alpha(n)), &(4)\end{aligned}$$

where $U_0 \equiv U(\mathbf{R}_{n,s})$, $U^{s,t}_{\alpha,\beta}(m-n) \equiv \frac{\partial^2 U}{\partial u^s_\alpha(m)\partial u^t_\beta(n)}$, the linear term vanished by virtue of the expansion around the minimum $\mathbf{R}_{n,s}$, dependence on $m-n$ is due to *discrete* lattice translational invariance, and in the last equality we utilized the *continuous* uniform translational invariance of the whole crystal, $\mathbf{u}^s(m) \to \mathbf{u}^s(m) + \boldsymbol{\epsilon}$, which requires $\sum_{m,s} U^{s,t}_{\alpha,\beta}(m,n) = 0$ (vanishing energy of uniform translation).

An equivalent description (but slightly less general since it is possible for the interaction not to be purely pairwise-additive or be of purely central form) is in terms of the pair potential $U_{pair}(|\mathbf{R}_{ij}|)$:

$$U(\{\mathbf{R}_i\}) = \frac{1}{2}\sum_{\mathbf{R}_{m,s},\mathbf{R}_{n,t}}^{N,p} U_{pair}(|\mathbf{R}_{m,s} - \mathbf{R}_{n,t} + \mathbf{u}(\mathbf{R}_{m,s}) - \mathbf{u}(\mathbf{R}_{n,t})|), \tag{5}$$

$$\approx U_0 + \frac{1}{4}\sum_{\mathbf{R},\mathbf{R}'}^{N,p} U_{\alpha\beta}^{s,t}(|\mathbf{R}-\mathbf{R}'|)(u_{\mathbf{R}}^{\alpha} - u_{\mathbf{R}'}^{\alpha})(u_{\mathbf{R}}^{\beta} - u_{\mathbf{R}'}^{\beta}), \tag{6}$$

$$\approx U_0 + \frac{1}{2}\sum_{\mathbf{k}\in BZ} D_{\alpha\beta}^{s,t}(\mathbf{k})\tilde{u}_{-\mathbf{k},s}^{\alpha}\tilde{u}_{\mathbf{k},t}^{\beta} \tag{7}$$

where with $r \equiv |\mathbf{R}_{m,s} - \mathbf{R}_{n,t}|$, we have force constants matrix given by

$$U_{\alpha\beta}^{s,t}(r) = \delta_{\alpha\beta}\frac{1}{r}\frac{\partial U_{pair}(r)}{\partial r} + \left(\frac{\partial^2 U_{pair}(r)}{\partial r^2} - \frac{1}{r}\frac{\partial U_{pair}(r)}{\partial r}\right)\frac{r_\alpha r_\beta}{r^2}, \tag{8}$$

and its Fourier transform, the dynamical matrix

$$D_{\alpha\beta}^{s,t}(\mathbf{k}) = \sum_{\mathbf{R}_n}^{N} U_{\alpha\beta}^{s,t}(|\mathbf{R}_{m,s} - \mathbf{R}_{n,t}|)\left(1 - e^{i\mathbf{k}\cdot(\mathbf{R}_{m,s}-\mathbf{R}_{n,t})}\right), \tag{9}$$

Within this harmonic approximation the equation of motion together with the kinetic energy

$$T_{kin} = \sum_{\mathbf{R}} \frac{1}{2} M_s \dot{\mathbf{u}}_{\mathbf{R}}^2, \tag{10}$$

$$= \sum_{\mathbf{R}} \frac{\mathbf{P}_{\mathbf{R}}^{\mathbf{2}}}{2M_s}, \tag{11}$$

is straightforwardly obtained (via Hamiltonian or Lagrangian formalisms):

$$M_s \ddot{u}_{\mathbf{R}_{m,s}}^{\alpha} = -\sum_{\mathbf{R}_{n,t}}^{N,p} U_{\alpha\beta}^{s,t}(|\mathbf{R}_{m,s} - \mathbf{R}_{n,t}|)(u_{\mathbf{R}_{m,s}}^{\beta} - u_{\mathbf{R}_{n,t}}^{\beta})$$

which in 3d corresponds to $3Np$ coupled harmonic oscillator equations. Because of discrete (lattice) translational symmetry, as we will see these can be decoupled using normal modes that are nothing else but the Fourier series coefficients labelled by $3Np$ discrete values of $\mathbf{k}$.

B. One-dimensional atomic chain

1. *Normal modes decoupling*

To get a feel for these expressions as a warm-up we will first consider a 1d monoatomic (no basis, $p = 1$), harmonic chain, illustrated in Fig.(1).

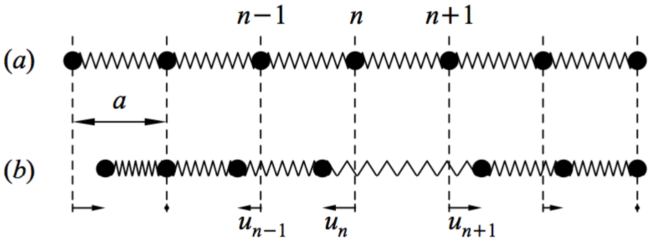

FIG. 1: A one-dimensional monatomic chain with springs representing the elastic forces between the atoms, (a) in equilibrium, (b) distorted by a fluctuation from equilibrium state.

Because typically interactions between atoms fall off strongly (short-ranged), it is often sufficient to approximate the interaction by nearest neighbors only. In this case the Hamiltonian reduces to

$$H_{1d} = \sum_{n=1}^{N} \frac{P_n^2}{2M} + \frac{1}{2} B \sum_{n=1}^{N} (u_{n+1} - u_n)^2, \tag{12}$$

with the corresponding equation of motion

$$\begin{aligned} M\ddot{u}_n &= -B(2u_n - u_{n+1} - u_{n-1}), & (13)\\ &= \nabla_n^2 u_n, & (14) \end{aligned}$$

and the elastic modulus $B \equiv M\omega_0^2 = \partial^2 U_{pair}(x)/\partial x^2$, ∇_n^2 a discrete second derivative. For convenience we take the system to have periodic boundary conditions (corresponding to atoms on a ring), with $u_{N+1} = u_1$.

Given the translational invariance of the system, the oscillations are decoupled in terms of Fourier normal modes

$$u_n = \frac{1}{\sqrt{N}} \sum_{p=-N/2}^{p=N/2} \tilde{u}_p e^{in2\pi p/N}, \tag{15}$$

where (i) $1/\sqrt{N}$ is a convenient normalization and (ii) the phase factor can be written in a more familiar, $in2\pi p/N = i(na)(2\pi p/(Na)) = ix_n k_p$, ($a$ the lattice) convenient for taking the continuum limit where $a \to 0$, $N \to \infty$, but $Na \equiv L$ fixed. We note that k_p is limited to a 1st Brillouin zone range, $-\pi/a < k_p \leq \pi/a$, corresponding to $-N/2 < p \leq N/2$, as can be seen from the fact that $p = N$ does not correspond to a physically distinct lattice distortion u_n.

Using this representation inside the equation of motion, and also Fourier transforming in time, we find

$$-M\omega^2\tilde{u}_k(\omega) = -B(2 - e^{-ika} - e^{ika})\tilde{u}_k(\omega), \tag{16}$$

$$= -2B(1 - \cos ka)\tilde{u}_k(\omega), \tag{17}$$

which gives the acoustic phonon dispersion

$$\omega(k) = \sqrt{\frac{2B}{M}(1 - \cos ka)} = 2\left(\frac{B}{M}\right)^{1/2} |\sin(\frac{1}{2}ka)|, \tag{18}$$

illustrated in Fig.2.

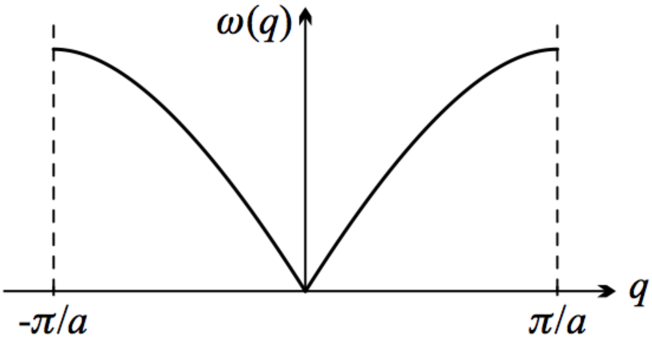

FIG. 2: A dispersion of a one-dimensional monatomic harmonic chain.

In the long-wavelength limit, $1/k \gg a$, the dispersion is linear

$$\omega(k) \approx \left(\frac{B}{M}\right)^{1/2} a|k| \equiv c|k|, \tag{19}$$

with sound group velocity $c = \left(\frac{B}{M}\right)^{1/2} a = \omega_0 a$ and dispersive group velocity $c_g(k) = |\partial\omega/\partial k|$ away from $k = 0$. This vanishing dispersion property is quite general and is a reflection of the underlying translational symmetry that is spontaneous "broken" by crystallization, with the phonon u_R the corresponding Goldstone mode.[1–3]

In building up to quantum field theory of solid state systems, it is more convenient to diagonalize the Hamiltonian directly (rather than the equation of motion). Expressing H in Eq.(12) in terms of the normal modes $\tilde{u}_k$, we find

$$H_{1d} = \sum_{n=1}^{N} \frac{P_n^2}{2M} + \frac{M\omega_0^2}{2N} \sum_{n=1}^{N} \sum_{p_1,p_2} \tilde{u}_{p_1}\tilde{u}_{p_2} e^{i2\pi n(p_1+p_2)/N} \left(e^{i2\pi p_1/N} - 1\right)\left(e^{i2\pi p_2/N} - 1\right) \tag{20}$$

Applying a simple identity

$$\sum_{n=1}^{N} e^{i2\pi n(p_1+p_2)/N} = N\delta_{p_1+p_2,0} \tag{21}$$

the Hamiltonian reduces to

$$\begin{aligned} H_{1d} &= \sum_{n=1}^{N} \frac{1}{2M} P_n^2 + \sum_{p=-N/2}^{N/2} \frac{1}{2} M\omega_p^2 |\tilde{u}_p|^2, & (22) \\ &= \sum_{k=-\pi/a}^{\pi/a} \left[\frac{1}{2M}|\tilde{P}_k|^2 + \frac{1}{2}M\omega_k^2|\tilde{u}_k|^2\right], & (23) \\ &= \sum_{k=-\pi/a}^{\pi/a} \left[\frac{1}{2M}\tilde{P}_k^\dagger\tilde{P}_k + \frac{1}{2}M\omega_k^2\tilde{u}_k^\dagger\tilde{u}_k\right], & (24) \end{aligned}$$

with

$$\omega_k = 2\omega_0|\sin(ka/2)|.$$

Although to decouple the Hamiltonian, it is sufficient to just Fourier transform the displacement $u_n \rightarrow \tilde{u}_k$, as we did in the second form above, we are forced to also transform the momentum $P_n \rightarrow \tilde{P}_k$, in order to maintain the canonical commutation relation, $[\tilde{u}_{k_1}, \tilde{P}_{k_2}] = i\hbar\delta_{k_1,-k_2}$, giving

$$[\tilde{u}_k, \tilde{P}_k^\dagger] = i\hbar,$$

where because the fields in coordinate space are real, $\tilde{P}_k^\dagger = \tilde{P}_{-k}$, as can be straightforwardly verified.

Thus Fourier representation indeed diagonalizes the Hamiltonian, decoupling it into N independent harmonic oscillators with frequency ω_k identical to that we found from the equation of motion.

For homework we will study a chain with two-atom basis that requires a diaogonalization of a 2×2 matrix even after Fourier transform and leads to two, optical and acoustic bands. (also see Solyom Sec. 11.2)

2. Normal modes quantization

It is now straightforward to quantize oscillations of the crystal lattice by simply treating it as a sum of N independent quantum harmonic oscillators. The answer can be written automatically, given that $H_{1d} = \sum_k H_k$ is a sum of independent harmonic oscillator Hamiltonians, given in the Fock occupation $\{n_k\}$ basis for each k by

$$H_k|n_k\rangle = E_{n_k}|n_k\rangle,$$

where $|\{n_k\}\rangle = \prod_k |n_k\rangle$, with the many-body spectrum

$$E(\{n_k\}) = \sum_k E_{n_k} = \sum_k \hbar\omega_k(n_k + 1/2).$$

For completeness we diagonalize the crystal Hamiltonian by expressing it in terms of creation and annihilation operators for each H_k following standard procedure. Namely, we express u_k and P_k in terms of a_k and $a_k^\dagger$, with latter satisfying bosonic commutation relation $[a_k, a_k^\dagger] = 1$ and $a_k|n_k\rangle = \sqrt{n_k}|n_k - 1\rangle$, $a_k^\dagger|n_k\rangle = \sqrt{n_k+1}|n_k + 1\rangle$.

Generically the normal mode k harmonic Hamiltonian H_k is given by

$$\begin{aligned} H_k &= \frac{1}{2}\alpha_k\tilde{P}_k^\dagger\tilde{P}_k + \frac{1}{2}\beta_k\tilde{u}_k^\dagger\tilde{u}_k, & (25)\\ &= \frac{1}{2}\hbar\sqrt{\alpha_k\beta_k}\left[\frac{1}{\hbar^2}\sqrt{\frac{\hbar^2\alpha_k}{\beta_k}}\tilde{P}_k^\dagger\tilde{P}_k + \sqrt{\frac{\beta_k}{\hbar^2\alpha_k}}\tilde{u}_k^\dagger\tilde{u}_k\right], & (26)\\ &\equiv \hbar\omega_k\left(a_k^\dagger a_k + 1/2\right), & (27)\end{aligned}$$

where we identified the natural frequency and a quantum oscillator length

$$\omega_k = \sqrt{\alpha_k\beta_k}, \quad u_{0k} = \left(\hbar^2\frac{\alpha_k}{\beta_k}\right)^{1/4} \tag{28}$$

and introduced creation and annihilation operators in terms of dimensionless displacement $\hat{u}_k \equiv \tilde{u}_k/u_0$ and momentum $\hat{P}_k \equiv \tilde{P}_k/(\hbar/u_{0k})$

$$a_k = \sqrt{\frac{1}{2}}(\hat{u}_k + i\hat{P}_k), \quad a_k^\dagger = \sqrt{\frac{1}{2}}(\hat{u}_k^\dagger - i\hat{P}_k^\dagger), \tag{29}$$

$$\tag{30}$$

obeying canonical commutation relation $[a_k, a_k^\dagger] = 1$. Equivalently,

$$\tilde{u}_k = u_{0k}\sqrt{\frac{1}{2}}(a_k + a_{-k}^\dagger), \quad \tilde{P}_k = -i\frac{\hbar}{u_{0k}}\sqrt{\frac{1}{2}}(a_k - a_{-k}^\dagger). \tag{31}$$

In real space the field operators are then given by

$$u_R = \sqrt{\frac{1}{2N}}\sum_{k=-\pi/a}^{k=\pi/a} u_{0k}(a_k e^{ikR} + a_k^\dagger e^{-ikR}), \quad P_R = -i\sqrt{\frac{1}{2N}}\sum_{k=-\pi/a}^{k=\pi/a}\frac{\hbar}{u_{0k}}(a_k e^{ikR} - a_k^\dagger e^{-ikR}). \tag{32}$$

C. Continuum elastic formulation

For a many applications, it is convenient to take a continuum limit of the above formulation, valid for acoustic mode in the limit of small k, i.e., $ka \ll 1$. In this limit, the general lattice form (7) simplifies by approximating phonon differences by a gradient expansion

$$\mathbf{u}(\mathbf{R}_m) - \mathbf{u}(\mathbf{R}_n) \approx \left((\mathbf{R}_m - \mathbf{R}_n) \cdot \boldsymbol{\nabla}_r\right) \mathbf{u}(\mathbf{r})|_{\mathbf{r}=\mathbf{R}_n},$$

giving

$$U_{el}[\mathbf{u}(\mathbf{r})] \;\approx\; \frac{1}{2}\int d\mathbf{r} C_{\alpha\beta,\gamma\delta}\; u_{\alpha\beta}u_{\gamma\delta} \tag{33}$$

where (going to continuum with unit cell v)

$$C_{\alpha\beta,\gamma\delta} = \frac{1}{2v}\sum_{\mathbf{R}_m}(\mathbf{R}_m - \mathbf{R}_n)_\alpha U^{s,t}_{\beta\delta}(|\mathbf{R}_m - \mathbf{R}_n|)(\mathbf{R}_m - \mathbf{R}_n)_\gamma \tag{34}$$

is the elastic structure constant, whose detailed form is determined by crystal symmetry, but generically by construction symmetric on the first two and last two indices, and under interchange of the pairs of indices

$$C_{\alpha\beta,\gamma\delta} = C_{\beta\alpha,\gamma\delta} = C_{\alpha\beta,\delta\gamma} = C_{\gamma\delta,\alpha\beta},$$

and

$$u_{\alpha\beta} \;=\; \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha + \partial_\alpha \mathbf{u}\cdot\partial_\beta \mathbf{u}), \tag{35}$$

$$\approx\; \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha) \equiv \varepsilon_{\alpha\beta} \tag{36}$$

is a symmetric strain tensor, where in the second line we approximated it by its harmonic form, $\varepsilon_{\alpha\beta}$. Strain's general structure is gauranteed by the underlying lattice rotational invariance, demanding that at harmonic level the elastic energy cannot dependent on the antisymmetric part $\frac{1}{2}(\partial_\alpha u_\beta - \partial_\beta u_\alpha)$ that corresponds to lattice rotation. The diagonal elements u_{xx}, u_{yy}, u_{zz} represent bond length change, while the off-diagonal elements u_{xy}, u_{yz}, u_{xz} correspond to shear. As a generalization of Hooke's law the elastic structure constant relates strain to stress

$$\sigma_{\alpha\beta} = C_{\alpha\beta,\gamma\delta}\; u_{\gamma\delta}.$$

1. *Elasticity in different crystal symmetries*

In three dimensions there are 6 independent components of the strain tensor, $\varepsilon_1 = u_{xx}, \varepsilon_2 = u_{yy}, \varepsilon_3 = u_{zz}, \varepsilon_4 = 2u_{yz}, \varepsilon_5 = 2u_{zx}, \varepsilon_6 = 2u_{xy}$ with the elastic energy density given by

$$\mathcal{U}_{el} \approx \frac{1}{2} c_{i,j} \varepsilon_i \varepsilon_j, \tag{37}$$

For *triclinic* crystals this leads to $6 \times 7/2 = 21$ elastic components. This number gets significantly reduced down to 13 components in a *monoclinic* crystal system, by invariance $x \to -x$, $y \to -y$, $z \to z$ forbidding odd appearance of ε_4 and ε_5. In the *orthorhombic* crystal the additional 180^0 rotation about each of the three axes reduces the count down to 9 elastic constants by forbidding odd occurence of ε_6 and ε_4. In *tetragonal* crystals, 90^0 rotations around z-axis, $x \to y, y \to -x, z \to z$ reduces the number of elastic constants down to 6, with the elastic energy density

$$\mathcal{U}_{el}^{tetra} = \frac{1}{2} c_{11}(u_{xx}^2 + u_{yy}^2) + \frac{1}{2} c_{33} u_{zz}^2 + c_{12} u_{xx} u_{yy} + c_{13}(u_{xx} u_{zz} + u_{yy} u_{zz}) + 2c_{44}(u_{xz}^2 + u_{yz}^2) + 2c_{44} u_{xy}^2. \tag{38}$$

Adding 90^0 rotations about x- and y-axes in a cubic crystal reduces the energy density to

$$\mathcal{U}_{el}^{cubic} = \frac{1}{2} c_{11}(u_{xx}^2 + u_{yy}^2 + u_{zz}^2) + c_{12}(u_{xx} u_{yy} + u_{xx} u_{zz} + u_{yy} u_{zz}) + 2c_{44}(u_{xy}^2 + u_{xz}^2 + u_{yz}^2). \tag{39}$$

2. *Elasticity of "isotropic" solid*

In the case of an isotropic (noncrystalline) solid, the elasticity is characterized by only two elastic constants traditionally called the Lame' constants, μ and λ, with

$$C_{\alpha\beta,\gamma\delta} = \lambda \delta_{\alpha\beta} \delta_{\gamma\delta} + \mu(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}).$$

In this notation the the shear modulus $G = \mu$, the bulk modulus $B = \lambda + 2\mu/3$, the inverse of the compressibility κ, Poisson ratio $\nu = \frac{\lambda}{2(\mu+\lambda)}$, Young's modulus $E = \frac{\mu(2\mu+3\lambda)}{\mu+\lambda}$, and the elastic energy density reduces to

$$\mathcal{U}_{el}^{iso} = \mu u_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2} \lambda u_{\alpha\alpha} u_{\beta\beta}, \tag{40}$$

expressed in terms of two scalars, $\mathrm{Tr}[u]$ and $\mathrm{Tr}[u^2]$. The corresponding stress is given by

$$\sigma_{\alpha\beta} = \lambda\delta_{\alpha\beta}u_{\gamma\gamma} + 2\mu u_{\alpha\beta}.$$

For further analysis it is important to express this elastic energy in terms of the phonon displacement degrees of freedom, $\mathbf{u}(\mathbf{r})$ and then decouple it through normal modes analysis, that corresponds to Fourier transformation. To this end we use (36) inside (40), finding

$$\begin{aligned} U_{el}^{iso} &= \frac{1}{2}\int_{\mathbf{r}} u_\alpha(\mathbf{r})\left[\mu(-\nabla^2)P^T_{\alpha\beta} + (2\mu+\lambda)(-\nabla^2)P^L_{\alpha\beta}\right]u_\beta(\mathbf{r}), & (41)\\ &= \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\tilde{u}_\alpha(-\mathbf{k})\left[\mu k^2 P^T_{\alpha\beta}(\mathbf{k}) + (2\mu+\lambda)k^2P^L_{\alpha\beta}(\mathbf{k})\right]\tilde{u}_\beta(\mathbf{k}), & (42)\\ &\equiv \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\tilde{u}_\alpha(-\mathbf{k})D_{\alpha\beta}(\mathbf{k})\tilde{u}_\beta(\mathbf{k}), & (43)\end{aligned}$$

where we utilized normal modes $\tilde{\mathbf{u}}(\mathbf{k})$

$$\mathbf{u}(\mathbf{r}) = \int\frac{d^3k}{(2\pi)^3}\tilde{\mathbf{u}}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{44}$$

decomposition to decouple the Hamiltonian, and defined transverse and longitudinal projection operators, transverse and along $\mathbf{k}$, respectively

$$P^T_{\alpha\beta}(\mathbf{k}) = \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}, \quad P^L_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2}. \tag{45}$$

Because the projection operators are independent, the inverse of the dynamic matrix $D_{\alpha\beta}(\mathbf{k})$ (that we will need for study of thermodynamics and correlation functions) is easily obtained

$$D^{-1}_{\alpha\beta}(\mathbf{k}) = \frac{1}{\mu k^2}P^T_{\alpha\beta}(\mathbf{k}) + \frac{1}{(2\mu+\lambda)k^2}P^L_{\alpha\beta}(\mathbf{k}), \tag{46}$$

as can be straightforwardly verified using $P^T_{\alpha\gamma}P^T_{\gamma\beta} = P^T_{\alpha\beta}$, $P^L_{\alpha\gamma}P^L_{\gamma\beta} = P^L_{\alpha\beta}$, $P^T_{\alpha\gamma}P^L_{\gamma\beta} = 0$.

Interestingly, a two-dimensional hexagonal lattice is also characterized by such isotropic elasticity, despite being a crystal, with only higher order nonlinear elastic terms distinguishing it from a truly isotropic, amorphous solid.

A related but more general observation that we will use over and over in converting a Hamiltonian from real-space $\phi(\mathbf{r})$ to Fourier $\tilde{\phi}(\mathbf{k})$ degrees of freedom is:

$$\begin{aligned} H &= \frac{1}{2}\int d^drd^dr'\phi(\mathbf{r})\Gamma(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}'), & \\ &= \frac{1}{2}\int\frac{d^dk}{(2\pi)^d}\tilde{\phi}(-\mathbf{k})\tilde{\Gamma}(\mathbf{k})\tilde{\phi}(\mathbf{k}), & (47)\end{aligned}$$

that is straightforwardly established by Fourier transformation.

Having established the field theory of elastic degrees of freedom, we now turn to the computation of variety of physical properties, such as thermodynamics and correlation functions.

II. THERMODYNAMICS

To analyze the thermodynamics it is convenient to work in canonical ensemble, where much can be extracted from the partition function or corresponding correlation function:

$$
\begin{aligned}
\mathcal{Z}_{phonons}^{classical} &= \int [d\mathbf{P}][d\mathbf{u}]e^{-\beta H[\mathbf{P},\mathbf{u}]}, && (48)\\
\langle ... \rangle &= \frac{1}{\mathcal{Z}_{phonons}^{classical}} \int [d\mathbf{P}][d\mathbf{u}]...e^{-\beta H[\mathbf{P},\mathbf{u}]}, && (49)\\
\mathcal{Z}_{phonons}^{quantum} &= \mathrm{Tr}\left[e^{-\beta \hat{H}[\hat{\mathbf{P}},\hat{\mathbf{u}}]}\right], && (50)\\
\langle ... \rangle &= \frac{1}{\mathcal{Z}_{phonons}^{quantum}} \mathrm{Tr}\left[...e^{-\beta \hat{H}[\hat{\mathbf{P}},\hat{\mathbf{u}}]}\right], && (51)
\end{aligned}
$$

where as usual $\beta = 1/(k_B T)$, the normalization by $2\pi\hbar$ per degree of freedom is implicitly, and in the quantum case the degrees of freedom $\hat{\mathbf{P}}, \hat{\mathbf{u}}$ are operators with the Trace taken over any complete set of states in the Hilbert space.

Before turning to the calculation of thermodynamics, we pause to develop the very important theoretical tool of Gaussian integrals, that we will utilize over and over again here and throughout the course.

A. Gaussian integrals

Given that the harmonic oscillator is a work-horse of theoretical physics, it is not suprising that Gaussian integrals are the key tool of theoretical physics. It is certainly clear in the computation of the partition function of the classical harmonic oscillator as it involves Gaussian integration over fields $\mathbf{P}$ and $\mathbf{u}$. However, as we will see, utilizing Feynman's path-integral formulation of quantum mechanics, Gaussian integrals are also central for computation in quantum statistical mechanics and more generally in quantum field theory.

1. *one-dimension*

Let us start out slowly with standard scalar Gaussian integrals

$$Z_0(a) = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}}, \tag{52}$$

$$Z_1(a) = \int_{-\infty}^{\infty} dx x^2 e^{-\frac{1}{2}ax^2} = -2\frac{\partial}{\partial a}Z_0(a) = \frac{1}{a}\sqrt{\frac{2\pi}{a}} = \frac{1}{a}Z_0, \tag{53}$$

$$Z_n(a) = \int_{-\infty}^{\infty} dx x^{2n} e^{-\frac{1}{2}ax^2} = \frac{(2n-1)!!}{a^n}Z_0, \tag{54}$$

that can be deduced from dimensional analysis, relation to the first basic integral $Z_0(a)$ (that can in turn be computed by a standard trick of squaring it and integrating in polar coordinates) or another generating function and Γ-functions

$$Z(a,h) = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2+hx} = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}a(x-h/a)^2} e^{\frac{1}{2}h^2/a} = Z_0(a)e^{\frac{1}{2}h^2/a}, \tag{55}$$

$$= \sum_{n=0} \frac{h^{2n}}{(2n)!}Z_n(a). \tag{56}$$

Quite clearly, odd powers of x vanish by symmetry.

A useful generalization of above Gaussian integral calculus is to integrals over complex numbers. Namely, from above we have

$$I_0(a) = \int_{-\infty}^{\infty} \frac{dxdy}{\pi} e^{-a(x^2+y^2)} = \frac{1}{a} = \int \frac{d\bar{z}dz}{2\pi i} e^{-a\bar{z}z}, \tag{57}$$

where in above we treat $\bar{z}, z$ as independent complex fields and the normalization is determined by the Jacobian of the transformation from x, y pair. This integral will be envaluable for path integral quantization and analysis of bosonic systems described by complex fields, $\overline{\psi}, \psi$.

2. *d-dimensions*

This calculus can be straightforwardly generalized to multi-variable Gaussian integrals characterized by an $N \times N$ matrix $(\mathbf{A})_{ij}$,

$$Z_0(\mathbf{A}) = \int_{-\infty}^{\infty} [d\mathbf{x}] e^{-\frac{1}{2}\mathbf{x}^T\cdot\mathbf{A}\cdot\mathbf{x}} = \prod_{i=1}^{N}\sqrt{\frac{2\pi}{a_i}} = \sqrt{\frac{(2\pi)^N}{\det\mathbf{A}}}, \tag{58}$$

$$Z_1^{ij}(\mathbf{A}) = \int_{-\infty}^{\infty} [d\mathbf{x}] x_i x_j e^{-\frac{1}{2}\mathbf{x}^T\cdot\mathbf{A}\cdot\mathbf{x}} = Z_0\mathbf{A}_{ij}^{-1}, \tag{59}$$

$$Z(\mathbf{A},\mathbf{h}) = \int_{-\infty}^{\infty} [d\mathbf{x}] e^{-\frac{1}{2}\mathbf{x}^T\cdot\mathbf{A}\cdot\mathbf{x}+\mathbf{h}^T\cdot\mathbf{x}} = Z_0(\mathbf{A})e^{\frac{1}{2}\mathbf{h}^T\cdot\mathbf{A}^{-1}\cdot\mathbf{h}}, \tag{60}$$

computed by diagonalizing the symmetric matrix $\mathbf{A}$ and thereby decoupling the N-dimensional integral into a product of N independent scalar Gaussian integrals (54), each characterized by eigenvalue a_i.

As a corollary of these Gaussian integral identities we have two more very important results, namely, that for a Gaussian random variable $\mathbf{x}$ obeying Gaussian statistics, with variance $\mathbf{A}^{-1}_{ij}$, we have

$$\langle \mathbf{x}_i \mathbf{x}_j \rangle \equiv G_{ij} = \frac{1}{Z_0}\int_{-\infty}^{\infty}[d\mathbf{x}]x_i x_j e^{-\frac{1}{2}\mathbf{x}^T\cdot\mathbf{A}\cdot\mathbf{x}} = \mathbf{A}^{-1}_{ij}, \tag{61}$$

$$\langle e^{\mathbf{h}^T\cdot\mathbf{x}} \rangle = e^{\frac{1}{2}\langle(\mathbf{h}^T\cdot\mathbf{x})^2\rangle} = e^{\frac{1}{2}\mathbf{h}^T\cdot\mathbf{G}\cdot\mathbf{h}}, \tag{62}$$

with second identity the relative of the Wick's theorem, which will be extremely important for computation of x-ray and neutron scattering structure function.

3. discrete vs continuum description

Throughout our lectures we will go back and forth between discrete and continuum description of the degrees of freedom. In all calculations, even when done in the continuum limit, it is quite important to keep in mind the discrete and therefore finite nature of the degrees of freedom, with the continuum description being simply an efficient pnemonic for the underlying lattice model. This guarantees that no true short-scale (ultra-violet, uv) divergences actually ever arise, cutoff by the physical lattice structure always present in any condensed matter system.

Given that a volume of a unit cell is v and reciprocal space is quantized in units of $2\pi/L$, the relations between sums and integrals in real and reciprocal spaces are given by

$$\sum_{\mathbf{R}}\ldots = \frac{1}{v}\int d^d r\ldots, \tag{63}$$

$$\sum_{\mathbf{k}}\ldots = L^d\int\frac{d^d k}{(2\pi)^d}\ldots. \tag{64}$$

Also, we note the relation between the Kronecker δ and δ-function identities,

$$\sum_{\mathbf{R}}^{N} e^{i\mathbf{k}\cdot\mathbf{R}} = N\delta_{\mathbf{k},0}, \tag{65}$$

$$\sum_{\mathbf{R}}^{N} v e^{i\mathbf{k}\cdot\mathbf{R}} = vN\delta_{\mathbf{k},0}, \tag{66}$$

$$\int d^d r e^{i\mathbf{k}\cdot\mathbf{r}} = V\delta_{\mathbf{k},0} = \frac{(2\pi)^d}{(2\pi/L)^d}\delta_{\mathbf{k},0} = (2\pi)^d\delta^d(\mathbf{k}), \tag{67}$$

where $V = vN$.

4. density of states

There will be many instances where our result is represented as a sum over the normal eigenmodes $\mathbf{k}$. If the summand is only a function the normal-mode frequency $\omega_{\mathbf{k}}$ (as will often be the case) it is convenient to replace the sum over $\mathbf{k}$ by an integral over ω, with the Jacobian of this transformation being the density of states $g(\omega)$, defined according to:

$$F = \sum_{\mathbf{k},\alpha} f(\omega_{\mathbf{k}}) = \int d\omega \left(\sum_{\mathbf{k},\alpha} \delta(\omega - \omega_{\mathbf{k}})\right) f(\omega), \tag{68}$$

$$= \int d\omega g(\omega) f(\omega), \tag{69}$$

where the number of states $\mathbf{k}$ per interval $d\omega$ around ω is given by density of states

$$g(\omega) = d\sum_{\mathbf{k}} \delta(\omega - \omega_{\mathbf{k}}) = dL^d \int \frac{d^d k}{(2\pi)^d}\delta(\omega - \omega_{\mathbf{k}}), \tag{70}$$

where there are d polarizations that we have taken to be degenerate. We note that sometimes $g(\omega)$ is defined without the volume factor L^d, corresponding to density of states per unit of volume. Also, by construction, $g(\omega)$ satisfies the sum rule $\int d\omega g(\omega) = N$.

The limit on large k is given by G set by the first BZ, corresponding to uv cutoff by the lattice spacing in $\mathbf{R}_n$. There is also infrared cutoff set by the system size, L or equivalently in momentum space by discreteness of $k = \frac{2\pi}{L}p$.

There are two canonical models of phonons, the Debye model with $\omega_k = ck$ and the Einstein model with $\omega_k = \omega_0$. The density of states for these "toy" models are straightforwardly computed to be

$$\begin{aligned}
g_{Debye}(\omega) &= dL^d \int \frac{d^dk}{(2\pi)^d}\delta(\omega - ck), & (71)\\
&= L^d \frac{dS_d}{(2\pi)^d c^d}\ \omega^{d-1}, \quad \text{for } 0 < \omega < \omega_{Debye} & (72)\\
g_{Einstein}(\omega) &= dL^d \int \frac{d^dk}{(2\pi)^d}\delta(\omega - \omega_o), & (73)\\
&= dN\delta(\omega - \omega_o), & (74)
\end{aligned}$$

where $S_d = 2\pi^{d/2}/\Gamma(d/2)$ is a surface area of a d-dimensional sphere and ω_D is defined by $dN = \int_0^{\omega_D} d\omega g_{Debye}(\omega)$.

B. Phonon thermodynamics

Armed with these tools, we now apply them to compute the free energy of a crystal lattice associated with atomic vibrations.

1. *classical treatment*

In the classical limit, we compute the partition function $\mathcal{Z}^c_{ph}$ in (48) by integrating over functional phase space of momentum and phonon displacement fields, $\mathbf{P}, \mathbf{u}$ using (60). In the classical limit, these are decoupled and the integral over the momentum field just gives an overall $3N$-th power of the thermal deBroglie wavelength, $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$. The remaining phonon integral is also straightforwardly done in terms of the normal phonon modes, giving

$$\begin{aligned}
\mathcal{Z}^c_{ph} &= \int [d\tilde{\mathbf{P}}_{\mathbf{k}}] e^{-\beta \int_{\mathbf{k}} \frac{|\tilde{\mathbf{P}}_{\mathbf{k}}|^2}{2M}} \int [d\tilde{\mathbf{u}}_{\mathbf{k}}] e^{-\beta \int_{\mathbf{k}} \frac{1}{2}\tilde{\mathbf{u}}^T_{-\mathbf{k}}\cdot\mathbf{D}_{\mathbf{k}}\cdot\tilde{\mathbf{u}}_{\mathbf{k}}}, & (75)\\
&= \prod_{\mathbf{k}} \left(\frac{M}{\hbar^2}\right)^{3/2} \frac{(k_BT)^3}{(\det \mathbf{D}_{\mathbf{k}})^{1/2}}, & (76)
\end{aligned}$$

The resulting Helmholtz free energy $\mathcal{F} = -k_BT \ln \mathcal{Z}$ is then given by

$$\mathcal{F}^c_{ph} = \frac{1}{2}k_BT \sum_{\mathbf{k}} \ln\left(\det \mathbf{D}_{\mathbf{k}}\right) + const. \qquad (77)$$

where the const. part comes from the momentum degrees of freedom, unimportant to us here, particularly because (due to lack of phase space discreteness) an additive constant to the free energy (and entropy) is not very meaningful in *classical* statistical mechanics.

The energy is also easily computed by averaging the classical Hamiltonian and utilizing the Gaussian integrals in (60). This directly leads to equipartition for the average energy and heat capacity

$$E = 3Nk_BT, \quad C_V = \left.\frac{\partial E}{\partial T}\right|_V = 3Nk_B. \tag{78}$$

The phonon correlation function is also directly given by the Gaussian integrals above,

$$\langle u^\alpha_{\mathbf{k}} u^\beta_{\mathbf{k}'}\rangle = k_BTD^{-1}_{\alpha\beta}(\mathbf{k})(2\pi)^3\delta^3(\mathbf{k}+\mathbf{k}'), \tag{79}$$

and in particular for "isotropic" solid is given by (46). In coordinate space it is given Fourier transform, (44)

$$\langle u^\alpha_{\mathbf{r}} u^\beta_{\mathbf{r}'}\rangle = k_BT\int\frac{d^3k}{(2\pi)^3}D^{-1}_{\alpha\beta}(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}, \tag{80}$$

a result that we will use extensively.

2. *quantum treatment*

We compute quantum thermodynamics utilizing canonical quantization, generalizing the 1d elastic chain treatement of Sec.(I B) to higher dimensions here. Normal modes decomposition (with eigenvectors $\hat{\mathbf{e}}_i$)

$$\mathbf{u}_{\mathbf{R}} = \sqrt{\frac{1}{N}}\sum_{\mathbf{k}\in 1BZ}\tilde{\mathbf{u}}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{81}$$

$$= \sqrt{\frac{1}{2N}}\sum_{i,\mathbf{k}\in 1BZ}u_{0ki}\hat{\mathbf{e}}_i(a_{\mathbf{k},i}e^{i\mathbf{k}\cdot\mathbf{R}} + a^\dagger_{\mathbf{k},i}e^{-i\mathbf{k}\cdot\mathbf{R}}), \tag{82}$$

$$\mathbf{P}_{\mathbf{R}} = \sqrt{\frac{1}{N}}\sum_{\mathbf{k}\in 1BZ}\tilde{\mathbf{P}}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{83}$$

$$= -i\sqrt{\frac{1}{2N}}\sum_{i,\mathbf{k}\in 1BZ}\frac{\hbar}{u_{0ki}}\hat{\mathbf{e}}_i(a_{\mathbf{k},i}e^{i\mathbf{k}\cdot\mathbf{R}} - a^\dagger_{\mathbf{k},i}e^{-i\mathbf{k}\cdot\mathbf{R}}). \tag{84}$$

gives a harmonic phonon Hamiltonian

$$H_{ph} = \sum_{\mathbf{k}\in 1BZ}\left[\frac{1}{2M}\tilde{\mathbf{P}}^\dagger_{\mathbf{k}}\cdot\tilde{\mathbf{P}}_{\mathbf{k}} + \frac{1}{2}\tilde{\mathbf{u}}^\dagger_k\cdot\mathbf{D}_{\mathbf{k}}\cdot\tilde{\mathbf{u}}_k\right], \tag{85}$$

$$= \sum_{i,\mathbf{k}\in 1BZ}\left[\frac{1}{2M}\tilde{P}^\dagger_{\mathbf{k},i}\tilde{P}_{\mathbf{k},i} + \frac{1}{2}M\omega^2_{\mathbf{k},i}\tilde{u}^\dagger_{\mathbf{k},i}\tilde{u}_{\mathbf{k},i}\right], \tag{86}$$

$$\equiv \sum_{\mathbf{k}\in 1BZ}\hbar\omega_{\mathbf{k},i}\left(a^\dagger_{\mathbf{k},i}a_{\mathbf{k},i} + 1/2\right), \tag{87}$$

where we identified the natural frequency $\omega_{\mathbf{k},i} = \sqrt{d_{\mathbf{k},i}/M}$ with eigenvalues $d_{\mathbf{k},i}$ of the dynamical matrix $\mathbf{D}_{\mathbf{k}}$ and a quantum oscillator length

$$u_{0ki} = \sqrt{\frac{\hbar}{M\omega_{\mathbf{k},i}}}, \tag{88}$$

and introduced creation and annihilation operators in terms of dimensionless displacement $\hat{u}_{\mathbf{k},i} \equiv \tilde{u}_{\mathbf{k},i}/u_{0ki}$ and momentum $\hat{P}_{\mathbf{k},i} \equiv \tilde{P}_{\mathbf{k},i}/(\hbar/u_{0ki})$

$$a_{\mathbf{k},i} \;=\; \sqrt{\frac{1}{2}}(\hat{u}_{\mathbf{k},i} + i\hat{P}_{\mathbf{k},i}), \quad a^{\dagger}_{\mathbf{k},i} = \sqrt{\frac{1}{2}}(\hat{u}^{\dagger}_{\mathbf{k},i} - i\hat{P}^{\dagger}_{\mathbf{k},i}), \tag{89}$$

obeying canonical commutation relation $[a_{\mathbf{k},i}, a^{\dagger}_{\mathbf{k}',j}] = \delta_{ij}\delta_{\mathbf{k},\mathbf{k}'}$.

To obtain the dynamics we recall that the time dependence of the Heisenberg operators is given by $O_H(t) = e^{iHt/\hbar}O_H(0)e^{-iHt/\hbar}$, or equivalently given by the solution of the Heisenberg equation of motion, $i\hbar\frac{dO_H}{dt} = [O_H, H]$. Applying this to the creation and annihilation operators, we obtain

$$a_{\mathbf{k}}(t) \;=\; a_{\mathbf{k}}e^{-i\omega_{\mathbf{k}}t}, \quad a^{\dagger}_{\mathbf{k}}(t) = a^{\dagger}_{\mathbf{k}}e^{i\omega_{\mathbf{k}}t}. \tag{90}$$

The trace in (51) can be computed in the occupation basis $|\{n_{\mathbf{k},i}\}\rangle$, (eigenstates of the Hamiltonian, (87), and is given by (summing the geometric series)

$$\mathcal{Z}^{q}_{ph} \;=\; \sum_{n_{\mathbf{k}}} \langle\{n_{\mathbf{k}}\}|e^{-\beta\hat{H}[\{a^{\dagger}_{\mathbf{k}}, a_{\mathbf{k}}\}]}|\{n_k\}\rangle, \tag{91}$$

$$= \prod_{\mathbf{k}} \sum_{n_{\mathbf{k}}=0}^{\infty} e^{-\beta\hbar\omega_k(n_{\mathbf{k}}+1/2)}, \tag{92}$$

$$= \prod_{\mathbf{k}} \frac{e^{-\frac{1}{2}\beta\hbar\omega_k}}{1 - e^{-\beta\hbar\omega_k}}, \tag{93}$$

and the associated free energy, $\mathcal{F}_{ph} = -k_BT\ln\mathcal{Z}_{ph}$

$$\mathcal{F}^{q}_{ph} \;=\; k_BT\sum_{\mathbf{k}} \ln\left(1 - e^{-\beta\hbar\omega_k}\right) + \sum_{\mathbf{k}} \frac{1}{2}\hbar\omega_k, \tag{94}$$

$$= k_BT\int d\omega g(\omega)\ln\left(1 - e^{-\beta\hbar\omega}\right) + \int d\omega g(\omega)\frac{1}{2}\hbar\omega, \tag{95}$$

$$\tag{96}$$

with the last term the zero-point energy. In above, for simplicity of notation we implicitly incorporated the eigenvector index i into the mode label $\mathbf{k}$ and will restore it later as necessary.

Another important observable is the occupation number of momentum mode $\mathbf{k}$, given by the famous Bose-Einstein distribution,

$$\begin{aligned} N_{\mathbf{k}} &= \langle \hat{n}_{\mathbf{k}} \rangle = \frac{1}{\mathcal{Z}^q_{ph}} \mathrm{Tr}\left[\hat{n}_{\mathbf{k}} e^{-\beta \hat{H}[\{\hat{n}_{\mathbf{k}}\}]}\right] = -\frac{\partial \mathcal{F}^q_{ph}}{\partial \mu_{\mathbf{k}}}, \quad (97)\\ &= (1-e^{-\beta\hbar\omega_k}) \sum_{n_{\mathbf{k}}} \langle n_{\mathbf{k}}|a^\dagger_{\mathbf{k}} a_{\mathbf{k}}|n_k\rangle e^{-\beta\hbar\omega_k n_k} = (1-e^{-\beta\hbar\omega_k}) \sum_{n_{\mathbf{k}}} n_{\mathbf{k}} e^{-\beta\hbar\omega_k n_{\mathbf{k}}}, \quad (98)\\ &= \frac{1}{e^{\beta\hbar\omega_k}-1}. \quad (99) \end{aligned}$$

In the classical (large number of thermally excited quanta) and quantum (thermal energy well below the excitation gap) limits are respectively given by

$$N_{\mathbf{k}} \approx \begin{cases} \frac{k_B T}{\hbar\omega_k}, & \text{for } k_B T \gg \hbar\omega_k, \\ e^{-\beta\hbar\omega_k}, & \text{for } k_B T \ll \hbar\omega_k, \end{cases} \quad (100)$$

with the first limit confirming the equipartition theorem and the total number of excitations simply given by

$$N_{phonons} = \sum_{\mathbf{k}} N_{\mathbf{k}} = \int d\omega g(\omega) \frac{1}{e^{\beta\hbar\omega_k}-1}. \quad (101)$$

We note that here phonons are not conserved, thus in contrast to the treatment of bosonic atoms in the next set of lectures, where μ enforces a fixed number of atoms, here the chemical potential does not appear and the number of excitations, $N_{phonons}$ is not fixed, rather controlled by temperature.

The total energy E is also straightforwardly computed either directly (with each mode $\mathbf{k}$ assigned energy $\hbar\omega_{\mathbf{k}}$) or from the free energy, in 3d for the Debye model given by

$$\begin{aligned} E_{ph} &= \langle \hat{H}_{ph} \rangle = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}_{ph} = \sum_{\mathbf{k}} E_{\mathbf{k}} = \sum_{\mathbf{k}} \frac{\hbar\omega_{\mathbf{k}}}{e^{\beta\hbar\omega_k}-1}, \quad (102)\\ &= \int d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}, \quad (103)\\ &= \frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} d\omega \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}, \quad (104)\\ &= 3Nk_B T \left(\frac{T}{T_D}\right)^3 f\left(\frac{T_D}{T}\right), \quad (105)\\ &\approx \begin{cases} 3Nk_B T \left(\frac{T}{T_D}\right)^3 = \sigma_{SB} T^4, & \text{for } T \ll T_D, \\ 3Nk_B T, & \text{for } T \gg T_D, \end{cases} \quad (106) \end{aligned}$$

as expected, in low- and high-temperature limits giving black-body (here, with phonons replacing photons) and equipartition results, respectively. The finite bandwidth ω_D is the crucial distinquishing feature, here, that is infinite in the case of photons. In above we defined the Debye temperature by the corresponding frequency, $k_BT_D \equiv \hbar\omega_D$ and used the low- and low-temperature limits of scaling function $f(T_D/T)$ given by

$$f(x) = 3\int_0^x d\omega \frac{\omega^3}{e^\omega - 1}, \tag{107}$$

$$\approx \begin{cases} 1, & \text{for } x \gg 1, \\ x^3, & \text{for } x \ll 1, \end{cases} \tag{108}$$

The corresponding (constant volume) heat capacity is given by

$$C_V^{ph} = \frac{\partial E_{ph}}{\partial T}, \tag{109}$$

$$= k_B \int d\omega g(\omega) \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}, \tag{110}$$

$$\approx \begin{cases} 3Nk_BT\left(\frac{T}{T_D}\right)^3 = \sigma_{SB}T^4, & \text{for } T_D \gg T, \\ 3Nk_BT, & \text{for } T_D \ll T, \end{cases} \tag{111}$$

showing the "freeze out" of modes at low temperature and equipartition at high, as compared with the Debye temperature.

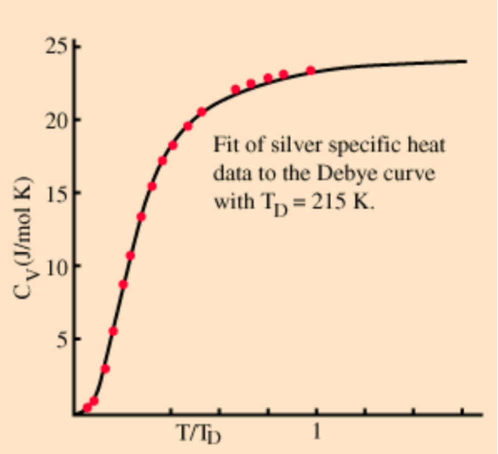

FIG. 3: Heat capacity of a Debye three-dimensional crystal, showing equipartition result at high temperature (classical) limit and a freeze out of vibrational degrees of freedom in the low temperature, $T < T_{Debye}$ (quantum) regime.

III. CORRELATION FUNCTIONS AND X-RAY SCATTERING

A. Phonon correlation function

The phonon correlation function $\langle u^\alpha_{\mathbf{R}} u^\beta_{\mathbf{R}'}\rangle$ can now be computed, utilizing our normal mode decomposition and quantization, (84) above and giving the quantum counter part of the classical result in (80).

$$\begin{aligned}
\langle u^\alpha_{\mathbf{R}} u^\beta_{\mathbf{R}'}\rangle &= \frac{1}{N}\sum_{\mathbf{k}\in 1BZ} \langle u^\dagger_{\mathbf{k},\alpha} u_{\mathbf{k},\beta}\rangle e^{i\mathbf{k}(\cdot\mathbf{R}-\mathbf{R}')}, & (112)\\
&= \frac{1}{2N}\sum_{i,j,\mathbf{k},\mathbf{k}'\in 1BZ} u_{0ki}u_{0kj}\hat{e}^\alpha_i \hat{e}^\beta_j \langle (a_{\mathbf{k},i}+a^\dagger_{-\mathbf{k},i})(a_{\mathbf{k}',j}+a^\dagger_{-\mathbf{k}',j})\rangle e^{i\mathbf{k}\cdot\mathbf{R}+i\mathbf{k}'\cdot\mathbf{R}'} & (113)\\
&= \frac{1}{2N}\sum_{i,j,\mathbf{k}\in 1BZ} u_{0ki}u_{0kj}\hat{e}^\alpha_i \hat{e}^\beta_j \langle (a_{\mathbf{k},i}a^\dagger_{\mathbf{k},j}+a^\dagger_{-\mathbf{k},i}a_{-\mathbf{k},j}\rangle e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & (114)\\
&= \frac{1}{2N}\sum_{i,j,\mathbf{k}\in 1BZ} u_{0ki}u_{0kj}\hat{e}^\alpha_i \hat{e}^\beta_j (2N_{\mathbf{k},i}+1) e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & (115)\\
&= \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ} u_{0ki}u_{0ki}\hat{e}^\alpha_i \hat{e}^\beta_i \coth(\frac{\hbar\omega_{\mathbf{k},i}}{2k_BT}) e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & (116)\\
&= \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ} \frac{\hbar}{M\omega_{\mathbf{k},i}}\hat{e}^\alpha_i \hat{e}^\beta_i \coth(\frac{\hbar\omega_{\mathbf{k},i}}{2k_BT}) e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & (117)\\
&\approx \frac{1}{N}\sum_{i,\mathbf{k}\in 1BZ} \begin{cases} \frac{k_BT}{M\omega^2_{\mathbf{k},i}}\hat{e}^\alpha_i \hat{e}^\beta_i e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & \text{for } \hbar\omega_{\mathbf{k},i} \ll 2k_BT, \text{ classical,}\\ \frac{1}{2N}\frac{\hbar}{M\omega_{\mathbf{k},i}}\hat{e}^\alpha_i \hat{e}^\beta_i e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')}, & \text{for } \hbar\omega_{\mathbf{k},i} \gg 2k_BT, \text{ quantum,}\end{cases} & (118)
\end{aligned}$$

where we used $\tilde{\mathbf{u}}_{-\mathbf{k}} = \tilde{\mathbf{u}}^\dagger_{\mathbf{k}}$, lattice translational invariance, and finite T normal modes occupation $N_{\mathbf{k}}$, (99).

For the scalar product this simplies to

$$\langle \mathbf{u}_{\mathbf{R}}\cdot\mathbf{u}_{\mathbf{R}'}\rangle = \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ}\frac{\hbar}{M\omega_{\mathbf{k},i}}\coth(\frac{\hbar\omega_{\mathbf{k},i}}{2k_BT})e^{i\mathbf{k}\cdot(\mathbf{R}-\cdot\mathbf{R}')} \qquad (119)$$

where we used orthonormality of the eigenvectors $\hat{\mathbf{e}}_i\cdot\hat{\mathbf{e}}_i = 1$.

B. Structure function

1. *scattering*

The atomic structure of liquids and solids can be probed using a variety of scattering techniques such as x-ray and neutron scattering. Atoms introduce a scattering potential

$V(\mathbf{r}) = \sum_{i=1}^{N} V_{atom}(\mathbf{r}-\mathbf{R}_i)$, that is proportional to their density distribution. X-rays photons interact with electron density in the outer atomic shell, with the scattering potential with $V_{atom}(\mathbf{r}-\mathbf{R}_i) \propto \rho_e(\mathbf{r}-\mathbf{R}_i)$, where $\rho_e(\mathbf{r})$ is the charge distribution on atom i at $\mathbf{R}_i$. In constrast neutrons interact with the nearly point-like nuclei with the potential well-represented by $V_{atom}(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} a_s \delta^3(\mathbf{r} - \mathbf{R}_i)$, where a_s single atom scattering length. We are interested in the probability of the scattering process of an incoming plane wave $\mathbf{k}$ into the outgoing plane wave $\mathbf{k}'$, with a scattering amplitude

$$\begin{aligned} \langle \mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle &= \frac{1}{Nv}\int_{\mathbf{r}} V(\mathbf{r}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, && (120)\\ &= \frac{1}{N}\sum_i e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_i} \frac{1}{v}\int_{\mathbf{r}} V_{atom}(\mathbf{r}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, && (121)\\ &= V_{\mathbf{q}}^{atom} \frac{1}{N}\sum_i e^{-i\mathbf{q}\cdot\mathbf{R}_i} = V_{\mathbf{q}}^{atom}\rho_{\mathbf{q}}, && (122) \end{aligned}$$

where $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ is the scattering wavevector (momentum transfer to the photon) and $V_{\mathbf{q}}^{atom}$ is the Fourier transform of the single atom potential, determining the form factor at high momenta. It is the second factor that is of most interest to us as it determines the distribution of *centers* of atomic positions and is the Fourier transform $\rho_{\mathbf{q}}$ of the atomic density of point atoms $\rho(\mathbf{r}) = \sum_i^N \delta^3(\mathbf{r} - \mathbf{R}_i)$ at a scattering wavevector $\mathbf{q}$.

The diffraction scattering intensity is characterized by the differential cross-section that is derived using the Fermi's Golden rule and is given by

$$\frac{d\sigma}{d\Omega} = N|V_{\mathbf{q}}^{atom}|^2 S(\mathbf{q}), \qquad (123)$$

where

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N}\sum_{i,j}\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\rangle, && (124)\\ &= \langle \rho_{-\mathbf{q}}\rho_{\mathbf{q}}\rangle && (125) \end{aligned}$$

is the *static* structure function, with correlations computed at equal times. In above we recognized the fact that in principle $\mathbf{R}_i$ are quantum, thermally fluctuating variables and therefore need to be averaged over to relate the result to the measured diffraction signal. A generalization of this central quantity to unequal time correlator of $\rho_{\mathbf{q}}(t) = \frac{1}{\sqrt{N}}\sum_i e^{-i\mathbf{q}\cdot\mathbf{R}_i(t)}$ gives the dynamic structure function

$$S(\mathbf{q}, t) = \frac{1}{N}\sum_{i,j}\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_i(t)-\mathbf{R}_j(0))}\rangle,$$

that is measured in elastic scattering, where in addition to momentum $\mathbf{q}$, the energy $\hbar\omega$ is also transferred between the probing particle (e.g., x-ray photon or a neutron) and the atomic system.

The structure function is useful for characterization of density distribution whether the material is a fluid or a solid. However, here will focus on a crystalline solid, in which $\mathbf{R}_i = \mathbf{R}_n + \mathbf{u}_{\mathbf{R}_n}$ with the fluctuating nature of atomic vibrations encoded through the phonons $\mathbf{u}_R$ degrees of freedom, whose dynamics is characterized by a elastic Hamiltonian discussed in previous sections.

We first note that for small fluctuations (heavy ions at low temperature) we can approximate the structure fuction by neglecting the phonon fluctuatins, i.e., taking $\mathbf{u}_R = 0$. In this case we find

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N}\sum_{\mathbf{R}_n,\mathbf{R}_m} e^{-i\mathbf{q}\cdot(\mathbf{R}_n-\mathbf{R}_m)}, && (126)\\ &= \frac{1}{N}\sum_{\mathbf{R}_n}\sum_{\mathbf{R}_n-\mathbf{R}_m} e^{-i\mathbf{q}\cdot(\mathbf{R}_n-\mathbf{R}_m)}, && (127)\\ &= \sum_{\mathbf{G}_p} N\delta_{\mathbf{q},\mathbf{G}_p} = (2\pi)^3 v \sum_{\mathbf{G}_p}\delta^3(\mathbf{q}-\mathbf{G}_p), && (128) \end{aligned}$$

a crucial result of lattice Bragg (δ-function) peaks appearing at the reciprocal lattice points $\mathbf{G}_p$ (defined by $e^{i\mathbf{G}_p\cdot\mathbf{R}_n} = 1$), characterizing the perfect a crystalline order. It is this key property that makes scattering such an effective tool for analyzing the crystal structure and deviation from it. The latter comes from lattice defects and fluctuations that are incorporated into phonons $\mathbf{u}_R$, to which we now turn.

2. scattering with phonon fluctuations

To go beyond the above idealized approximation we now include phonons in (125) in the structure function

$$S(\mathbf{q},t) = \frac{1}{N}\sum_{\mathbf{R},\mathbf{R}'} e^{-i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}\langle e^{-i\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}}(t)} e^{i\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}'}(0)}\rangle, \qquad (129)$$

where $\mathbf{u}_R$ is a quantum field and the average is over both its quantum and thermal fluctuations. In above we returned to the original definition of the structure function as a two-point correlator of a Fourier transformed density $\rho_{\mathbf{q}}$, and avoided combining the noncommuting phonon operators in the exponential.

A very useful identity, valid for quadratic (Gaussian) operator fields is given by

$$\langle e^A e^B \rangle = e^{\frac{1}{2}\langle A^2\rangle + \frac{1}{2}\langle B^2\rangle + \langle AB\rangle}, \tag{130}$$

that can be derived by using Baker-Hausdorff formula (valid for operators whose commutator is a c-number)

$$e^A e^B = e^{A+B} e^{\frac{1}{2}[A,B]} \tag{131}$$

together with a formula

$$\langle e^{\phi} \rangle = e^{\frac{1}{2}\langle \phi^2\rangle},$$

that we have derived for classical harmonic (Gaussian) fields using Gaussian integrals, but can also be shown to hold for quantum harmonic fields using path-integral formulation.

Taking $A = -i\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}}(t)$, $B = i\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}'}(0)$, and utilizing identity (130), we obtain for the dynamic structure function

$$S(\mathbf{q},t) \;=\; \frac{1}{N}\sum_{\mathbf{R},\mathbf{R}'} e^{-i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} e^{-C_{\mathbf{R}-\mathbf{R}'}(t)}, \tag{132}$$

where

$$\begin{aligned}
C_{\mathbf{R}-\mathbf{R}'}(t) &= \langle (\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}}(t))^2\rangle - \langle (\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}}(t))(\mathbf{q}\cdot\mathbf{u}_{\mathbf{R}'}(0))\rangle, & (133)\\
&= \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ} |u_{0ki}|^2 (\mathbf{q}\cdot\hat{\mathbf{e}}_{\mathbf{k},i})^2 \left[\langle a_{\mathbf{k},i} a^{\dagger}_{\mathbf{k},i}\rangle \left(1 - e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}') - i\omega_{\mathbf{k}} t}\right)\right. \\
&\quad \left. + \langle a^{\dagger}_{\mathbf{k},i} a_{\mathbf{k},i}\rangle \left(1 - e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}') + i\omega_{\mathbf{k}} t}\right)\right], & (134)\\
&= \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ} \frac{\hbar}{M\omega_{i,\mathbf{k}}} (\mathbf{q}\cdot\hat{\mathbf{e}}_{\mathbf{k},i})^2 \left[(N_{\mathbf{k},i}+1)\left(1 - e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}') - i\omega_{\mathbf{k}} t}\right)\right. \\
&\quad \left. + N_{\mathbf{k},i}\left(1 - e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}') + i\omega_{\mathbf{k}} t}\right)\right], \\
&= \frac{1}{2N}\sum_{i,\mathbf{k}\in 1BZ} \frac{\hbar}{M\omega_{i,\mathbf{k}}} (\mathbf{q}\cdot\hat{\mathbf{e}}_{\mathbf{k},i})^2 \coth\!\left(\frac{\hbar\omega_{\mathbf{k},i}}{2k_B T}\right)\left(1 - e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}') - i\omega_{\mathbf{k}} t}\right). & (135)
\end{aligned}$$

we took advantage of the translational invariance of the connected phonon correlation function, invariance of the summand under $\mathbf{k}\to -\mathbf{k}$, and used the time dependence of the normal modes based on the Heisenberg equation of motion (90) that gives

$$\mathbf{u}_{\mathbf{R}}(t) \;=\; \sqrt{\frac{1}{2N}}\sum_{i,\mathbf{k}\in 1BZ} u_{0ki}\hat{\mathbf{e}}_{\mathbf{k},i}\left(a_{\mathbf{k},i} e^{i\mathbf{k}\cdot\mathbf{R} - i\omega_{\mathbf{k}} t} + a^{\dagger}_{\mathbf{k},i} e^{-i\mathbf{k}\cdot\mathbf{R} + i\omega_{\mathbf{k}} t}\right). \tag{136}$$

For isotropic crystal, $\hat{\mathbf{e}}^{\alpha}_i \hat{\mathbf{e}}^{\beta}_i$ (no sum over i) gives $P^{L,T}_{\alpha\beta}(k)$ for $i = L, T$, respectively.

Time Fourier transform of $S(\mathbf{q},t)$ gives the dynamic structure $S(\mathbf{q},\omega)$ measured in elastic scattering with energy transfer of $\hbar\omega$.

Specializing to the equal time correlator $t = 0$, gives the static function, $S(\mathbf{q})$, with exponent $C_{\mathbf{R}-\mathbf{R}'}(t = 0)$. At large spatial separations, the oscillating averages out and the correlator asymptotes to a constant W given by

$$\begin{aligned}
C_{\mathbf{R}-\mathbf{R}'}(0) &= W, \quad |\mathbf{R}-\mathbf{R}'| \gg a, && (137)\\
&= \frac{1}{N}\sum_{i,\mathbf{k}\in 1BZ}\frac{\hbar}{2M\omega_{i,\mathbf{k}}}(\mathbf{q}\cdot\hat{\mathbf{e}}_{\mathbf{k},i})^2\coth(\frac{\hbar\omega_{\mathbf{k},i}}{2k_BT}), && (138)\\
&= a^d\int\frac{d^dk}{(2\pi)^d}\sum_{i=L,T}\frac{\hbar}{2M\omega_{i,\mathbf{k}}}q_\alpha q_\beta P^i_{\alpha\beta}\coth(\frac{\hbar\omega_{\mathbf{k},i}}{2k_BT}), && (139)\\
&= q^2a^dd\int\frac{d^dk}{(2\pi)^d}\frac{\hbar}{2Mc_sk}\coth(\frac{\hbar c_sk}{2k_BT}), && (140)
\end{aligned}$$

where we went over to the continuum limit and for simplicity specialized to an isotropic lattice and then taken $\lambda = -\mu$ so that longitudinal transverse speeds of sound are degenerate, $c_L = c_T$.

In the *quantum* limit, $\hbar\omega_{\mathbf{k}} \gg k_BT$ (note that for acoustic phonons where ω_k vanishes as $k \to 0$, this requires ultra-low $T \to 0$), the $\coth(\frac{\hbar c_sk}{2k_BT})$ factor is 1 and for $d > 1$, W reduces to

$$\begin{aligned}
W &\approx q^2\frac{dC_d}{d-1}\frac{\hbar}{2Mc_sa^{-1}},\\
&= q^2\frac{\hbar}{M\omega_D}\frac{dC_d}{2(d-1)} = c_dq^2u_{0D}^2 && (141)
\end{aligned}$$

where $c_d \equiv \frac{dC_d}{2(d-1)}$, $u_{0D}^2 \equiv \frac{\hbar}{M\omega_D}$ is the quantum oscillator length at the BZ edge scale π/a, we cutoff the upper limit of the integral by the BZ edge, $k = \pi/a \equiv \Lambda$, and denoted surface area $S_d = 2\pi^{d/2}/\Gamma(d/2)$ of a d-dimensional unit sphere ($S_2 = \pi, S_3 = 4\pi$) divided by $(2\pi)^d$ by C_d. Note that for $d \leq 1$, the integral diverges in the infrared, i.e., with system size L according to $W(L) \sim L^{(1-d)}$ ($\sim \ln L/a$, for $d = 1$), which is a reflection of the Hohenberg-Mermin-Wagner theorem of the absence of long range order (breaking of continuous symmetry at $T = 0$ in one dimension and below.

In the *classical* limit, $\hbar\omega_{\mathbf{k}} \ll k_BT$ (note that for this to be true for all of $\mathbf{k}$, this actually requires the condition on the highest frequency $\hbar\omega_\Lambda \equiv \hbar\omega_D \ll k_BT$) the $\coth(\frac{\hbar c_sk}{2k_BT}) \approx 2k_BT/(\hbar c_sk)$ and for $d \leq 2$, W reduces to

$$W \approx q^2a^2\frac{dC_d}{d-2}\frac{k_BT}{Mc_s^2} = b_Dq^2a^2\frac{T}{T_D}, \qquad (142)$$

where $b_D \equiv \frac{dC_d}{d-2}$. Note that for $d \leq 2$, the integral diverges in the infrared, i.e., with system size L according to $W(L) \sim L^{(2-d)}$ ($\sim \ln L/a$, for $d = 2$), which is a reflection of the Hohenberg-Mermin-Wagner theorem of the absence of long range order (breaking of continuous symmetry at finite T in two dimensions and below.

Since at $T = 0$ (finite $T > 0$) in $d > 1$ (in $d > 2$), $C_{\mathbf{R}-\mathbf{R}'}(0)$ asymptotes to the above finite value W, the static structure function from (132), $S(\mathbf{q}) \equiv S(\mathbf{q}, t = 0)$ reduces to

$$S(\mathbf{q}) \approx \frac{1}{N}\sum_{\mathbf{R},\mathbf{R}'} e^{-i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} e^{-W_q}, \tag{143}$$

$$= \sum_{\mathbf{G}_p} e^{-W_{G_p}} N\delta_{\mathbf{q},\mathbf{G}_p} = v\sum_{\mathbf{G}_p} e^{-W_{G_p}}(2\pi)^3\delta^3(\mathbf{q}-\mathbf{G}_p), \tag{144}$$

retaining perfect Bragg (δ-function) peaks even in the presense of thermal and quantum phonon fluctuations, that simply reduce it by the so-called Debye-Waller q-dependent Gaussian form factor, e^{-W_q}.

On the other hand for $T = 0$ (finite $T > 0$) in $d \leq 1$ (in $d \leq 2$), $C_{\mathbf{R}-\mathbf{R}'}(0)$ is a growing function of $|\mathbf{R}-\mathbf{R}'|$, that leads to $S(\mathbf{q})$ that exhibits broadenned, finite width (in critical dimension $d = 1$ ($d = 2$) quasi-Bragg) peaks at $\mathbf{G}_p$'s, demonstrating short-range crystalline order in these lower dimensions.

Indeed in 2D (crystalline film) evaluating above correlator $C_{\mathbf{R}-\mathbf{R}'}$ in the continuum classical limit, for simplicity specializing to an isotropic crystal with $\lambda = -\mu$, with linear dispersion (Debye model) gives

$$C_{\mathbf{R}-\mathbf{R}'} \approx \eta_q(T)\ln\left(|\mathbf{R}-\mathbf{R}'|/a\right), \tag{145}$$

where the exponent $\eta_q(T)$ is given by

$$\eta_q(T) = q^2a^2\frac{T}{\pi T_D} = q^2\frac{k_BT}{\pi\mu}, \tag{146}$$

with the shear modulus μ carrying units of energy per length-squared in 2D.

Using this inside (132) (with $t = 0$) together with the Poisson summation formula

$$\sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} = \sum_{\mathbf{G}}(2\pi)^d\delta^d(\mathbf{q}-\mathbf{G})$$

to evaluate the sum over $\mathbf{R}$, we find a seminal result[5, 6] that

$$S(\mathbf{q}) \sim \sum_{\mathbf{G}_p}\frac{1}{|\mathbf{q}-\mathbf{G}|^{2-\eta_q}}. \tag{147}$$

It demonstrates that at finite temperature T, phonon fluctuations in a 2D crystal divergently large and lead to a structure function that no longer exhibits true (δ-function) Bragg peaks, but instead is characterized by *quasi*-Bragg power-law peaks, i.e., it exhibits translatonal *quasi*-long-range order, with $\mathbf{G}$ spanning a lattice reciprocal to the real-space lattice of $\mathbf{R}$.

IV. MELTING

A detailed theory of melting of a crystal can be quite elaborate, particularly because this transition is generically first-order and so depends on the microscopic details.[4] Two dimensional crystals melt via a (infinitely) continuous transition according to a beautiful and quite elaborate Kosterlitz-Thouless-Halperin-Nelson-Young theory[5–7] closely related to the Kosterlitz-Thouless Normal-Superfluid transition of 2D films.

However, one can estimate the melting temperature, T_m through a very simple criterion due to Lindemann named after him[8]. It very reasonably states that the melting of a crystal takes place when its root-mean phonon fluctuation become of order inter-atomic spacing a, namely

$$u_{rms}(T_m) \approx c_L a,$$

where c_L is a Lindemann phenomenological contant typically taken to be 0.1 but can very significantly between different crystals. Given the phenomenological nature of the Lindemann criterion, it is most useful for qualitative rather than quantitative estimates of the melting temperature T_m.

Using the classical, high-temperature limit result

$$u^2_{rms}(T) \;=\; 3\frac{k_B T}{2Mc_s^2}\,a^2 \approx \frac{k_B T}{\hbar\omega_D}\,a^2, \tag{148}$$

derived on the homework, inside the Lindemann criterion we obtain,

$$T_m \approx c_L \frac{\hbar\omega_D}{k_B} = c_L T_D.$$

Repeating the calculation of root-mean-squared fluctuations in a 2d crystal (as found on the homework) gives

$$u^2_{rms,2d} \approx \frac{k_B T}{\hbar\omega_D}\,a^2 \ln(L/a),$$

fluctuations that diverge logarithmically with the growing system size $L/a \to \infty$. This divergence is a manifestation of the so-called Hohenberg-Mermin-Wagner theorem, that in particle physics is referred to as the Coleman's theorem. It has profound implications of the absence of true long-range crystalline order in 2d crystals, that translates into absence of δ-function Bragg peaks in its static structure function $S(\mathbf{q})$, in contrast to that of a 3d crystal, that well-described by (128).

V. NONLINEAR ELASTICITY

Although so far we have treated the elasticity within harmonic approximation, real crystals exhibit nonlinear elasticity, that is essential to include to capture a number of physical phenomena.

Recall that the elastic crystal energy to quadratic order in the elastic strain $u_{\alpha\beta}$ is given by

$$H_{el}[\mathbf{u}(r)] = \frac{1}{2}\int d^d r C_{\alpha\beta,\gamma\delta}\, u_{\alpha\beta}u_{\gamma\delta}. \tag{149}$$

Translational and rotational invariances of the underlying liquid from which a crystal spotaneously emerges guarantee that the strain is a *symmetric* tensor of the gradients of the phonon displacements $\mathbf{u}(\mathbf{r})$. While the above elastic energy is quadratic in $u_{\alpha\beta}$, the strain tensor itself is a nonlinear function of the phonon field u_α,

$$\begin{aligned} u_{\alpha\beta} &= \frac{1}{2}(\partial_\alpha \mathbf{R}\cdot\partial_\beta \mathbf{R} - \delta_{\alpha\beta}), && (150)\\ &= \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha + \partial_\alpha \mathbf{u}\cdot\partial_\beta \mathbf{u}), && (151)\\ & && (152)\end{aligned}$$

where in the first line we used the fact that the strain is the difference between the distortion-induced metric $g_{\alpha\beta}$ and the flat metric $\delta_{\alpha\beta}$ and expressed the position of an atom $\mathbf{r}$ that has been moved to $\mathbf{R}(\mathbf{r}) = \mathbf{r} + \mathbf{u}(\mathbf{r})$ in a deformed crystal in terms of the phonon field $\mathbf{u}(\mathbf{r})$.

Expressing the elastic Hamiltonian in terms of the phonon fields $\mathbf{u}$, and keeping nonlinearities for the case of an isotropic crystal, we find

$$\begin{aligned} \mathcal{H}_{el} &= \mu u_{\alpha\beta}u_{\alpha\beta} + \frac{1}{2}\lambda u_{\alpha\alpha}u_{\beta\beta}, && (153)\\ &= \mu(\varepsilon_{\alpha\beta} + \frac{1}{2}\partial_\alpha\mathbf{u}\cdot\partial_\beta\mathbf{u})(\varepsilon_{\alpha\beta} + \frac{1}{2}\partial_\alpha\mathbf{u}\cdot\partial_\beta\mathbf{u}) + \frac{\lambda}{2}(\varepsilon_{\alpha\alpha} + \frac{1}{2}\partial_\alpha\mathbf{u}\cdot\partial_\alpha\mathbf{u})^2, && (154)\\ &= \mu\varepsilon_{\alpha\beta}\varepsilon_{\alpha\beta} + \frac{\lambda}{2}\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta} + \mathcal{H}_{nonlin} = \mathcal{H}^0_{el} + \mathcal{H}_{nonlin}, && (155)\end{aligned}$$

where

$$\begin{aligned}\mathcal{H}_{nonlin} &= \mu(\partial_\alpha u_\beta)(\partial_\alpha \mathbf{u}\cdot\partial_\beta \mathbf{u}) + \frac{\lambda}{2}(\partial_\alpha u_\alpha)(\partial_\beta \mathbf{u}\cdot\partial_\beta \mathbf{u}) \\ &\quad + \frac{\mu}{4}(\partial_\alpha \mathbf{u}\cdot\partial_\beta \mathbf{u})(\partial_\alpha \mathbf{u}\cdot\partial_\beta \mathbf{u}) + \frac{\lambda}{8}(\partial_\alpha \mathbf{u}\cdot\partial_\alpha \mathbf{u})(\partial_\beta \mathbf{u}\cdot\partial_\beta \mathbf{u}), \qquad (156)\end{aligned}$$

are the cubic and quartic nonlinearities, and $\mathcal{H}_{el}^0$ is the harmonic energy density from (43).

For low T and small fluctuations (away from the melting transition or any structural instabilities), contributions of these nonlinearities will typically be small. Thus they can be accounted for in physical properties (e.g., the free energy, thermal expansion, structure function, etc.) by Taylor-expanding the Boltzmann weight (or a quantum evolution operator) in terms of $\mathcal{H}_{nonlin}$, averaging over it with the Gaussian weight based on $\mathcal{H}_{el}^0$.

As a concrete example, we can consider a computation of a thermal expansion of a crystal. This is given by the change in the volume V due to fluctuations and distortions, characterized by metric $g_{\alpha\beta} = \delta_{\alpha\beta} + 2u_{\alpha\beta}$

$$\begin{aligned}\delta V &= \langle \int d^d r(\sqrt{\det \mathbf{g}} - 1)\rangle, & (157)\\ &= \langle \int d^d r(\sqrt{\det(1+2\mathbf{u})} - 1)\rangle, & (158)\\ &\approx \langle \int d^d r(\sqrt{(1+2\mathrm{Tr}(\mathbf{u}))} - 1)\rangle, & (159)\\ &\approx \int d^d r\langle \mathrm{Tr}(\mathbf{u})\rangle, & (160)\\ &\approx \int d^d r(\langle \partial_\alpha u_\alpha\rangle + \frac{1}{2}\langle \partial_\alpha \mathbf{u}\cdot\partial_\alpha \mathbf{u}\rangle), & (161)\end{aligned}$$

where in general the average is done with the Boltzmann weight, characterized by a quantum Hamiltonian H_{el}, above. It can typically be computed perturbatively in H_{nonlin}. This involves, for a classical regime a computation of various Gaussian averages of powers of $\mathbf{u}(\mathbf{r})$ and for a quantum case averages over powers of $a_{\mathbf{k}}, a_{\mathbf{k}}^\dagger$. We will not pursue this further here.

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[1] *Fundamentals of the Physics of Solids I*, Electronic Properties, J. Solyom.

[2] *Quantum Field Theory of Many-body Systems*, by Xiao-Gang Wen.

[3] *Principles of Condensed Matter Physics*, by P. M. Chaikin and T. C. Lubensky.

[4] L.D. Landau, Phys. Z. Sowjetunion **II**, 26 (1937); see also S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1984).

[5] J.M. Kosterlitz and D.J. Thouless, J. Phys. C **6**, 1181 (1973); see also, V.L. Berezinskii, Zh. Eksp. Teor. Fiz. **59**, 907 (1970) [Sov. Phys. JETP **32**, 493 (1971)]; Zh. Eksp. Teor. Fiz. **61**, 1144 (1971) [Sov. Phys. JETP **34**, 610 (1972)];

[6] B.I. Halperin and D.R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D.R. Nelson and B.I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[7] A.P. Young, Phys. Rev. B **19**, 1855 (1979).

[8] F. A. Lindemann, "The calculation of molecular vibration frequencies", Physik. Z. **11**, 609-612 (1910).