

Condensed Matter Physics

Part 1. Atomic System

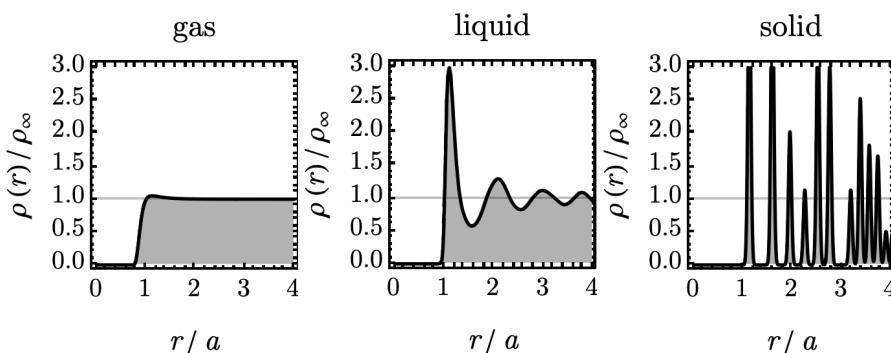
Crystal Geometry

■ Crystal Formation

■ Atomic Orders

Gas, liquid, and solid are *states of matter* in our everyday life. They are all made of **atoms** (and/or molecules), yet their macroscopic behaviors are very different.

- **Atomic order:** how *atoms* are *arranged* in the matter.
 - **Gas** (no order) - atoms are *well separated*, no regular arrangement.
 - **Liquid** (*short-ranged* order) - atoms are *close together*, no regular arrangement.
 - **Solid** (*long-ranged* order) - atoms are *tightly packed* in a *regular pattern* (in particular, atoms form a *regular lattice* in a **crystal**).
- The atomic order is characterized by the radial density distribution $\rho(r)$ - density ρ of atoms as a function of the distance r from a reference atom (in unit of average inter-atomic spacing a).



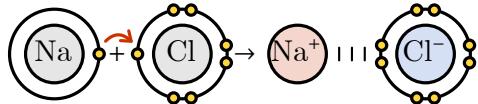
- Many macroscopic behaviors can be explained

	shape	volume	fluidity	compressibility
gas	✗	✗	high	high
liquid	✗	✓	high	low
solid	✓	✓	low	low

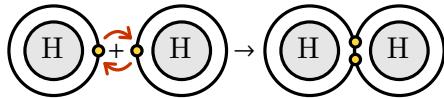
■ Atomic Interaction

But why do atoms order? What is the underlying mechanism or energetic reason?

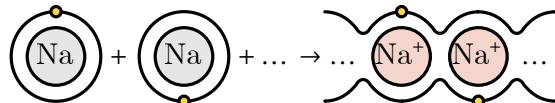
- Order always arise from **interaction**.
- Atoms (or molecules) interact in many different ways (i.e. different **chemical bounds**):
- **Ionic bound.**



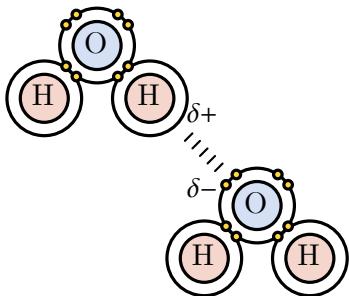
- **Covalent bound.**



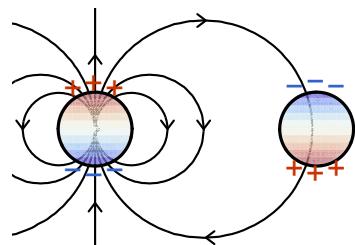
- **Metallic bound.**



- **Hydrogen bound.**



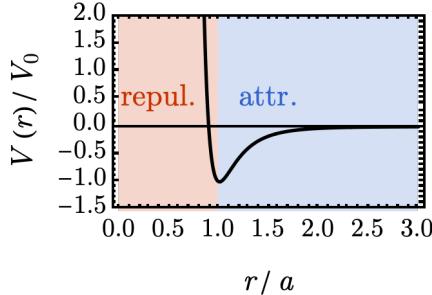
- **Van der Waals force** (Molecular bound).



- All types of **atomic forces** are the *residual* of the **electrostatic force** of electrons and nuclei.

- They are generally *repulsive* at *short range*, and *attractive* at *longer range*. The pair-wise interaction can be described by the **inter-atomic potential energy** $V(r)$ (where r is the inter-atom distance). One famous phenomenological model (the 6-12 potential) is

$$V(r) = V_0 \left(\frac{1}{(r/a)^{12}} - \frac{2}{(r/a)^6} \right). \quad (1)$$



- They can be *isotropic* (ionic bounds, metallic bounds, Van der Waals) or *directional* (most covalent bounds, hydrogen bounds).

■ Statistical Mechanics of Atoms

Consider a collection of atoms interacting with each other.

- Let \mathbf{r}_i be the **position** of the i th atom.
- The *total potential energy* of all atoms is

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j), \quad (2)$$

(summing the potential energy over all pairs of atoms).

- For isotropic interaction, $V(\mathbf{r})$ only depends on $r = |\mathbf{r}|$, and is often denoted as $V(r)$.
- For directional interaction, $V(\mathbf{r})$ also depends on the direction of \mathbf{r} . [But we generally assume the inversion symmetry $V(\mathbf{r}) = V(-\mathbf{r})$, i.e. the action and reaction are always equal in magnitude and opposite in direction (Newton's third law).]
- By *Boltzmann distribution*, the probability (density) to observe the atoms at positions $\{\mathbf{r}_i\}$ is given by

$$\begin{aligned} p(\mathbf{r}_1, \mathbf{r}_2, \dots) &= \frac{1}{Z} \exp\left(-\frac{V(\mathbf{r}_1, \mathbf{r}_2, \dots)}{k_B T}\right), \\ Z &= \int d\mathbf{r}_1 d\mathbf{r}_2 \dots \exp\left(-\frac{V(\mathbf{r}_1, \mathbf{r}_2, \dots)}{k_B T}\right). \end{aligned} \quad (3)$$

k_B - Boltzmann constant, T - temperature.

- High-temperature limit* ($T \rightarrow \infty$): $p(\mathbf{r}_1, \mathbf{r}_2, \dots) = 1/Z$. The atoms can appear anywhere with equal probability *independently*. \Rightarrow **Gas phase**.

- *Low-temperature limit* ($T \rightarrow 0$): the probability is dominated by the configuration of the lowest energy. The atoms will arrange themselves to *minimize* the total potential energy

$$\min_{\{\mathbf{r}_i\}} V(\mathbf{r}_1, \mathbf{r}_2, \dots). \quad (4)$$

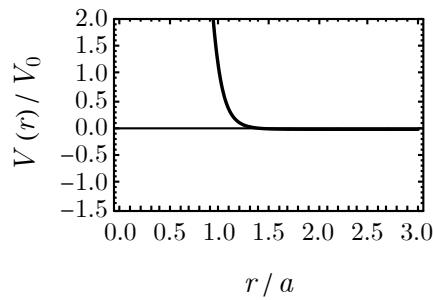
This leads to crystal formation. \Rightarrow **Solid phase.**

■ Minimal Energy Configurations

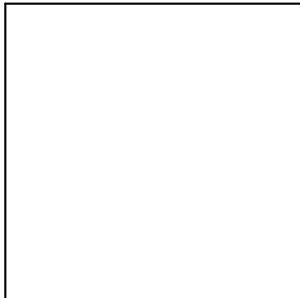
□ Isotropic Repulsive Interaction

Inter-atomic potential:

$$V(r) = \frac{V_0}{(r/a)^{12}}. \quad (5)$$



Searching for minimal energy configurations ...

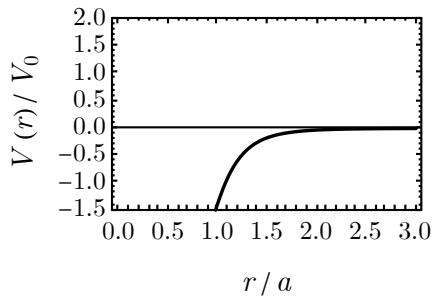


Observation: under purely *repulsive* interaction, all atoms fly apart (if not restricted by a container). \rightarrow Doesn't look physical.

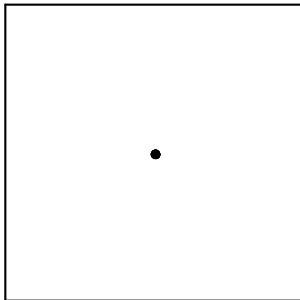
□ Isotropic Attractive Interaction

Inter-atomic potential:

$$V(r) = -\frac{2 V_0}{(r/a)^6}. \quad (6)$$



Searching for minimal energy configurations ...

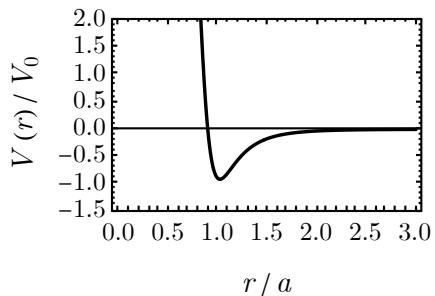


Observation: under purely *attractive* interaction, all atoms will collapse to a single point and takes up no volume (this could happen for a black-hole). → Doesn't look physical either.

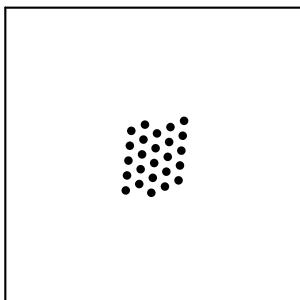
□ Isotropic Interaction with Both Attraction and Repulsion

Inter-atomic potential:

$$V(r) = V_0 \left(\frac{1}{(r/a)^{12}} - \frac{2}{(r/a)^6} \right). \quad (7)$$



Searching for minimal energy configurations ...



A crystal is formed at low-temperature!

Observation:

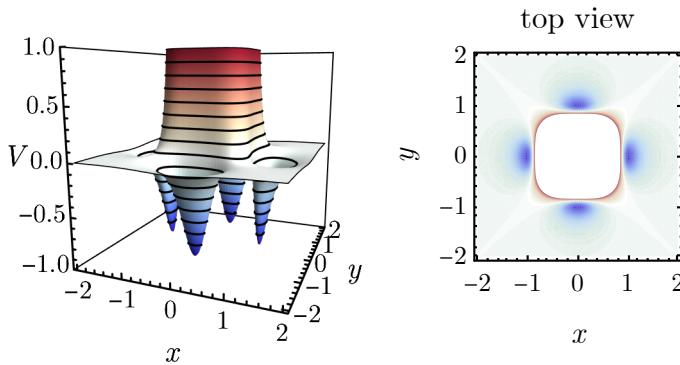
- Need *short-range repulsion + long-range attraction* to crystallize.
⇒ The existence of *crystals* implies that the *inter-atomic interaction* is neither purely repulsive (unlike electric force) nor purely attractive (unlike gravity).
 - We can infer *microscopic* laws of physics by observing their *macroscopic* consequences.
- The crystal always have roughly the *same* volume.
 - Because the **atomic spacing** is determined by the equilibrium position $r = a$ of the inter-atomic potential (the distance where interaction switch from repulsive to attractive). ⇒ Explains why a solid is hard to compress.
- The crystal always assume the same **triangular lattice** structure.
 - Because triangular lattice is the **closest packed structure** in 2D.
 - **Spontaneous symmetry breaking:** although the microscopic interaction is *isotropic* (continuous rotation symmetry, no special bound angle), the resulting low-energy configuration (the crystal lattice) *spontaneously* breaks the *continuous* rotation symmetry to a *discrete* (6-fold) rotation symmetry with an *emergent* 30° bound angle. ⇒ Explains why a solid is rigid (has a fixed shape).
 - This is an **emergent phenomenon**. No where in the microscopic theory can we see why 30° bound angle should be special. ⇒ Demonstrates that *reductionism* doesn't always work.

□ Directional Interaction

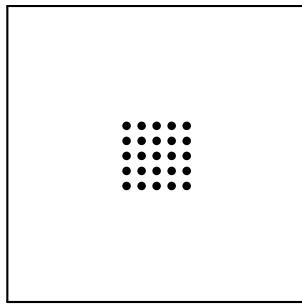
How can we realize other lattice structures? - Need directional inter-atomic interactions.
Consider

$$V(\mathbf{r}) = V_0 \left(\frac{1}{(r/a)^{12}} - \frac{1 + \cos 4\theta}{(r/a)^6} \right), \quad (8)$$

where r, θ is the polar representation of $\mathbf{r} = r(\cos \theta, \sin \theta)$.



Searching for minimal energy configurations ...



A **square lattice** crystal is formed at low-temperature!

Observations:

- The **explicit symmetry breaking** in the microscopic inter-atomic potential already breaks the continuous rotation symmetry to *4-fold discrete* rotation symmetry.
- The *square* lattice is compatible with the 4-fold rotation symmetry and gains energy from bounds in all four directions.
- The *triangular* lattice is incompatible with the 4-fold rotation symmetry, and can not gain as much energy, thus it ceases to be the minimal energy configuration.

**HW
1**

Given the atomic spacing $a = 1$ as unit length, show that the volume V of the triangular lattice scales as the number N of sites as $V = (\sqrt{3} / 2) N \approx 0.866 N$, whereas for square lattice, the scaling is $V = N$. This verifies that the triangular lattice is at least closer packed compared to square lattice.

■ Gas-Solid Transition

How does temperature drives the gas-solid transition?

Consider a **canonical ensemble** of atoms specified by (N, V, T)

- N : *number* of atoms in the system,
- V : *volume* of the system,
- T : *temperature* of the system (in equilibrium with a thermal bath).

The equilibrium state is determined by *minimizing* the **free energy** F

$$F = E - T S, \quad (9)$$

- E : *total energy* of the system,
- S : *entropy* of the system,

$$S = k_B \ln \Omega, \quad (10)$$

Ω : number of microscopic configurations

- **Gas phase:** every atom can reach every point in the space, number of configurations for a single atom $\propto V$, number of configurations for N atoms $\propto V^N$; however, permutations of atoms does not lead to new configurations, thus a factor $N!$ must be divided,

$$\Omega_{\text{gas}} = \frac{V^N}{N!}$$

$$\Rightarrow S_{\text{gas}} = k_B(N \ln V - \ln N!)$$

$$\simeq k_B(N \ln V - N \ln N + N)$$
(11)

- **Solid phase:** every atom typically travels within the V/N volume surrounding its equilibrium position on the lattice, total number of configurations $\propto (V/N)^N$. Moreover, atoms are distinguishable by their lattice coordinates, hence there is no permutation redundancy.

$$\Omega_{\text{solid}} = \left(\frac{V}{N}\right)^N$$

$$\Rightarrow S_{\text{solid}} = k_B(N \ln V - N \ln N)$$
(12)

Free energy difference

$$F_{\text{gas}} - F_{\text{solid}}$$

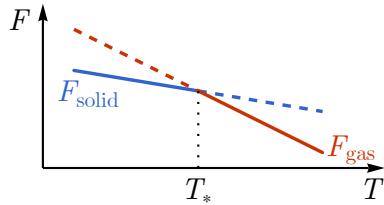
$$= (E_{\text{gas}} - E_{\text{solid}}) - T(S_{\text{gas}} - S_{\text{solid}})$$

$$= E_{\text{bind}} - N k_B T$$
(13)

- E_{bind} is the binding energy, i.e. the energy released when atoms binds to solid. It defines a temperature scale

$$T_* = \frac{E_{\text{bind}}}{N k_B}.$$
(14)

- When $T < T_*$, $F_{\text{gas}} > F_{\text{solid}}$, the system is in the *solid* phase,
- When $T > T_*$, $F_{\text{gas}} < F_{\text{solid}}$, the system is in the *gas* phase,
- Therefore T_* is the gas-solid transition temperature.



- The transition is generally a *first order* transition, because the first order derivative of the free energy $\partial F / \partial T$ is *discontinuous* at the transition.
- Note: this simple argument assumes that each atom fluctuates in a mean-field potential, which is not valid in 1D and 2D. In low dimensions, collective fluctuations of atoms will destroy the crystal order (to be discussed later).

■ Lattice Structure

■ Lattice

Lattice: a collection of *repeating* sets of points in the space. Each lattice point is called a **site**.

- A simple math model of lattice is a set of points as *integer* combinations of *linearly independent primitive lattice vectors* \mathbf{a}_i .

- 1D ($n \in \mathbb{Z}$)

$$R_n = n \mathbf{a}. \quad (15)$$

- 2D ($n_1, n_2 \in \mathbb{Z}$)

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2. \quad (16)$$

- 3D ($n_1, n_2, n_3 \in \mathbb{Z}$)

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3. \quad (17)$$

- **Bravais lattice** in dimension D is described by

$$\mathbf{R}_n = \sum_{i=1}^D n_i \mathbf{a}_i. \quad (18)$$

- Closure: if \mathbf{R}_n and \mathbf{R}_m are two sites on the Bravais lattice, $\mathbf{R}_n + \mathbf{R}_m = \mathbf{R}_{n+m}$ is also a site.
- Homogeneity: every site on the Bravais lattice is equivalent. We can start with a representative site (say $\mathbf{R}_0 = \mathbf{0}$) and reach all the other sites by translation.
- **General lattice** (inhomogeneous): if the repeating structure contains more than one site, different types of sites (labeled by s) are further translated by different **sub-lattice vectors** \mathbf{r}_s .

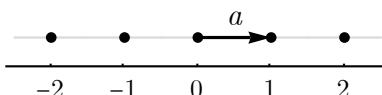
$$\mathbf{R}_{n,s} = \mathbf{R}_n + \mathbf{r}_s. \quad (19)$$

Examples:

- **Chain lattice** (1D) ($n \in \mathbb{Z}$)

$$a = 1. \quad (20)$$

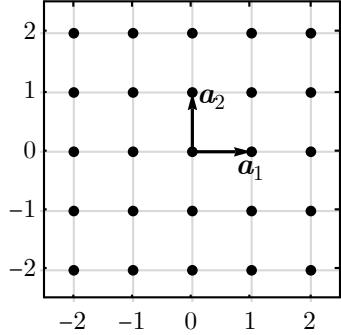
$$R_n = n a = n. \quad (21)$$



- **Square lattice** (2D) ($n_1, n_2 \in \mathbb{Z}$)

$$\begin{cases} \mathbf{a}_1 = (1, 0) \\ \mathbf{a}_2 = (0, 1) \end{cases}. \quad (22)$$

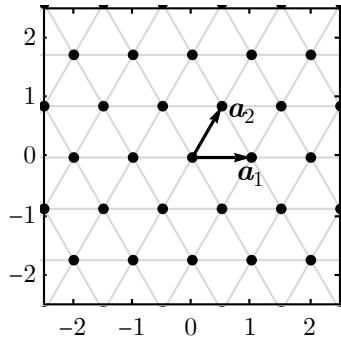
$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 = (n_1, n_2). \quad (23)$$



- **Triangular lattice (2D)** ($n_1, n_2 \in \mathbb{Z}$)

$$\begin{cases} \mathbf{a}_1 = (1, 0) \\ \mathbf{a}_2 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \end{cases}. \quad (24)$$

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 = \left(n_1 + \frac{n_2}{2}, \frac{n_2 \sqrt{3}}{2}\right). \quad (25)$$

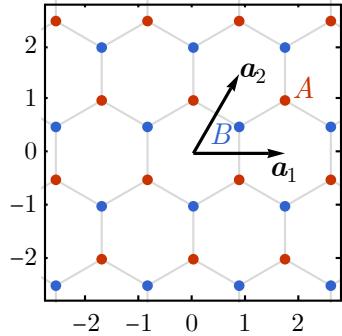


- **Honeycomb lattice (2D)** ($n_1, n_2 \in \mathbb{Z}$)

$$\begin{cases} \mathbf{a}_1 = (\sqrt{3}, 0) \\ \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, \frac{3}{2}\right) \end{cases}, \quad \begin{cases} \mathbf{r}_A = (\sqrt{3}, 1) \\ \mathbf{r}_B = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \end{cases}. \quad (26)$$

$$\begin{aligned} \mathbf{R}_{n,A} &= n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \mathbf{r}_A \\ &= \left(\sqrt{3} n_1 + \frac{\sqrt{3} n_2}{2} + \sqrt{3}, \frac{3 n_2}{2} + 1\right), \end{aligned} \quad (27)$$

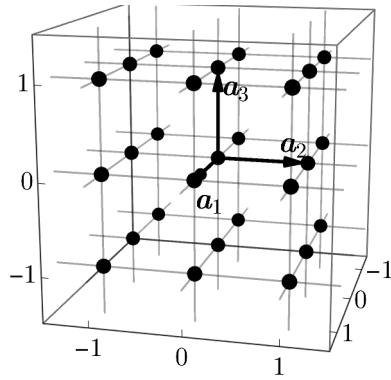
$$\begin{aligned} \mathbf{R}_{n,B} &= n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \mathbf{r}_B \\ &= \left(\sqrt{3} n_1 + \frac{\sqrt{3} n_2}{2} + \frac{\sqrt{3}}{2}, \frac{3 n_2}{2} + \frac{1}{2}\right). \end{aligned}$$



- **Cubic lattice (3D)** ($n_1, n_2, n_3 \in \mathbb{Z}$)

$$\begin{cases} \mathbf{a}_1 = (1, 0, 0) \\ \mathbf{a}_2 = (0, 1, 0) \\ \mathbf{a}_3 = (0, 0, 1) \end{cases} \quad (28)$$

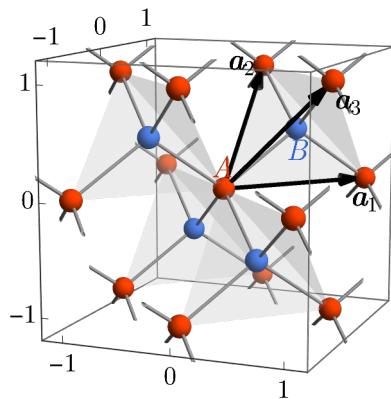
$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 = (n_1, n_2, n_3). \quad (29)$$



- **Diamond lattice (3D)** ($n_1, n_2, n_3 \in \mathbb{Z}$)

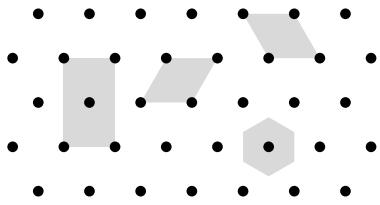
$$\begin{cases} \mathbf{a}_1 = (1, 1, 0) \\ \mathbf{a}_2 = (0, 1, 1) \\ \mathbf{a}_3 = (1, 0, 1) \end{cases}, \quad \begin{cases} \mathbf{r}_A = (0, 0, 0) \\ \mathbf{r}_B = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \end{cases}. \quad (30)$$

$$\begin{aligned} \mathbf{R}_{n,A} &= n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 + \mathbf{r}_A \\ &= (n_1 + n_3, n_1 + n_2, n_2 + n_3), \\ \mathbf{R}_{n,B} &= n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 + \mathbf{r}_B \\ &= \left(n_1 + n_3 + \frac{1}{2}, n_1 + n_2 + \frac{1}{2}, n_2 + n_3 + \frac{1}{2}\right). \end{aligned} \quad (31)$$

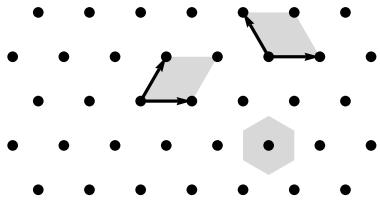


■ Unit Cell

Unit cell: the repeated building block of the lattice, which can tile the full space under lattice translation.



- **Primitive unit cell:** a unit cell of *minimal volume*, e.g. parallelogram (parallelepiped) spanned by *primitive lattice vectors* \mathbf{a}_i .



- The choice of primitive lattice vectors for a lattice is *not* unique, hence the primitive unit cell is also *not* unique.
- However, the *volume* of the primitive unit cell is unique, which is given by the absolute value of the determinant of the matrix A formed by all primitive lattice vectors (see Wikipedia Parallelepiped:Volume)

$$\Omega = |\det A|,$$

$$A = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \dots \end{pmatrix}.$$

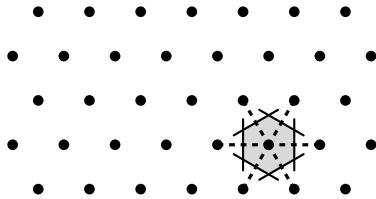
(32)

- In 2D, $\Omega = |\mathbf{a}_1 \times \mathbf{a}_2|$.
- In 3D, $\Omega = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$.

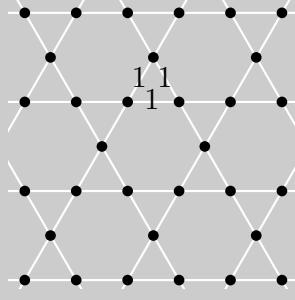
Exc 1

Calculate the volume of primitive unit cell for the triangular lattice defined in Eq. (24).

- **Wigner-Seitz cell** (Voronoi cell): a primitive unit cell enclosed by perpendicular bisectors between a Bravais lattice point and all its neighbors.



Calculate the volume of primitive unit cell for the **Kagome lattice** (figure below), assuming that the nearest neighbor links are all of unit length. [Hint: first find the primitive lattice vectors and then use Eq. (32)]

HW 2

■ Lattice Symmetry

Lattice symmetry: coordinate transformations which leave the lattice *invariant*.

- General form of **coordinate transformation** (affine transformation)

$$\mathbf{R} \rightarrow \mathbf{R}' = \mathbf{R} A + \mathbf{b}, \quad (35)$$

where

- A - matrix (to implement rotations, reflections, inversions),
- \mathbf{b} - vector (to implement translation).

▫ Translation Symmetry

Every lattice (by definition) is invariant under the translation by any Bravais lattice vector (i.e. $\mathbf{b} = \mathbf{R}_m$).

$$\mathbf{R}_{n,s} \rightarrow \mathbf{R}'_{n,s} = \mathbf{R}_{n,s} + \mathbf{R}_m = \mathbf{R}_{n+m,s} \quad (36)$$

▫ Point Group Symmetry

Lattice symmetry that preserves a fixed point.

- **Rotation** by angle θ along an axis. The rotation is said to be k -fold if the angle is $\theta = 2\pi/k$. In 2D, rotation axis reduces to a point, and the rotation about the origin is implemented by

$$\mathbf{R} \rightarrow \mathbf{R} \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}. \quad (37)$$

In 3D, a rotation about axis \mathbf{N} (specified by a unit vector) by θ angle is implemented by

$$\mathbf{R} \rightarrow \mathbf{R} \cos \theta + (\mathbf{R} \cdot \mathbf{N}) \mathbf{N}(1 - \cos \theta) + \mathbf{N} \times \mathbf{R} \sin \theta. \quad (38)$$

- **Reflection** about a mirror plane (in 3D; reduces to a line in 2D). The mirror plane can be specified by the normal vector \mathbf{N} (the unit vector perpendicular to the mirror plane).

$$\mathbf{R} \rightarrow \mathbf{R} - 2(\mathbf{R} \cdot \mathbf{N}) \mathbf{N}. \quad (39)$$

Exc 2

Show the composition of two reflections induced by normal vectors \mathbf{N}_1 and \mathbf{N}_2 is a rotation along the axis $(\mathbf{N}_1 \times \mathbf{N}_2)/\sin \theta$ by the angle 2θ , where θ is the angle between \mathbf{N}_1 and \mathbf{N}_2 (i.e. $\mathbf{N}_1 \cdot \mathbf{N}_2 = \cos \theta$).

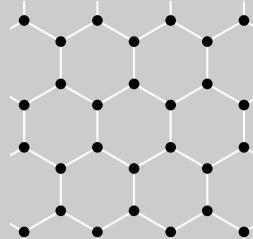
- **Inversion** about an inversion center. In 2D an inversion is equivalent to a 2-fold rotation. Inversion about the origin is implemented by

$$\mathbf{R} \rightarrow -\mathbf{R}. \quad (51)$$

Exc 3

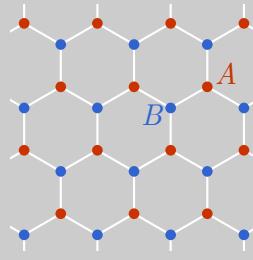
If the inversion center \mathbf{r}_c is not at the origin, how does the lattice coordinate transform under the inversion?

The honeycomb lattice, as defined by Eq. (26), has a six-fold and a three-fold rotation symmetry, assuming all sites are made of the same type of atoms (like in graphene).



HW 3

- Write how the six-fold and the three-fold rotations are implemented as coordinate transformations [answer not unique, up to lattice translation].
- What happens to the six-fold rotation symmetry if A and B sites are made of different atoms (like in hexagonal boron nitride)?



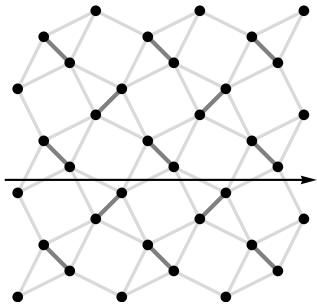
□ Nonsymmorphic Symmetry

Lattice symmetry that involves a non-trivial translation followed by a non-trivial point group

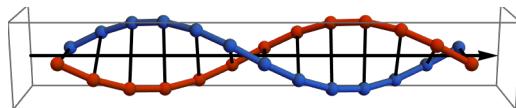
transformation.

- **Glide reflection:** translate along an axis followed by a reflection about the same axis.

Example: **Shastry-Sutherland lattice.**



- **Screw displacement:** translation along an axis followed by a rotation around the same axis.



■ Reciprocal Lattice

■ Wave Propagating on Lattice

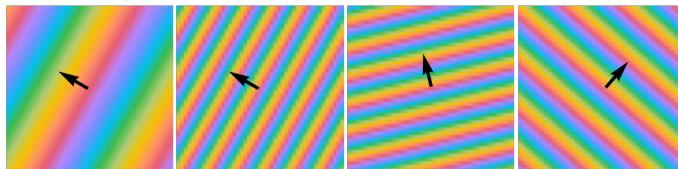
Plane wave propagating in the *continuous space*:

$$\psi_k(r) = e^{i k \cdot r} \quad (53)$$

labeled by the **wave vector** (or **wave momentum**) k :

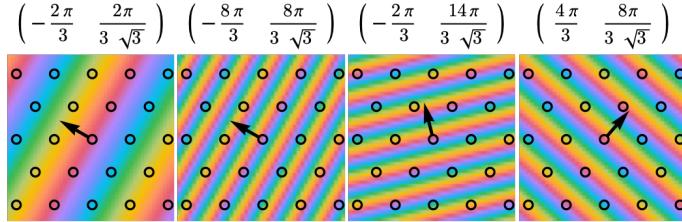
- length of k - *wave number* $|k| = 2\pi/\lambda$, reciprocal to the *wave length* λ ,
- direction of k - *wave propagation direction*.

$$\left(-\frac{2\pi}{3}, \frac{2\pi}{3\sqrt{3}} \right), \left(-\frac{8\pi}{3}, \frac{8\pi}{3\sqrt{3}} \right), \left(-\frac{2\pi}{3}, \frac{14\pi}{3\sqrt{3}} \right), \left(\frac{4\pi}{3}, \frac{8\pi}{3\sqrt{3}} \right)$$

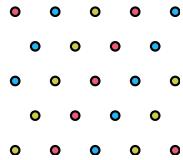


(Rainbow colors are used to indicate the phase of the wave).

However, when the waves are defined on (or restricted to) a *lattice*, different wave vectors may look the *same*. For example,



all look like:



- Two waves of wave vectors \mathbf{k} and \mathbf{k}' are *equivalent* (indistinguishable) on a lattice, if their wave momentum difference $\mathbf{G} = \mathbf{k}' - \mathbf{k}$ satisfies

$$e^{i \mathbf{G} \cdot \mathbf{R}} = 1 \quad (54)$$

for *all* lattice points \mathbf{R} .

- Because, in this case,

$$\psi_{\mathbf{k}'}(\mathbf{R}) = e^{i \mathbf{k}' \cdot \mathbf{R}} = e^{i (\mathbf{k} + \mathbf{G}) \cdot \mathbf{R}} = e^{i \mathbf{k} \cdot \mathbf{R}} e^{i \mathbf{G} \cdot \mathbf{R}} = \psi_{\mathbf{k}}(\mathbf{R}). \quad (55)$$

Note: this does not mean $\psi_{\mathbf{k}'}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$ for any point \mathbf{r} in the space, but the equality only holds for discrete lattice points \mathbf{R} .

- The solutions \mathbf{G} of Eq. (54) are called **lattice momenta** of the lattice. It turns out that all solutions of \mathbf{G} also forms a lattice in the *momentum space*, called the **reciprocal lattice**.

■ Reciprocal Lattice (Definition)

Reciprocal lattice: every **Bravais lattice** (in the real space) has a dual lattice in the momentum space, made of points \mathbf{G} that satisfies

$e^{i \mathbf{G} \cdot \mathbf{R}_n} = 1,$

(56)

for all points \mathbf{R}_n ($n \in \mathbb{Z}^D$) on the Bravais lattice.

- Recall Eq. (18): every Bravais lattice vector $\mathbf{R}_n = \sum_{i=1}^D n_i \mathbf{a}_i$ is an integer combination of primitive lattice vectors \mathbf{a}_i . Then $e^{i \mathbf{G} \cdot \mathbf{R}_n} = 1$ implies

$$\mathbf{G} \cdot \mathbf{R}_n = \sum_{i=1}^D n_i \mathbf{G} \cdot \mathbf{a}_i \in 2\pi\mathbb{Z}, \quad (57)$$

and this must hold for *any* choice of \mathbf{n} .

- Suppose we choose $\mathbf{n} = (1, 0, \dots)$, Eq. (57) implies $\mathbf{G} \cdot \mathbf{a}_1 \in 2\pi\mathbb{Z}$,
Suppose we choose $\mathbf{n} = (0, 1, \dots)$, Eq. (57) implies $\mathbf{G} \cdot \mathbf{a}_2 \in 2\pi\mathbb{Z}$,
... (enumerating over all dimensions).

- In summary,

$$\mathbf{G} \cdot \mathbf{a}_j = 2\pi m_j \quad (58)$$

with $m_j \in \mathbb{Z}$ (for $j = 1, 2, \dots, D$). This is a *necessary* and *sufficient* condition for \mathbf{G} to be a reciprocal lattice point

- *Necessity:* if any condition in Eq. (58) is not satisfied, we can take the corresponding choice of \mathbf{n} to construct a violation of $e^{i \mathbf{G} \cdot \mathbf{R}_n} = 1$.
- *Sufficiency:* as long as all conditions in Eq. (58) is satisfied, we have

$$\mathbf{G} \cdot \mathbf{R}_n = 2\pi \left(\sum_{i=1}^D m_i n_i \right) \in 2\pi \mathbb{Z}, \quad (59)$$

such that $e^{i \mathbf{G} \cdot \mathbf{R}_n} = 1$.

- Therefore, every integer vector $\mathbf{m} \in \mathbb{Z}^D$ labels a solution of the reciprocal lattice point \mathbf{G}_m via Eq. (58). Components of \mathbf{m} are also called **Miller indices**.
- Let us define a set of special solutions (where Miller indices \mathbf{m} are unit vectors)

$$\begin{aligned} \mathbf{b}_1 &= \mathbf{G}_{(1,0,\dots)}, \\ \mathbf{b}_2 &= \mathbf{G}_{(0,1,\dots)}, \\ &\dots, \end{aligned} \quad (60)$$

which, according to Eq. (58), means

$$\boxed{\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}} \quad (61)$$

- These \mathbf{b}_j vectors actually form the *primitive lattice vectors* of the *reciprocal lattice*, since any reciprocal lattice point \mathbf{G}_m can be written as

$$\boxed{\mathbf{G}_m = \sum_{i=1}^D m_i \mathbf{b}_i.} \quad (62)$$

- Because in this way,

$$\mathbf{G}_m \cdot \mathbf{a}_j = \sum_{i=1}^D m_i \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \sum_{i=1}^D m_i \delta_{ij} = 2\pi m_j, \quad (63)$$

meaning that Eq. (62) is indeed the general solution of the condition Eq. (58), hence also the general solution of the reciprocal lattice point.

■ Reciprocal Lattice (Construction)

Now the remaining problem is: given a set of \mathbf{a}_i how to find the set of \mathbf{b}_i to satisfy Eq. (61)?

- Represent the primitive lattice vectors as matrices for both the direct and the reciprocal lattice

$$A \stackrel{\text{def}}{=} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \dots \end{pmatrix}, B \stackrel{\text{def}}{=} \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \\ \dots \end{pmatrix}. \quad (64)$$

- Then Eq. (61) can be written as a matrix equation

$$B A^T = 2\pi \mathbb{1}, \quad (65)$$

where $\mathbb{1}$ stands for the $D \times D$ identity matrix.

- As \mathbf{a}_i are linearly independent, the matrix A is invertible (so does A^T), thus the solution for B is given by the matrix inversion

$$B = 2\pi (A^T)^{-1}. \quad (66)$$

- The name “reciprocal” becomes clear now, as their primitive lattice vectors are *reciprocal* (as *matrix inversion*) to each other. When the direct lattice expands, the reciprocal lattice will shrink, and vice versa.

Explicit formulae:

- 1D lattice

$$b = \frac{2\pi}{a}. \quad (67)$$

- 2D lattice $\Omega = |\mathbf{a}_1 \times \mathbf{a}_2|$,

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{\Omega} \mathbf{a}_2 \times \hat{\mathbf{z}}, \\ \mathbf{b}_2 &= -\frac{2\pi}{\Omega} \mathbf{a}_1 \times \hat{\mathbf{z}}, \end{aligned} \quad (68)$$

where $\hat{\mathbf{z}}$ is the unit vector normal to the 2D lattice plane.

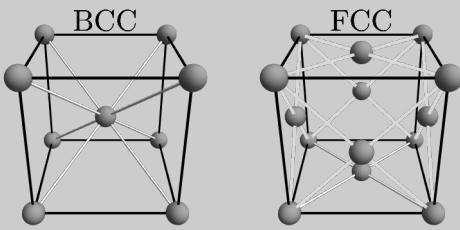
- 3D lattice $\Omega = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$,

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3, \\ \mathbf{b}_2 &= \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1, \\ \mathbf{b}_3 &= \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2. \end{aligned} \quad (69)$$

Exc 4 Find the primitive lattice vectors of the reciprocal lattice of the triangular lattice as defined by Eq. (24). Plot the reciprocal lattice.

Show that the **body-centered cubic** (BCC) lattice and the **face-centered cubic** (FCC) lattice are reciprocal lattices of each other.

HW
4



■ Brillouin Zone

Brillouin zone (BZ): a *primitive unit cell* of the *reciprocal lattice*.

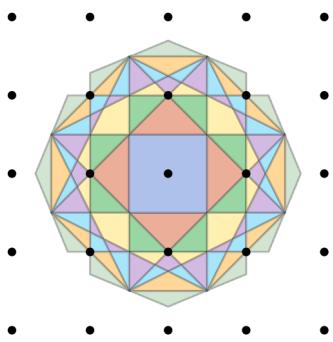
- The **first Brillouin zone** (1st BZ): the *Wigner-Seitz cell* centered at $\mathbf{G} = 0$ on the *reciprocal lattice*; also as the set of all points \mathbf{k} in the momentum space, that are closest to $\mathbf{G} = 0$ than another points \mathbf{G} on the reciprocal lattice.
- The **n th Brillouin zone**: the set of all points \mathbf{k} in the momentum space, that are n th closest to $\mathbf{G} = 0$ among another points \mathbf{G} on the reciprocal lattice.

Examples of Brillouin zones (see [1] for the construction algorithm):

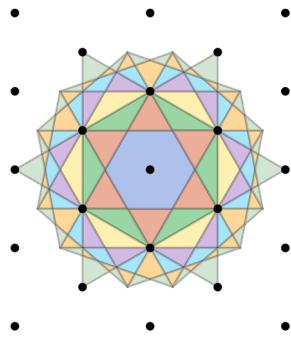
- On 1D reciprocal lattice



- On 2D *square* reciprocal lattice



- On 2D *triangular* reciprocal lattice



Properties:

- The 1st BZ provides a *complete* set of *inequivalent* wave vectors. Any wave vector outside the 1st BZ will be equivalent to one inside the 1st BZ (related by certain lattice momentum).
- Every BZ has exactly the *same volume* (in the momentum space):

$$\det |B| = \frac{(2\pi)^n}{\det |A|} = \frac{(2\pi)^n}{\Omega}. \quad (73)$$

- Higher BZ can be *folded* to the 1st BZ.
- Any physical property (e.g. frequency, group velocity) of the wave propagating on a lattice can be fully described within the 1st BZ.

[1] Smith, Philip. Geometric and Topological Methods for Applications to Materials and Data Skeletonisation. PhD thesis, University of Liverpool (2021).

■ Scattering Experiment

■ Elastic Scattering

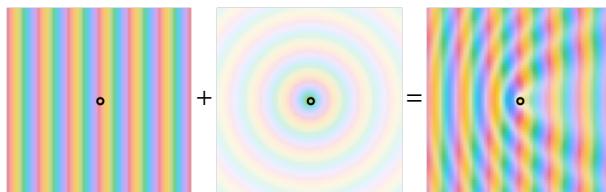
How do we probe the lattice structure? - Scattering experiment.

- **X-ray** scattering.
- **Neutron** scattering.
- **Electron** scattering.

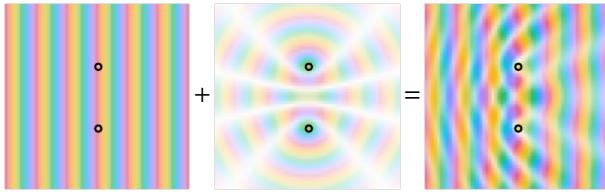
Note: Particles are waves. — Quantum Mechanics

□ Real Space Picture

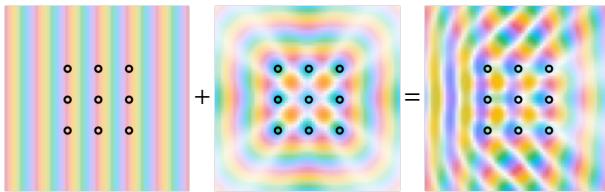
- *Plane wave* hits an atom, the atom responds with a *spherical wave*.



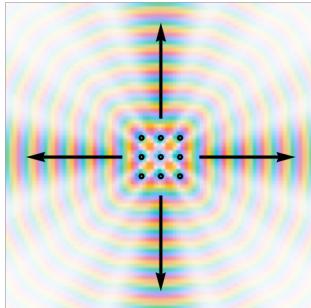
- Each atom behaves like an *independent scatterer* for the incident wave (to the leading order, ignoring the fact that the atoms can continue to scatter the wave that was scattered from other atoms).



- If there is an *array* of atoms, the scattering wave emitted from each atom can *interfere* → leading to **Bragg diffraction**.



As we zoom out, the wave scattered off the crystal looks like beams of plane waves along special directions.



Question: Why the scattering amplitude is strong along these directions? How to determine these directions?

□ Momentum Space Picture

- **Plane wave** of *wave momentum* \mathbf{k} (length of \mathbf{k} - $2\pi/\lambda$, direction of \mathbf{k} - propagation direction)

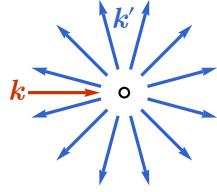
$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}}. \quad (74)$$

- **Spherical wave** = superposition of *plane waves* of the *same wave length* in *all directions*

$$\begin{aligned} \phi_{\mathbf{k}}(\mathbf{r}) &= \int_{|\mathbf{k}|=k} \psi_{\mathbf{k}}(\mathbf{r}) = \int_{|\mathbf{k}|=k} e^{i \mathbf{k} \cdot \mathbf{r}} \\ &= \frac{1}{2\pi} \int d\theta e^{i k r \cos \theta} = J_0(k r). \end{aligned} \quad (75)$$

An atom scatters a plane wave of momentum \mathbf{k} to a spherical wave of the same wave number k

\Leftrightarrow to a equal-probability superposition of plane waves of all possible momentum \mathbf{k}' , as long as $|\mathbf{k}'| = |\mathbf{k}| = k$ (the wave length does not change, as it is fixed by the wave frequency).



Scattering rate $\Gamma(\mathbf{k} \rightarrow \mathbf{k}')$: the *probability* (transition rate) to scatter a wave from momentum \mathbf{k} to momentum \mathbf{k}' by a set of scatterers of the density distribution $\rho(\mathbf{r})$. According to Fermi's golden rule,

$$\Gamma(\mathbf{k} \rightarrow \mathbf{k}') \propto |\langle \mathbf{k}' | \rho | \mathbf{k} \rangle|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}), \quad (76)$$

where

- the scattering amplitude $\langle \mathbf{k}' | \rho | \mathbf{k} \rangle$ is given by the **wave function overlap**

$$\begin{aligned} \langle \mathbf{k}' | \rho | \mathbf{k} \rangle &= \int_r \psi_{\mathbf{k}'}^*(\mathbf{r}) \rho(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \\ &= \int_r \rho(\mathbf{r}) e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} \\ &= \tilde{\rho}(\mathbf{k}' - \mathbf{k}) \end{aligned} \quad (77)$$

- $\psi_{\mathbf{k}}(\mathbf{r})$ - incident wave,
- $\rho(\mathbf{r})$ - scatterer density distribution (\sim atomic density distribution),
- $\rho(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r})$ - incident wave enveloped by the atomic density (no atom no scattering, more atom stronger scattering),
- $\int_r \psi_{\mathbf{k}'}^*(\mathbf{r}) \dots$ - inner product with $\psi_{\mathbf{k}'}(\mathbf{r})$ to extract the amplitude of wave in the \mathbf{k}' momentum component.
- The integration result can be expressed in terms of the *Fourier transform* of the density distribution

$$\tilde{\rho}(\mathbf{q}) \equiv \int_r \rho(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (78)$$

the term $\delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$ imposes the *energy conservation*, which requires $|\mathbf{k}'| = |\mathbf{k}|$ (the **on-shell condition**).

In conclusion, the scattering rate is given by

$$\Gamma(\mathbf{k} \rightarrow \mathbf{k}') \propto |\tilde{\rho}(\mathbf{k}' - \mathbf{k})|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}). \quad (79)$$

- Apply to a *single atom* at the origin: $\rho(\mathbf{r}) = \delta(\mathbf{r})$,

$$\tilde{\rho}(\mathbf{q}) = \int_r \delta(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} = e^{-i\mathbf{q} \cdot \mathbf{0}} = 1. \quad (80)$$

Therefore the scattering rate is *constant* for all \mathbf{k}' as long as it is on-shell

$$\Gamma(\mathbf{k} \rightarrow \mathbf{k}') \propto \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \propto \delta(|\mathbf{k}'| - |\mathbf{k}|). \quad (81)$$

This matches the intuition that an atom scatters a *plane wave* to a *spherical wave*.

■ Fourier Transform of Lattice

Let us explore the behavior of the Fourier transform Eq. (78).

$$\tilde{\rho}(\mathbf{q}) \equiv \int_{\mathbf{r}} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}}. \quad (82)$$

- 1D lattice $R_n = n a$,
- Real-space density distribution (modeled by a sequence of Dirac peaks)

$$\rho(r) = \frac{1}{N} \sum_{n \in \mathbb{Z}} \delta(r - R_n) = \frac{1}{N} \sum_{n \in \mathbb{Z}} \delta(r - n a) \quad (83)$$

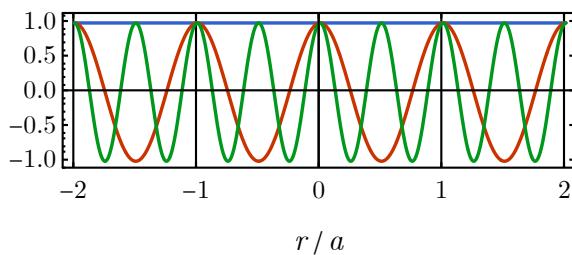
- Momentum-space density distribution

$$\begin{aligned} \tilde{\rho}(q) &= \frac{1}{N} \sum_{n \in \mathbb{Z}} e^{-i q R_n} = \frac{1}{N} \sum_{n \in \mathbb{Z}} e^{-i q n a} \\ &= \frac{2\pi}{N a} \sum_{m \in \mathbb{Z}} \delta\left(q - \frac{2\pi m}{a}\right) = \frac{2\pi}{V} \sum_{m \in \mathbb{Z}} \delta(q - G_m). \end{aligned} \quad (84)$$

Also a sequence of Dirac peaks located at **reciprocal lattice** sites:

$$G_m = \frac{2\pi}{a} m. \quad (85)$$

- Argument: constructive interference from all lattice sites happens only when the wave length $\lambda = a/m$ is an integer fraction of the lattice spacing a .

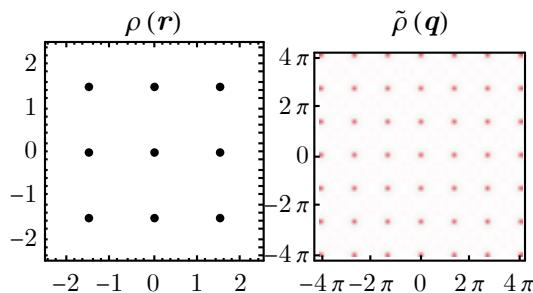
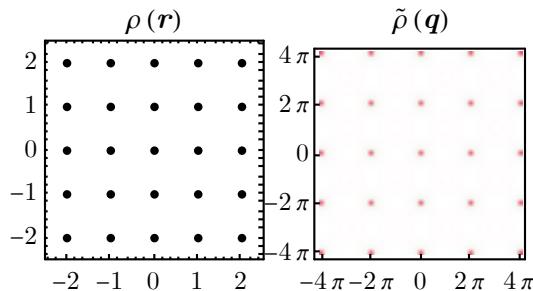


**Exc
5**

Show that in the functional sense

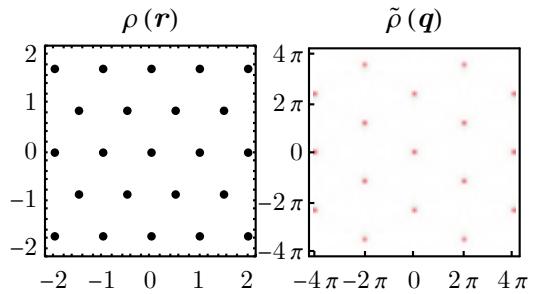
- $\sum_{n \in \mathbb{Z}} e^{-i n \theta} = 2\pi \sum_{m \in \mathbb{Z}} \delta(\theta - 2\pi m)$,
- $\delta(q a) = \frac{1}{a} \delta(q)$.

- 2D lattices (numerical examples)
- Square lattice \rightarrow square lattice



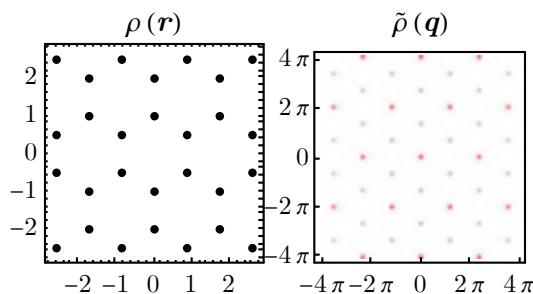
Direct lattice *expands* in the **real space** \Leftrightarrow reciprocal lattice *shrinks* in the **momentum space** (hence the name “reciprocal”). Reason: *momentum* and *coordinate* scales are reciprocal to each other ($q \sim a^{-1}$).

- Triangular lattice \rightarrow triangular lattice



Reciprocal lattice shares the *same point group symmetry* as the direct lattice. (In this case, six-fold rotation, horizontal and vertical reflections).

- Honeycomb lattice (triangular Bravais lattice + sub-lattice structure) \rightarrow triangular lattice with non-trivial **structure factor**.



red dot - positive peak, green dot - negative peak. Non-trivial *sub-lattice structure* leads to non-trivial *structure factor* (To be discussed in more details).

- In general, for atoms at $\mathbf{R}_{n,s}$ on a lattice, the scatterer density distribution can be modeled by

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{n,s} f_s \delta(\mathbf{r} - \mathbf{R}_{n,s}), \quad (93)$$

where

- f_s is the scattering amplitude of the type- s atom (different types of atom can scatter the wave with different amplitudes). Normalization: $\sum_s f_s = 1$.
- N - number of unit cells. Assume thermodynamic limit $N \rightarrow \infty$. The average $\frac{1}{N} \sum_R \dots$ has a well-defined limit as $N \rightarrow \infty$. The normalization condition is $\int_r \rho(\mathbf{r}) = 1$.

Therefore by Eq. (78),

$$\begin{aligned} \tilde{\rho}(\mathbf{q}) &= \int_r \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \frac{1}{N} \int_r \sum_{n,s} f_s \delta(\mathbf{r} - \mathbf{R}_{n,s}) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \frac{1}{N} \sum_{n,s} f_s e^{-i\mathbf{q}\cdot\mathbf{R}_{n,s}}. \end{aligned} \quad (94)$$

Given $\mathbf{R}_{n,s} = \mathbf{R}_n + \mathbf{r}_s$ (recall Eq. (19)), the summation can be split into two parts

$$\tilde{\rho}(\mathbf{q}) = \frac{1}{N} \sum_n e^{-i\mathbf{q}\cdot\mathbf{R}_n} \sum_s f_s e^{-i\mathbf{q}\cdot\mathbf{r}_s}. \quad (95)$$

- If the lattice is a *Bravais lattice*, there is only one type of atom (no sub-lattice structure), the second summation is just a trivial factor f , which may be rescaled to $f = 1$, such that the scattering amplitude $\tilde{\rho}(\mathbf{q})$ is given by the Fourier series

$$\tilde{\rho}(\mathbf{q}) = \frac{1}{N} \sum_n e^{-i\mathbf{q}\cdot\mathbf{R}_n}. \quad (96)$$

- Expect $\tilde{\rho}(\mathbf{q})$ to peak at multiple points arranged *periodically* in the *momentum space*, forming the **reciprocal lattice**.

■ Scattering Amplitude

Recall that the scattering rate is given by Eq. (79),

$$\Gamma(\mathbf{k} \rightarrow \mathbf{k}') \propto |\tilde{\rho}(\mathbf{k}' - \mathbf{k})|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}), \quad (97)$$

where the scattering amplitude is (recall Eq. (95))

$$\tilde{\rho}(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{n}} e^{-i \mathbf{q} \cdot \mathbf{R}_n} \sum_s f_s e^{-i \mathbf{q} \cdot \mathbf{r}_s}. \quad (98)$$

- Given the knowledge of reciprocal lattice, the first summation can be evaluated as (use (Exc. 5) results and generalize to higher dimensions)

$$\sum_{\mathbf{n}} e^{-i \mathbf{q} \cdot \mathbf{R}_n} = \frac{(2\pi)^D}{\Omega} \sum_{\mathbf{m}} \delta(\mathbf{q} - \mathbf{G}_m), \quad (99)$$

- D - space dimension.
- Ω - unit cell volume, as defined in Eq. (32).
- \mathbf{G}_m - reciprocal lattice vectors, as in Eq. (62), labeled by Miller indices \mathbf{m} .
- If \mathbf{q} is a reciprocal lattice point, $e^{-i \mathbf{q} \cdot \mathbf{R}_n}$ will be unity and the sum is infinite, however if \mathbf{q} is not on the reciprocal lattice, the sum will be zero due to the phase cancellation of $e^{-i \mathbf{q} \cdot \mathbf{R}_n}$. Such behavior is exactly described by the delta function on the right-hand-side.
- Then Eq. (98) can be written as (note $N\Omega = V$ is the total volume)

$$\begin{aligned} \tilde{\rho}(\mathbf{q}) &= \frac{(2\pi)^D}{V} \sum_{\mathbf{m}} \delta(\mathbf{q} - \mathbf{G}_m) \sum_s f_s e^{-i \mathbf{q} \cdot \mathbf{r}_s} \\ &= \frac{(2\pi)^D}{V} \sum_{\mathbf{m}} \delta(\mathbf{q} - \mathbf{G}_m) \sum_s f_s e^{-i \mathbf{G}_m \cdot \mathbf{r}_s} \end{aligned} \quad (100)$$

where we are free to replace \mathbf{q} by \mathbf{G}_m because $\tilde{\rho}(\mathbf{q})$ is non-vanishing only when $\mathbf{q} = \mathbf{G}_m$ (when the replacement is valid).

In summary, the scattering amplitude takes the form of

$$\begin{aligned} \tilde{\rho}(\mathbf{q}) &= \frac{(2\pi)^D}{V} \sum_{\mathbf{m}} S_{\mathbf{m}} \delta(\mathbf{q} - \mathbf{G}_m), \\ S_{\mathbf{m}} &= \sum_s f_s e^{-i \mathbf{G}_m \cdot \mathbf{r}_s}. \end{aligned} \quad (101)$$

such that $\tilde{\rho}(\mathbf{q})$ contains

- a collection of peaks at $\mathbf{q} = \mathbf{G}_m$ described by $\delta(\mathbf{q} - \mathbf{G}_m)$,
- whose amplitude is given by the **structural factor** $S_{\mathbf{m}}$ (it is determined by the sub-lattice *structure*, and appears as a *factor* in front of the delta function peak, hence the name).

The direct lattice (atomic density distribution $\rho(\mathbf{r})$) can be restored from the scattering amplitude $\tilde{\rho}(\mathbf{q})$ by the *inverse Fourier transform*

$$\rho(\mathbf{r}) \equiv \frac{1}{(2\pi)^D} \int_{\mathbf{q}} \tilde{\rho}(\mathbf{q}) e^{i \mathbf{q} \cdot \mathbf{r}}. \quad (102)$$

Therefore the result of scattering experiment can be used to infer the lattice structure.

Exc 6 Show that Eq. (102) indeed restores Eq. (93) given Eq. (101).

■ Laue Condition

The scattering rate $\Gamma(\mathbf{k} \rightarrow \mathbf{k}')$ peaks (i.e. the scattering happens) when the following conditions are met

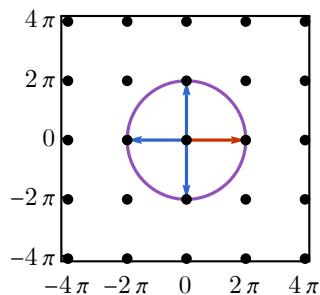
- conservation of *crystal momentum (Laue condition)*

$$\mathbf{k}' - \mathbf{k} = \mathbf{G}_m, \quad (106)$$

- conservation of *energy* (for X-ray $E_k = c \hbar |\mathbf{k}|$, for neutron / electron $E_k = \frac{\hbar^2}{2m} |\mathbf{k}|^2$)

$$|\mathbf{k}'| = |\mathbf{k}|. \quad (107)$$

Graphical method to determine \mathbf{k}' (scattered wave, in blue) from \mathbf{k} (incident wave, in red) given the reciprocal lattice.



- k - wave number $2\pi/\lambda$,
- θ - rotation angle of the crystal (reciprocal lattice rotates by the same amount as the direct lattice).

■ Lattice Momentum

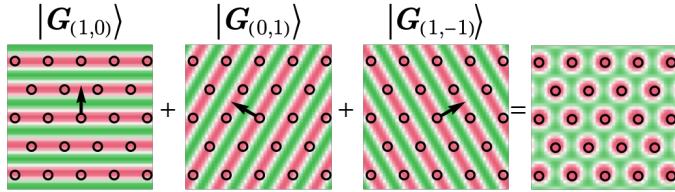
What is the physical meaning of the **lattice momentum** $\hbar\mathbf{G}$?

- Lattice (Bravais lattice) = the *intersection* of families of lattice planes of all lattice momenta \mathbf{G}

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_n \delta(\mathbf{r} - \mathbf{R}_n) = \frac{1}{V} \sum_m e^{i \mathbf{G}_m \cdot \mathbf{r}}, \quad (108)$$

see (Exc. 6) for derivation.

Take the triangular lattice for example:



- Each **family of lattice planes** is in one-to-one correspondence with the possible *directions* of reciprocal lattice vectors \mathbf{G} , to which they are *normal*.
- The *length* of \mathbf{G} is always an *integer* multiple of $2\pi/d$,

$$|\mathbf{G}| = \frac{2\pi m}{d}, \quad (109)$$

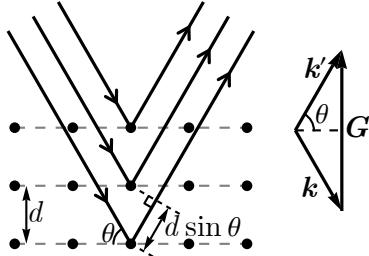
where d is the *spacing* between the lattice planes. (The corresponding wave length $\lambda = d/m$).

- The *particle* that carries the momentum $\hbar \mathbf{G}$ is the *condensed phonon* in the crystal (To be explained later).

■ Bragg Condition

Laue condition can also be interpreted as the scattering condition associated with a diffraction grating.

- An incoming wave is reflected off of a family of adjacent layers of atoms separated by the inter-layer distance d .



- The wave has been deflected by angle 2θ .
- Wave deflected from the next deeper layer travels *additional distance* $2d \sin \theta$ (extra $d \sin \theta$ accumulated on both the *incoming* and *outgoing* rays), compare to that from the previous layer.
- Condition for *constructive interference* (**Bragg condition**)

$$2d \sin \theta = m\lambda, \quad (110)$$

with $m \in \mathbb{Z}$.

Bragg condition and **Laue condition** are *equivalent*.

$$2d \sin \theta = m\lambda \Leftrightarrow \mathbf{k}' - \mathbf{k} = \mathbf{G}. \quad (111)$$

- Direction: the direction of $\mathbf{k}' - \mathbf{k}$ is always *normal* to the lattice plane, matching the direction of \mathbf{G} .
- Length: $|\mathbf{k}'| = |\mathbf{k}| = 2\pi/\lambda$, $|\mathbf{G}| = 2\pi m/d$.

$$2 \frac{2\pi}{\lambda} \sin \theta = \frac{2\pi m}{d} \Rightarrow 2 d \sin \theta = m \lambda. \quad (112)$$

■ Structural Factor

The Bragg/Laue condition determines the *positions* of diffraction peaks (at \mathbf{G}_m , labeled by *Miller indices* \mathbf{m}), the *intensity* $|S_m|^2$ of each peak \mathbf{m} is determined by the **structural factor** S_m (recall Eq. (101))

$$S_m = \sum_s f_s e^{-i \mathbf{G}_m \cdot \mathbf{r}_s}, \quad (113)$$

where

- f_s is the atomic form factor (scattering amplitude) of the type- s atom,
- \mathbf{r}_s is the sub-lattice vector of the type- s atom.

It is sometimes more convenient to represent the sub-lattice vector \mathbf{r}_s in the primitive lattice vector basis, by introducing $\mathbf{n}_s = (n_{s,1}, n_{s,2}, \dots)$,

$$\boxed{\mathbf{r}_s = \sum_{i=1}^D n_{s,i} \mathbf{a}_i.} \quad (114)$$

Given that $\mathbf{G}_m = \sum_{i=1}^D m_i \mathbf{b}_i$, Eq. (113) can be written as

$$\begin{aligned} S_m &= \sum_s f_s \exp\left(-i \sum_{i=1}^D m_i \mathbf{b}_i \cdot \sum_{j=1}^D n_{s,j} \mathbf{a}_j\right) \\ &= \sum_s f_s \exp\left(-i \sum_{i,j} m_i n_{s,j} \mathbf{b}_i \cdot \mathbf{a}_j\right) \\ &= \sum_s f_s \exp\left(-2\pi i \sum_{i,j} m_i n_{s,j} \delta_{ij}\right) \\ &= \sum_s f_s \exp\left(-2\pi i \sum_i m_i n_{s,i}\right), \end{aligned} \quad (115)$$

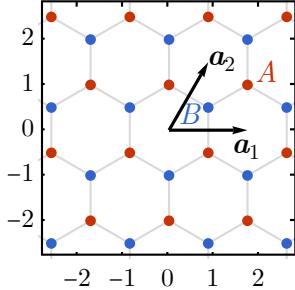
or in terms of a dot product

$$\boxed{S_m = \sum_s f_s e^{-2\pi i \mathbf{m} \cdot \mathbf{n}_s}.} \quad (116)$$

Examples:

- Honeycomb lattice (recall Eq. (26))

$$\begin{cases} \mathbf{a}_1 = (\sqrt{3}, 0) \\ \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, \frac{3}{2}\right) \end{cases}, \begin{cases} \mathbf{r}_A = (\sqrt{3}, 1) \\ \mathbf{r}_B = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \end{cases}. \quad (117)$$



- Rewrite \mathbf{r}_s to \mathbf{n}_s by Eq. (114),

$$\begin{cases} \mathbf{n}_A = \left(\frac{2}{3}, \frac{2}{3}\right) \\ \mathbf{n}_B = \left(\frac{1}{3}, \frac{1}{3}\right) \end{cases}. \quad (118)$$

- The structure factor is given by Eq. (116)

$$\begin{aligned} S_m &= f_A e^{-2\pi i 2(m_1+m_2)/3} + f_B e^{-2\pi i (m_1+m_2)/3} \\ &= f_A \varpi^{m_1+m_2} + f_B \varpi^{-(m_1+m_2)}. \end{aligned} \quad (119)$$

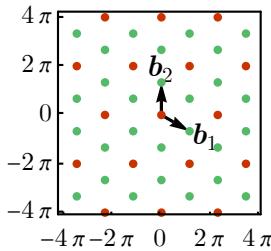
where $\varpi = e^{2\pi i/3}$ is the third root of unity.

- If $f_A = f_B = f$ (A, B sub-lattices are equivalent as in graphene)

$$S_m = \begin{cases} 2f & m_1 + m_2 \stackrel{\text{mod } 3}{=} 0 \\ -f & m_1 + m_2 \stackrel{\text{mod } 3}{=} 1, 2 \end{cases}. \quad (120)$$

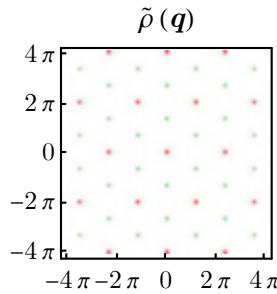
- The reciprocal lattice is given by $\mathbf{G}_m = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2$ with

$$\begin{cases} \mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}}, -\frac{2\pi}{3}\right) \\ \mathbf{b}_2 = \left(0, \frac{4\pi}{3}\right) \end{cases}. \quad (121)$$



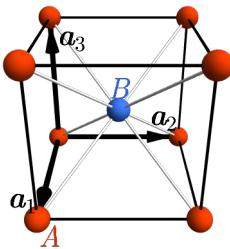
- red - $m_1 + m_2 \stackrel{\text{mod } 3}{=} 0 \Rightarrow S_m = 2f$,
- light green - $m_1 + m_2 \stackrel{\text{mod } 3}{=} 1, 2 \Rightarrow S_m = -f$.

Matching the numerical result of lattice Fourier transform.



- Cubic lattice (recall Eq. (28)) with both corner (A) and center (B) sites

$$\begin{cases} \mathbf{a}_1 = (1, 0, 0) \\ \mathbf{a}_2 = (0, 1, 0), \\ \mathbf{a}_3 = (0, 0, 1) \end{cases}, \quad \begin{cases} \mathbf{r}_A = (0, 0, 0) \\ \mathbf{r}_B = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \end{cases}. \quad (122)$$



- Rewrite \mathbf{r}_s to \mathbf{n}_s by Eq. (114),

$$\begin{cases} \mathbf{n}_A = (0, 0, 0) \\ \mathbf{n}_B = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \end{cases}. \quad (123)$$

- The structure factor is given by Eq. (116)

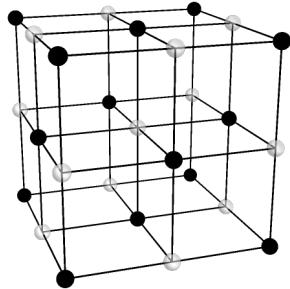
$$\begin{aligned} S_m &= f_A + f_B e^{-2\pi i (m_1 + m_2 + m_3)/2} \\ &= f_A + f_B (-1)^{m_1 + m_2 + m_3}. \end{aligned} \quad (124)$$

- If $f_A = f_B = f$ (A , B sub-lattices are equivalent as in body-centered cubic (BCC) lattice)

$$S_m = \begin{cases} 2f & m_1 + m_2 + m_3 \text{ is even} \\ 0 & m_1 + m_2 + m_3 \text{ is odd} \end{cases}. \quad (125)$$

- The reciprocal lattice is given by $\mathbf{G}_m = \sum_{i=1}^3 m_i \mathbf{b}_i$ with

$$\begin{cases} \mathbf{b}_1 = 2\pi(1, 0, 0) \\ \mathbf{b}_2 = 2\pi(0, 1, 0) \\ \mathbf{b}_3 = 2\pi(0, 0, 1) \end{cases}. \quad (126)$$



- Solid (black) - $m_1 + m_2 + m_3$ even $\Rightarrow S_m \neq 0$. They form a face-centered cubic (FCC) lattice, verifying the fact that the reciprocal lattice of BCC lattice is a FCC lattice (see (HW 4)).
- Transparent - $m_1 + m_2 + m_3$ odd $\Rightarrow S_m = 0$. These are called **extinction points** in the diffraction pattern, where the scattering wave is systematically absent.

- **Symmetry reason** for the *extinction* phenomenon

- When A , B sites are equivalent, the lattice symmetry is *enlarged*. For example, translation by the vector $\mathbf{r}_B = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ becomes a symmetry (which was not for a simple cubic lattice). This means

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{r}_B), \quad (127)$$

is a new property of the density distribution ρ .

- Under the symmetry action, the scattering amplitude $\tilde{\rho}(\mathbf{q})$ transforms as (according to Eq. (78))

$$\begin{aligned} \tilde{\rho}(\mathbf{q}) &= \int_{\mathbf{r}} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &\rightarrow \int_{\mathbf{r}} \rho(\mathbf{r} + \mathbf{r}_B) e^{-i\mathbf{q}\cdot(\mathbf{r} + \mathbf{r}_B)} \\ &= e^{-i\mathbf{q}\cdot\mathbf{r}_B} \int_{\mathbf{r}} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= e^{-i\mathbf{q}\cdot\mathbf{r}_B} \tilde{\rho}(\mathbf{q}). \end{aligned} \quad (128)$$

- Apply to the reciprocal lattice points

$$\begin{aligned} \tilde{\rho}(\mathbf{G}_m) &\rightarrow e^{-i\mathbf{G}_m \cdot \mathbf{r}_B} \tilde{\rho}(\mathbf{G}_m) \\ &= e^{-2\pi i \mathbf{m} \cdot \mathbf{n}_B} \tilde{\rho}(\mathbf{G}_m) \\ &= (-1)^{m_1+m_2+m_3} \tilde{\rho}(\mathbf{G}_m). \end{aligned} \quad (129)$$

Therefore, if $m_1 + m_2 + m_3$ is odd, Eq. (129) implies that $\tilde{\rho}(\mathbf{G}_m)$ will transform to $-\tilde{\rho}(\mathbf{G}_m)$. The only way to preserve $\tilde{\rho}(\mathbf{G}_m)$ under the symmetry transformation is to set $\tilde{\rho}(\mathbf{G}_m) = 0$, hence the extinction phenomenon.

■ Summary

- Relation between lattice and reciprocal lattice.

$$R_n = \sum_{i=1}^D n_i \, a_i \quad \xleftarrow[b_i \cdot a_j = 2\pi \delta_{ij}]{} \quad G_m = \sum_{i=1}^D m_i \, b_i$$

\downarrow sub-lattice

$$R_{n,s} = R_n + r_s$$

General lattice

- Volume of primitive unit cell

$$\Omega = |a_1 \cdot (a_2 \times a_3)|.$$

- Construct b_i from a_i

$$\mathbf{b}_i = \frac{2\pi}{\Omega} \frac{1}{2} \epsilon_{ijk} \mathbf{a}_j \times \mathbf{a}_k.$$

- Fourier transformation between atomic density distribution $\rho(\mathbf{r})$ and scattering amplitude $\tilde{\rho}(\mathbf{q})$

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{n}, s} f_s \delta(\mathbf{r} - \mathbf{R}_{\mathbf{n}, s}) \quad \frac{\tilde{\rho}(\mathbf{q}) = \int_{\mathbf{r}} \rho(\mathbf{r}) e^{-i \mathbf{q} \cdot \mathbf{r}}}{\rho(\mathbf{r}) = \frac{1}{(2\pi)^D} \int_{\mathbf{q}} \tilde{\rho}(\mathbf{q}) e^{i \mathbf{q} \cdot \mathbf{r}}} \quad \tilde{\rho}(\mathbf{q}) = \frac{(2\pi)^D}{V} \sum_{\mathbf{m}} S_{\mathbf{m}} \delta(\mathbf{q} - \mathbf{G}_{\mathbf{m}}) \\ (S_{\mathbf{m}} = \sum_s f_s e^{-i G_{\mathbf{m}} \cdot \mathbf{r}_s})$$

- $\tilde{\rho}(\mathbf{q})$ determines the scattering rate

$$\Gamma(\mathbf{k} \rightarrow \mathbf{k}') \propto |\tilde{\rho}(\mathbf{k}' - \mathbf{k})|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}).$$

- Diffraction spot location is determined by either the Laue condition or the Bragg condition (they are equivalent)

$$\begin{cases} \mathbf{k}' - \mathbf{k} = \mathbf{G}_m \\ |\mathbf{k}'| = |\mathbf{k}| \end{cases} \Leftrightarrow 2d \sin \theta = m\lambda.$$

- Diffraction spot intensity $|S_m|^2$ is determined by the structural factor

$$S_m = \sum_s f_s e^{-2\pi i m \cdot n_s}.$$

Diffraction spot can extinct when $S_m = 0$.

Phonon

■ Lattice Vibration

■ Hamiltonian of Atoms

The dynamics of a system of atoms is described by the Hamiltonian (kinetic energy + potential energy)

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \mathbf{r}_2, \dots), \quad (130)$$

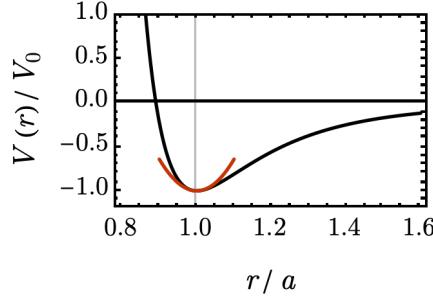
where

- \mathbf{p}_i - the *momentum* of the i th atom,
- \mathbf{r}_i - the *position* of the i th atom,
- m_i - the *mass* of the i th atom.

The total *potential energy* of atoms may be well modeled by pairwise inter-atomic interactions (recall Eq. (2))

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j), \quad (131)$$

where $V(r)$ generally takes the following shape (short-range repulsion + longer range attraction):



At *low energy* (low temperature), the atoms are expected to form a crystal (that minimizes the potential energy) and *oscillate* around their equilibrium positions (around the potential minimum). Suppose the oscillation *amplitude* is *small* (otherwise the crystal may melt), the inter-atomic potential energy can be approximated by its 2nd order expansion around the minimum

$$V(r) = V_0 + \frac{\kappa}{2} (r - a)^2 + \dots, \quad (132)$$

where $\kappa = \partial_r^2 V(r)_{r=a}$, as shown in the above figure as the red parabola.

■ Harmonic Approximation

This idea can be formulated more systematically:

- Let \mathbf{R}_i be the **equilibrium position** of the i th atom, and \mathbf{x}_i be the **displacement** of the i th atom from its equilibrium position, s.t.

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{x}_i. \quad (133)$$

- Assuming \mathbf{x}_i are small, expand the potential energy to the 2nd order of \mathbf{x}_i

$$\begin{aligned} V(\mathbf{r}_1, \mathbf{r}_2, \dots) &= V(\mathbf{R}_1 + \mathbf{x}_1, \mathbf{R}_2 + \mathbf{x}_2, \dots) \\ &= V(\mathbf{R}_1, \mathbf{R}_2, \dots) \end{aligned}$$

$$\begin{aligned}
& + \sum_i \mathbf{x}_i \cdot \nabla_{\mathbf{R}_i} V(\mathbf{R}_1, \mathbf{R}_2, \dots) \\
& + \frac{1}{2} \sum_{i,j} (\mathbf{x}_i \cdot \nabla_{\mathbf{R}_i}) (\mathbf{x}_j \cdot \nabla_{\mathbf{R}_j}) V(\mathbf{R}_1, \mathbf{R}_2, \dots) \\
& + \dots
\end{aligned}$$

where

- The 0th order term $V(\mathbf{R}_1, \mathbf{R}_2, \dots) = V_{\text{eq}}$ is a constant shift of energy, which can be dropped from the Hamiltonian without affecting dynamics.
- The 1st order term vanishes, because the gradient $\nabla_{\mathbf{R}_i} V = 0$ vanishes at equilibrium (by definition).
- The 2nd order term takes the form of

$$\frac{1}{2} \sum_{i,j} \mathbf{x}_i \cdot K_{ij} \cdot \mathbf{x}_j, \quad (135)$$

where K_{ij} is a matrix for every i, j , and is called the **elastic tensor**,

$$K_{ij} = \nabla_{\mathbf{R}_i} \nabla_{\mathbf{R}_j} V(\mathbf{R}_1, \mathbf{R}_2, \dots). \quad (136)$$

Thus the Hamiltonian in Eq. (130) can be approximated by

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j} \mathbf{x}_i \cdot K_{ij} \cdot \mathbf{x}_j.$$

(137)

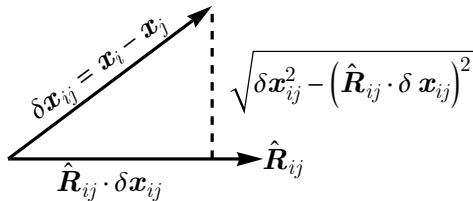
It describes a set of **coupled harmonic oscillators**, which models the lattice vibration.

- Apply to the pairwise interaction model Eq. (131), and assume the inter-atomic interaction $V(\mathbf{r}) = V(r)$ is *isotropic*, by Taylor expansion,

$$\frac{1}{2} \sum_{i,j} \mathbf{x}_i \cdot K_{ij} \cdot \mathbf{x}_j = \frac{1}{2} \sum_{i \neq j} \left(\kappa_{ij}^\perp (\mathbf{x}_i - \mathbf{x}_j)^2 + (\kappa_{ij}^\parallel - \kappa_{ij}^\perp) (\hat{\mathbf{R}}_{ij} \cdot (\mathbf{x}_i - \mathbf{x}_j))^2 \right), \quad (138)$$

where

- $\hat{\mathbf{R}}_{ij} = \mathbf{R}_{ij} / |\mathbf{R}_{ij}|$ is the unit vector along the bond displacement $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$,



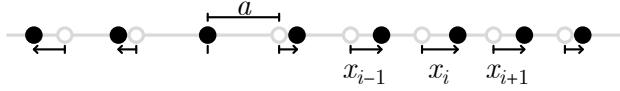
- κ_{ij}^\parallel and κ_{ij}^\perp are elastic constants along the parallel and perpendicular directions of the bond, which are defined by

$$\kappa_{ij}^{\parallel} = V''(R_{ij}), \quad \kappa_{ij}^{\perp} = \frac{V'(R_{ij})}{R_{ij}}. \quad (139)$$

Exc 7 | Derive Eq. (138).

■ Phonon Dispersion Relation

Consider an array of identical atoms forming a 1D lattice.



- White dots - equilibrium positions $R_i = i a$.
- Black dots - actual positions of atoms (the i th atom displaced by x_i).

The Hamiltonian in Eq. (137) reduces to (as $\hat{R}_{ij} = 1$ is trivial in 1D)

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \frac{\kappa}{2} (x_i - x_{i+1})^2. \quad (148)$$

or written as

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} K_{ij} x_i x_j, \quad (149)$$

with

$$K_{ij} = \kappa(2\delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1}). \quad (150)$$

- Equation of motion:

$$m \ddot{x}_i = - \sum_j K_{ij} x_j. \quad (151)$$

Exc 8 | Derive the equation of motion Eq. (151) from the Hamiltonian Eq. (148).

- Take the trial solution

$$x_i = u e^{-i\omega t + i q R_i}, \quad (154)$$

substitute into Eq. (151),

$$-m\omega^2 u e^{-i\omega t + i q R_i} = - \sum_j K_{ij} u e^{-i\omega t + i q R_j} \quad (155)$$

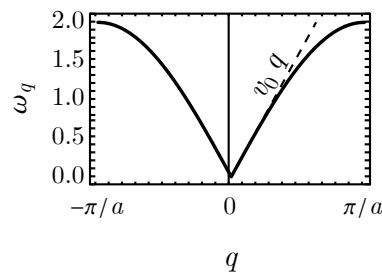
or

$$m\omega^2 = \sum_j K_{ij} e^{-i q (R_i - R_j)}$$

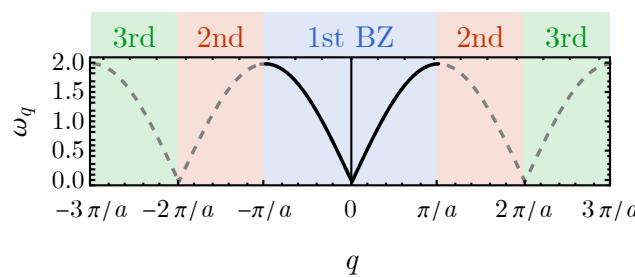
$$\begin{aligned}
&= \kappa \sum_j (2 \delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1}) e^{-i q a (i-j)} \\
&= \kappa (2 - e^{-i q a} - e^{+i q a}) \\
&= 2 \kappa (1 - \cos q a) \\
&= \kappa \left(2 \sin \frac{q a}{2} \right)^2.
\end{aligned}$$

Dispersion relation - the relationship between frequency (energy) and wavevector (momentum)

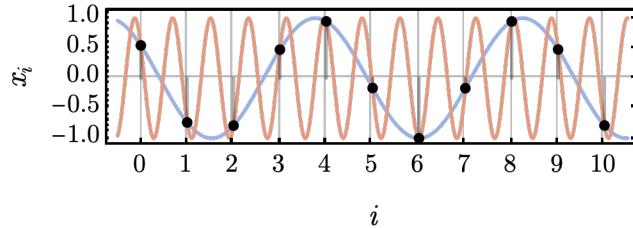
$$\omega_q = 2 \sqrt{\frac{\kappa}{m}} \left| \sin \frac{q a}{2} \right|. \quad (157)$$



- Each point on the dispersion relation corresponds to a **sound wave** mode (a normal mode of the 1D lattice vibration). The sound wave quantum is called a **phonon**. The dispersion relation indicates that a phonon excitation of **momentum** $\hbar q$ will carry **energy** $\hbar \omega_q$.
- It is sufficient to describe the dispersion relation within the **first Brillouin zone** $[-\pi/a, \pi/a]$.
 - Because $\omega_q = \omega_{q \pm (2\pi/a)}$ is *periodic* in the momentum space (with the same periodicity as the *reciprocal lattice*), the behavior of ω_q within the 1st BZ fully determines its behavior outside the 1st BZ.



- Because $q \pm (2\pi m/a)$ describe the same wave mode as q on the lattice (known as the **aliasing** of waves), there is no need to go beyond the 1st BZ.



Group velocity - how fast a wave packet propagates

$$v_q = \partial_q \omega_q = \frac{\text{sgn } q}{a} \sqrt{\frac{\kappa}{m}} \cos \frac{q a}{2}. \quad (158)$$

- *Low-frequency limit* (BZ center): linear dispersion $\omega_q = v_0 |q| \Rightarrow$ constant speed of sound

$$v_0 = \sqrt{\frac{\kappa}{m}}. \quad (159)$$

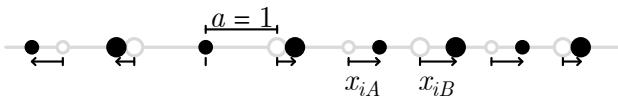
- *High-frequency limit* (BZ boundary):

- Group velocity vanishes at BZ boundary $q = \pm\pi/a$.
- **Inversion symmetry** requires $\omega_q = \omega_{-q}$ to be even in q , so its first order derivative $v_q = \partial_q \omega_q$ must be odd in q , i.e. $v_q = -v_{-q}$. Further consider the periodicity $v_q = v_{q-(2\pi/a)}$, we have $v_{q-(2\pi/a)} = -v_{-q}$. Set $q = \pi/a$ at the BZ boundary, this implies $v_{-(\pi/a)} = -v_{(\pi/a)}$, thus $v_{-(\pi/a)} = 0$ (if v_q is smooth at the BZ boundary). Similar argument applies to $v_{(\pi/a)} = 0$.
- **Bragg reflection**: $q = \pm\pi/a$ are related by a lattice momentum $G = (2\pi)/a$, strongly scattered to each other by the lattice \Rightarrow standing wave mode (equal-weight superposition of left- and right-moving modes):

$$e^{i(\pi/a)R_i} + e^{-i(\pi/a)R_i} \propto (-)^i. \quad (160)$$

■ Acoustic and Optical Modes

Consider the lattice vibration of 1D diatomic chain, where two types of atoms of different masses (m_A and m_B) are arranged alternatively on a 1D lattice.



Equilibrium positions

$$\begin{aligned} R_{iA} &= 2i, \\ R_{iB} &= 2i + 1. \end{aligned} \quad (161)$$

Hamiltonian (based on Eq. (137))

$$H = \sum_i \left(\frac{p_{iA}^2}{2m_A} + \frac{p_{iB}^2}{2m_B} \right) + \frac{\kappa}{2} \sum_i ((x_{iA} - x_{iB})^2 + (x_{iB} - x_{(i+1)A})^2). \quad (162)$$

- Introduce the following vectors in each unit cell (taking A, B as basis)

$$p_i = \begin{pmatrix} p_{iA} \\ p_{iB} \end{pmatrix}, \quad x_i = \begin{pmatrix} x_{iA} \\ x_{iB} \end{pmatrix}. \quad (163)$$

- The Hamiltonian Eq. (162) can be generally written as

$$H = \frac{1}{2} \sum_{i,j} \left(p_i^\top (M^{-1})_{ij} p_j + x_i^\top K_{ij} x_j \right), \quad (164)$$

where M and K matrices are

$$\begin{aligned} (M^{-1})_{ij} &= \begin{pmatrix} m_A^{-1} \delta_{ij} & 0 \\ 0 & m_B^{-1} \delta_{ij} \end{pmatrix}, \\ K_{ij} &= \kappa \begin{pmatrix} 2 \delta_{ij} & -\delta_{ij} - \delta_{i,j+1} \\ -\delta_{ij} - \delta_{i,j-1} & 2 \delta_{ij} \end{pmatrix}. \end{aligned} \quad (165)$$

Equation of motion

$$\sum_j M_{ij} \ddot{x}_j = - \sum_j K_{ij} x_j. \quad (166)$$

- Take the trial solution (labeled by q)

$$x_i = \begin{pmatrix} x_{iA} \\ x_{iB} \end{pmatrix} = e^{-i\omega t} \begin{pmatrix} u_A e^{i q R_{iA}} \\ u_B e^{i q R_{iB}} \end{pmatrix}, \quad (167)$$

substitute into Eq. (166),

$$\omega^2 \begin{pmatrix} m_A & 0 \\ 0 & m_B \end{pmatrix} \begin{pmatrix} u_A \\ u_B \end{pmatrix} = 2 \kappa \begin{pmatrix} 1 & -\cos q \\ -\cos q & 1 \end{pmatrix} \begin{pmatrix} u_A \\ u_B \end{pmatrix} \quad (168)$$

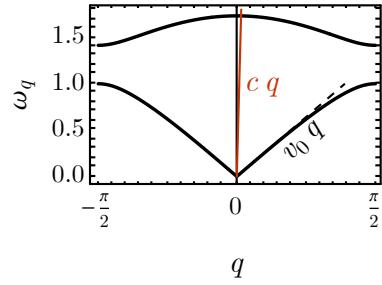
Exc 9

Derive Eq. (168).

Dispersion relation: solving the (generalized) eigen problem [2] of Eq. (168), two *branches* of solutions are found

$$\omega_{q,\pm} = \sqrt{\frac{\kappa}{m_A m_B}} \left(m_A + m_B \pm \sqrt{m_A^2 + m_B^2 + 2 m_A m_B \cos(2q)} \right)^{1/2} \quad (173)$$

For $\kappa = 1$, $m_A = 1$, $m_B = 2$:



- **Acoustic phonon:** the *lower* branch $\omega_{q,-}$ phonon modes (sound waves).
Definition: the branch that exhibits a *linear* dispersion as $q \rightarrow 0$ ($\omega_{q \rightarrow 0}$ is vanishing).

$$\omega_{q \rightarrow 0, -} = v_0 |q|,$$

$$v_0 = \sqrt{\frac{2 \kappa}{m_A + m_B}}. \quad (174)$$

- **Optical phonon:** the upper branch $\omega_{q,+}$ phonon modes (sound waves).
Definition: the branch that maintains a finite frequency ($\omega_{q \rightarrow 0}$ is non-vanishing), such that the mode can possibly couple to *light* (photon). Because the speed of light c is much larger than the speed of sound v_0 , such that the photon can transfer its energy-momentum to phonon only in the optical branch (hence the name “optical”).
- There is a **spectral gap** between the two branches of sound waves.

Mode wave functions - take the eigen vector $(u_A, u_B)^T$ at a given momentum q on a given branch, reconstruct

$$x_{iA} = u_A e^{-i \omega_{q,\pm} t + i q R_{iA}}, \quad x_{iB} = u_B e^{-i \omega_{q,\pm} t + i q R_{iB}} \quad (175)$$

- *Acoustic mode at $q = 0$ (BZ center),*

eigen value : $\omega_{0,-} = 0$,

$$\text{eigen vector : } \begin{pmatrix} u_A \\ u_B \end{pmatrix} \propto \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad (176)$$

meaning that

$$x_{iA} = x_{iB} = u, \quad (177)$$

which corresponds to a mode that translates all atoms uniformly (the long-wave length limit of sound wave).

- *Acoustic mode at $q = \pi/2$ (BZ boundary), (assuming $m_A < m_B$)*

$$\text{eigen value : } \omega_{\pi/2,-} = \sqrt{\frac{2 \kappa}{m_B}}, \quad (178)$$

$$\text{eigen vector : } \begin{pmatrix} u_A \\ u_B \end{pmatrix} \propto \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

meaning that only B atoms oscillate

$$x_{iA} = 0, \quad x_{iB} = u e^{-i \omega_{\pi/2,-} t + i \frac{\pi}{2}} R_{iB}. \quad (179)$$



- *Optical mode at $q = \pi/2$ (BZ boundary), (assuming $m_A < m_B$)*

$$\text{eigen value : } \omega_{\pi/2,+} = \sqrt{\frac{2 \kappa}{m_A}}, \quad (180)$$

$$\text{eigen vector : } \begin{pmatrix} u_A \\ u_B \end{pmatrix} \propto \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$

meaning that only A atoms oscillate

$$x_{iA} = u e^{-i \omega_{\pi/2,+} t + i \frac{\pi}{2}} R_{iA}, \quad x_{iB} = 0. \quad (181)$$



- At the BZ boundary, the oscillation mode transfers from B site (heavy atom, slower) to A site (light atom, faster), leading to a *jump* in the oscillation frequency \Rightarrow explains the spectral gap.

- *Optical mode at $q = 0$ (BZ center),*

$$\text{eigen value : } \omega_{0,+} = \sqrt{2 \kappa \left(\frac{1}{m_A} + \frac{1}{m_B} \right)}, \quad (182)$$

$$\text{eigen vector : } \begin{pmatrix} u_A \\ u_B \end{pmatrix} \propto \begin{pmatrix} m_B \\ -m_A \end{pmatrix},$$

meaning that

$$x_{iA} = m_B u e^{-i \omega_{0,+} t}, \quad x_{iB} = -m_A u e^{-i \omega_{0,+} t}. \quad (183)$$



[2] Eigendecomposition of a matrix. Wikipedia.

**HW
5**

Consider a diatomic chain where the atom masses m are the same, but the bond elastic constants are alternating between κ_1 and κ_2 , as described by

$$H = \frac{1}{2m} \sum_i (p_{iA}^2 + p_{iB}^2) + \frac{1}{2} \sum_i (\kappa_1 (x_{iA} - x_{iB})^2 + \kappa_2 (x_{iB} - x_{(i+1)A})^2).$$

(i) Find the phonon dispersion relation.

(ii) Determine the sound velocity as $q \rightarrow 0$ for acoustic phonons.

■ Longitudinal and Transverse Modes

Generalize to higher dimension. Consider identical atoms forming a 3D cubic lattice. Equilibrium positions are given by

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3,$$

$$\begin{cases} \mathbf{a}_1 = (1, 0, 0) \\ \mathbf{a}_2 = (0, 1, 0) \\ \mathbf{a}_3 = (0, 0, 1) \end{cases} \quad (184)$$

Take the pairwise interaction model Eq. (138) on nearest neighboring bonds, the Hamiltonian reads

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{\langle ij \rangle} \left(\kappa_{\perp} (\mathbf{x}_i - \mathbf{x}_j)^2 + (\kappa_{\parallel} - \kappa_{\perp}) (\hat{\mathbf{R}}_{ij} \cdot (\mathbf{x}_i - \mathbf{x}_j))^2 \right). \quad (185)$$

- A lattice site is labeled by the index i (or j), which is equivalent to the integer vector $\mathbf{n} \in \mathbb{Z}^3$.
- $\langle ij \rangle$ denotes that (i, j) are across the nearest neighboring bond on the cubic lattice.
- κ_{\parallel} - parallel elastic constants of the bond (Young's modulus),
 κ_{\perp} - perpendicular elastic constants of the bond (shear modulus),
such that suppose the bond $\hat{\mathbf{R}}_{ij}$ is along x -direction, the bond potential energy is given by

$$\frac{1}{2} (\mathbf{x}_i - \mathbf{x}_j) \cdot \begin{pmatrix} \kappa_{\parallel} & & \\ & \kappa_{\perp} & \\ & & \kappa_{\perp} \end{pmatrix} \cdot (\mathbf{x}_i - \mathbf{x}_j), \quad (186)$$

similar for y - and z -directions (by cyclic permuting the diagonal).

Rewrite the Hamiltonian in the general form of Eq. (137),

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \mathbf{x}_i \cdot K_{ij} \cdot \mathbf{x}_j, \quad (187)$$

The elastic tensor K_{ij} reads

$$K_{ij} = K_0 \delta_{\mathbf{R}_i, \mathbf{R}_j} - \sum_{l=1,2,3} K_l (\delta_{\mathbf{R}_i, \mathbf{R}_j + \mathbf{a}_l} + \delta_{\mathbf{R}_i, \mathbf{R}_j - \mathbf{a}_l}),$$

$$K_0 = 2(\kappa_{\parallel} + 2\kappa_{\perp}) \mathbf{1},$$

$$K_l = \kappa_{\perp} \mathbf{1} + (\kappa_{\parallel} - \kappa_{\perp}) \mathbf{a}_l \otimes \mathbf{a}_l,$$
(188)

where $\mathbf{1}$ stands for 3×3 identity matrix, and $\mathbf{a}_l \otimes \mathbf{a}_l$ is the tensor product of \mathbf{a}_l (spanning the vector to a matrix). More explicitly

$$K_0 = 2(\kappa_{\parallel} + 2\kappa_{\perp}) \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix},$$

$$K_1 = \begin{pmatrix} \kappa_{\parallel} & & \\ & \kappa_{\perp} & \\ & & \kappa_{\perp} \end{pmatrix},$$

$$K_2 = \begin{pmatrix} \kappa_{\perp} & & \\ & \kappa_{\parallel} & \\ & & \kappa_{\perp} \end{pmatrix},$$

$$K_3 = \begin{pmatrix} \kappa_{\perp} & & \\ & \kappa_{\perp} & \\ & & \kappa_{\parallel} \end{pmatrix}.$$

Exc 10 | Derive Eq. (188) from Eq. (185).

- Equation of motion:

$$m \ddot{\mathbf{x}}_i = - \sum_j K_{ij} \cdot \mathbf{x}_j. \quad (195)$$

- Take the trial solution

$$\mathbf{x}_i = \mathbf{u} e^{-i \omega t + i \mathbf{q} \cdot \mathbf{R}_i}, \quad (196)$$

substitute into Eq. (195),

$$\begin{aligned} m \omega^2 \mathbf{u} &= \sum_j K_{ij} \cdot \mathbf{u} e^{-i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \\ &= \sum_j \left(K_0 \delta_{\mathbf{R}_i, \mathbf{R}_j} - \sum_{l=1,2,3} K_l (\delta_{\mathbf{R}_i, \mathbf{R}_j + \mathbf{a}_l} + \delta_{\mathbf{R}_i, \mathbf{R}_j - \mathbf{a}_l}) \right) \cdot \mathbf{u} e^{-i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \\ &= \left(K_0 - \sum_{l=1,2,3} K_l (e^{-i \mathbf{q} \cdot \mathbf{a}_l} + e^{i \mathbf{q} \cdot \mathbf{a}_l}) \right) \cdot \mathbf{u} \\ &= \left(K_0 - \sum_{l=1,2,3} 2 K_l \cos(\mathbf{q} \cdot \mathbf{a}_l) \right) \cdot \mathbf{u} \\ &= K(\mathbf{q}) \cdot \mathbf{u}, \end{aligned} \quad (197)$$

given K_0 and K_l matrices in Eq. (189),

$$K(\mathbf{q}) = \begin{pmatrix} K_x(\mathbf{q}) & & \\ & K_y(\mathbf{q}) & \\ & & K_z(\mathbf{q}) \end{pmatrix},$$

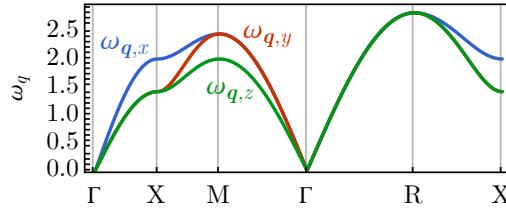
$$\begin{aligned} K_x(\mathbf{q}) &= \kappa_{\parallel} \left(2 \sin \frac{q_x}{2} \right)^2 + \kappa_{\perp} \left(2 \sin \frac{q_y}{2} \right)^2 + \kappa_{\perp} \left(2 \sin \frac{q_z}{2} \right)^2, \\ K_y(\mathbf{q}) &= \kappa_{\perp} \left(2 \sin \frac{q_x}{2} \right)^2 + \kappa_{\parallel} \left(2 \sin \frac{q_y}{2} \right)^2 + \kappa_{\perp} \left(2 \sin \frac{q_z}{2} \right)^2, \\ K_z(\mathbf{q}) &= \kappa_{\perp} \left(2 \sin \frac{q_x}{2} \right)^2 + \kappa_{\perp} \left(2 \sin \frac{q_y}{2} \right)^2 + \kappa_{\parallel} \left(2 \sin \frac{q_z}{2} \right)^2, \end{aligned} \quad (198)$$

Dispersion relation: The eigen equation $m \omega^2 \mathbf{u} = K(\mathbf{q}) \cdot \mathbf{u}$ in Eq. (197) has *three* eigen modes:

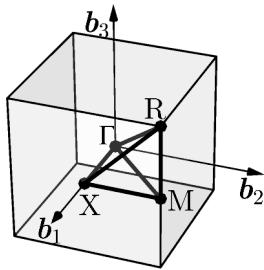
$$\begin{aligned}\alpha &= x \quad y \quad z \\ \mathbf{u}_\alpha &= (1, 0, 0) \quad (0, 1, 0) \quad (0, 0, 1) \\ \omega_{q,\alpha} &= \sqrt{\frac{K_x(\mathbf{q})}{m}} \quad \sqrt{\frac{K_y(\mathbf{q})}{m}} \quad \sqrt{\frac{K_z(\mathbf{q})}{m}}\end{aligned}$$

- α labels the **polarization** of the phonon modes (sound waves) in the 3D solid.

- Dispersion relation



plotted along high symmetry lines in the cubic lattice Brillouin zone



- **Longitudinal phonon:** polarization parallel to momentum ($\mathbf{u} \parallel \mathbf{q}$)
- **Transverse phonon:** polarization perpendicular to momentum ($\mathbf{u} \perp \mathbf{q}$)
- Phonon modes along Γ -X, i.e. $\mathbf{q} = q(1, 0, 0)$,
- Longitudinal mode (one branch)

$$\omega_{q,x} = 2 \sqrt{\frac{\kappa_{||}}{m}} \left| \sin \frac{q}{2} \right| \xrightarrow{q \rightarrow 0} v_L |q|. \quad (200)$$

Longitudinal speed of sound

$$v_L = \sqrt{\frac{\kappa_{||}}{m}}. \quad (201)$$

- Transverse mode (two branches)

$$\omega_{q,y} = \omega_{q,z} = 2 \sqrt{\frac{\kappa_{\perp}}{m}} \left| \sin \frac{q}{2} \right| \xrightarrow{q \rightarrow 0} v_T |q|. \quad (202)$$

Transverse speed of sound

$$v_T = \sqrt{\frac{\kappa_{\perp}}{m}}. \quad (203)$$

- Phonon modes along Γ -M, i.e. $\mathbf{q} = q(1, 1, 0) / \sqrt{2}$,
- Longitudinal mode (one branch)

$$\omega_{q,x+y} = 2 \sqrt{\frac{\kappa_{\parallel} + \kappa_{\perp}}{2m}} \left| \sin \frac{q}{2} \right| \xrightarrow{q \rightarrow 0} v_L |q|. \quad (204)$$

Longitudinal speed of sound

$$v_L = \sqrt{\frac{\kappa_{\parallel} + \kappa_{\perp}}{2m}}. \quad (205)$$

- Transverse mode (two branches)

$$\begin{aligned} \omega_{q,x-y} &= 2 \sqrt{\frac{\kappa_{\parallel} + \kappa_{\perp}}{2m}} \left| \sin \frac{q}{2} \right| \xrightarrow{q \rightarrow 0} v_{T1} |q|, \\ \omega_{q,z} &= 2 \sqrt{\frac{\kappa_{\perp}}{m}} \left| \sin \frac{q}{2} \right| \xrightarrow{q \rightarrow 0} v_{T2} |q|. \end{aligned} \quad (206)$$

Transverse speed of sound

$$\begin{aligned} v_{T1} &= \sqrt{\frac{\kappa_{\parallel} + \kappa_{\perp}}{2m}}, \\ v_{T2} &= \sqrt{\frac{\kappa_{\perp}}{m}}. \end{aligned} \quad (207)$$

- The degeneracy between v_L and v_{T1} is accidental. Including further neighboring bonds in the model will lift this degeneracy.

■ Specific Heat of Solid

■ Boltzmann Model

Specific heat (molar heat capacity): the rate that the average energy (per atom) increases with the raise of temperature.

$$c_V = \frac{\partial \langle \epsilon \rangle}{\partial T}. \quad (208)$$

- Specific heat often varies with temperature. Its temperature dependence reflects how energy is stored as excitations in the material.

How energy is stored in solid?

Boltzmann model: each atom in the solid sits in a harmonic well formed by the interaction with neighboring atoms.

- Energy of a harmonic oscillator

$$\epsilon(\mathbf{x}, \mathbf{p}) = \frac{1}{2m} \mathbf{p}^2 + \frac{\kappa}{2} \mathbf{x}^2. \quad (209)$$

- The oscillation frequency is $\omega = \sqrt{\kappa/m}$.
- Probability for the oscillator to be at the state (\mathbf{x}, \mathbf{p}) is

$$p(\mathbf{x}, \mathbf{p}) = \frac{1}{Z} e^{-\beta \epsilon(\mathbf{x}, \mathbf{p})}, \quad (210)$$

where Z is the partition function (classical, canonical ensemble)

$$\begin{aligned} Z &= \int d^D \mathbf{p} d^D \mathbf{x} e^{-\beta \epsilon(\mathbf{x}, \mathbf{p})} \\ &= \left(\frac{2\pi m}{\beta} \right)^{D/2} \left(\frac{2\pi}{\beta \kappa} \right)^{D/2} \\ &= \left(\frac{2\pi}{\beta \omega} \right)^D. \end{aligned} \quad (211)$$

- $\beta = 1/(k_B T)$: k_B - Boltzmann constant, T - temperature.
- D - dimension of space.
- Average energy

$$\begin{aligned} \langle \epsilon \rangle &= \int d^D \mathbf{p} d^D \mathbf{x} \epsilon(\mathbf{x}, \mathbf{p}) p(\mathbf{x}, \mathbf{p}) \\ &= -\partial_\beta \ln Z \\ &= D k_B T. \end{aligned} \quad (212)$$

- Specific heat

$$c_V = \frac{\partial \langle \epsilon \rangle}{\partial T} = D k_B. \quad (213)$$

For 3D materials ($D = 3$),

$$c_V = 3 k_B, \quad (214)$$

which is known as the **Dulong-Petit law**. Specific heats of some solids at room temperature and pressure:

Material	c_V / k_B
Gold (Au)	3.05
Antimony (Sb)	3.03
Zinc (Zn)	3.02
Iron (Fe)	3.02
Silver (Ag)	2.99

Lithium (Li)	2.98
Copper (Cu)	2.94
Aluminum (Al)	2.91
Diamond (C)	0.735 (why?)

The Dulong-Petit law works well for many crystalline materials above some characteristic temperature T_Θ around 200~500K. Below this temperature scale T_Θ , it fails dramatically (for diamond, room temperature is already below its T_Θ). The specific heat is found to decrease with temperature rapidly towards zero as $T \rightarrow 0$.

■ Einstein Model

Einstein realized that *quantum* mechanics is important to understand the *low-temperature* behavior of specific heat.

- Energy is quantized in quantum mechanics. For D -dimensional harmonic oscillator, its eigen energies (energy levels) are labeled by $\mathbf{n} \in \mathbb{N}^D$,

$$\epsilon_{\mathbf{n}} = \hbar \omega \sum_{i=1}^D \left(n_i + \frac{1}{2} \right). \quad (215)$$

- ω - oscillator frequency,
- \hbar - Planck constant.
- Probability to find the oscillator in the $\epsilon_{\mathbf{n}}$ energy level

$$p_{\mathbf{n}} = \frac{1}{Z} e^{-\beta \epsilon_{\mathbf{n}}}, \quad (216)$$

where Z is the partition function (quantum, canonical ensemble)

$$\begin{aligned} Z &= \sum_{\mathbf{n} \in \mathbb{N}^D} e^{-\beta \epsilon_{\mathbf{n}}} \\ &= (2 \sinh(\beta \hbar \omega / 2))^{-D}. \end{aligned} \quad (217)$$

**Exc
11**

Evaluate the partition function in Eq. (217).

- Average energy

$$\begin{aligned} \langle \epsilon \rangle &= \sum_{\mathbf{n} \in \mathbb{N}^D} \epsilon_{\mathbf{n}} p_{\mathbf{n}} \\ &= -\partial_{\beta} \ln Z \\ &= \frac{D \hbar \omega}{2} \coth\left(\frac{\beta \hbar \omega}{2}\right) \\ &= D \hbar \omega \left(n_B(\beta \hbar \omega) + \frac{1}{2} \right), \end{aligned} \quad (219)$$

- n_B is the **Bose-Einstein distribution** function

$$n_B(\beta \hbar \omega) = \frac{1}{e^{\beta \hbar \omega} - 1}, \quad (220)$$

describing the average number of bosons occupying the mode of energy $\hbar \omega$.

- Specific heat

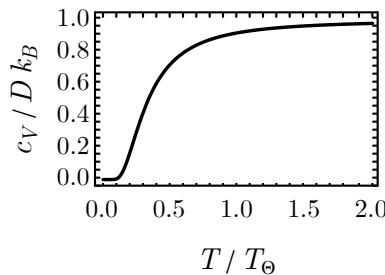
$$\begin{aligned} c_V &= \frac{\partial \langle \epsilon \rangle}{\partial T} \\ &= D k_B \left(\left(\frac{\beta \hbar \omega}{2} \right) \operatorname{csch} \left(\frac{\beta \hbar \omega}{2} \right) \right)^2. \end{aligned} \quad (221)$$

- Define a temperature scale (the **Einstein temperature**)

$$T_\Theta = \frac{\hbar \omega}{k_B}, \quad (222)$$

Eq. (221) can be written as

$$c_V = D k_B \left(\left(\frac{T_\Theta}{2T} \right) \operatorname{csch} \left(\frac{T_\Theta}{2T} \right) \right)^2. \quad (223)$$



- In the high-temperature limit ($T \gg T_\Theta$), the Dulong-Petit law $c_V = D k_B$ is recovered.
- However, at low-temperature ($T \ll T_\Theta$), the degrees of freedom “freeze out”. The energy level is discrete in quantum mechanics, when the temperature is too low compared to the excitation energy (the level spacing), the system will stuck in the ground state and can not absorb/release energy, hence no contribution to the specific heat.

■ Debye Model

The Einstein model takes into account the quantum effect. However, treating atoms in the solid as independent harmonic oscillators is a rather crude assumption. Debye further takes into account the fact that what really absorb/release energy in the solid are the *collective excitations* of atoms, i.e. *phonons* (sound waves).

- Phonon can have *different* frequencies, as described by the dispersion relation $\omega_{q,a}$, which depends on:
 - \mathbf{q} - phonon momentum,

- α - phonon band index (including acoustic/optical branches, and different polarizations).
- Following Eq. (221), the specific heat should also average over all phonon modes

$$c_V = \frac{k_B}{N} \sum_{\alpha} \sum_{q \in \text{BZ}} \left(\left(\frac{\beta \hbar \omega_{q,\alpha}}{2} \right) \operatorname{csch} \left(\frac{\beta \hbar \omega_{q,\alpha}}{2} \right) \right)^2. \quad (224)$$

- N - number of atoms, which is also the number of phonon modes (per polarization).
- At low-temperature, focus on *acoustic* phonons, its dispersion can be modeled by

$$\omega_q = v |\mathbf{q}|, \quad (225)$$

where v is the speed of sound.

- Here the dispersion is assumed to be *isotropic*, ignoring the velocity difference between longitudinal and transverse phonons.
- The frequency is bounded as \mathbf{q} varies in the Brillouin zone. So there must be some maximal frequency ω_{\max} (to be specified later).
- Under the isotropic assumption, the momentum summation can be written as integration

$$\begin{aligned} \frac{1}{N} \sum_{\alpha} \sum_{q \in \text{BZ}} &= \frac{D}{N} \left(\frac{L}{2\pi} \right)^D \int d^D q \\ &= \frac{D \Omega}{(2\pi)^D} \int A_D q^{D-1} dq \\ &= \int \frac{D A_D \Omega}{(2\pi v)^D} \omega_q^{D-1} d\omega_q \\ &= \int d\omega_q g(\omega_q) \end{aligned} \quad (226)$$

- D - space dimension (also the number of polarizations $\alpha = 1, \dots, D$)
- L - linear size of the system, which determined the momentum discretization unit ($2\pi/L$).
- Ω - volume of unit cell.
- $A_D = 2\pi^{D/2} / \Gamma\left(\frac{D}{2}\right)$ - area of a $(D-1)$ -dimensional unit sphere (in the D -dimensional space).
- Define the phonon **density of state**

$$g(\omega) = \frac{D A_D \Omega}{(2\pi v)^D} \omega^{D-1} = \frac{D^2 \omega^{D-1}}{\omega_{\Theta}^D}, \quad (227)$$

where the **Debye frequency** ω_{Θ} is introduced as a frequency scale

$$\omega_{\Theta}^D = \frac{D (2\pi v)^D}{A_D \Omega}, \quad (228)$$

or more explicitly

$$\omega_\Theta = \begin{cases} \frac{\pi}{\Omega} v & D = 1 \\ \left(\frac{4\pi}{\Omega}\right)^{1/2} v & D = 2 \\ \left(\frac{6\pi^2}{\Omega}\right)^{1/3} v & D = 3 \\ \dots & \dots \end{cases} \quad (229)$$

- The maximal frequency ω_{\max} must be such that the density of state integrates to the number of polarization modes

$$D = \int_0^{\omega_{\max}} d\omega g(\omega) = D \left(\frac{\omega_{\max}}{\omega_\Theta} \right)^D, \quad (230)$$

so it turns out that the Debye frequency is also the maximal frequency $\omega_{\max} = \omega_\Theta$.

- The specific heat Eq. (224) can then be evaluated as

$$c_V = k_B \int_0^{\omega_\Theta} d\omega g(\omega) \left(\left(\frac{\beta \hbar \omega}{2} \right) \operatorname{csch} \left(\frac{\beta \hbar \omega}{2} \right) \right)^2, \quad (231)$$

which can be organized as

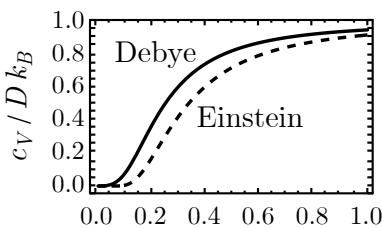
$$c_V = D k_B \left(\frac{T}{T_\Theta} \right)^D Y \left(\frac{T_\Theta}{T} \right),$$

$$Y \left(\frac{T_\Theta}{T} \right) = D \int_0^{T_\Theta/T} dx x^{D-1} \left(\frac{x}{2} \operatorname{csch} \left(\frac{x}{2} \right) \right)^2.$$

(232)

- T_Θ - **Debye temperature**, define as

$$T_\Theta = \frac{\hbar \omega_\Theta}{k_B}. \quad (233)$$



T / T_Θ

- Low-temperature limit $T \ll T_\Theta$,
- The specific heat Eq. (232) reads

$$\begin{aligned} c_V &= D k_B \left(\frac{T}{T_\Theta} \right)^D Y(\infty) \\ &= k_B \left(\frac{T}{T_\Theta} \right)^D D^2 \Gamma(D+2) \text{Li}(D+1, 1) \end{aligned} \quad (234)$$

or more explicitly

$$c_V = k_B \begin{cases} \left(\frac{T}{T_\Theta} \right) \frac{\pi^2}{3} & D = 1 \\ \left(\frac{T}{T_\Theta} \right)^2 24 \zeta(3) & D = 2 \\ \left(\frac{T}{T_\Theta} \right)^3 \frac{12\pi^4}{5} & D = 3 \\ \dots & \dots \end{cases}. \quad (235)$$

- In conclusion, the low-temperature specific heat from the acoustic phonon contribution scales with temperature as

$$c_V \sim T^D,$$

which is $c_V \sim T^3$ for $D = 3$.

**HW
6**

Suppose the dispersion of phonon is modified to $\omega_q \sim |\mathbf{q}|^z$ with some $z > 0$ in D -dimensional space, determine the power-law exponent α that the specific heat $c_V \sim T^\alpha$ scales with temperature T in the low-temperature limit (as $T \rightarrow 0$).

■ Stability of Crystal Order

■ Boltzmann Model

How much does an atom fluctuates around its equilibrium position in the solid?

Boltzmann model: each atom in the solid sits in a harmonic well formed by the interaction with neighboring atoms.

- Energy of a harmonic oscillator

$$\epsilon(\mathbf{x}, \mathbf{p}) = \frac{1}{2m} \mathbf{p}^2 + \frac{\kappa}{2} \mathbf{x}^2. \quad (237)$$

- Probability for the oscillator to be at the state (\mathbf{x}, \mathbf{p}) is

$$p(\mathbf{x}, \mathbf{p}) = \frac{1}{Z} e^{-\beta \epsilon(\mathbf{x}, \mathbf{p})}, \quad (238)$$

where Z is the partition function

$$\begin{aligned} Z &= \int d^D p d^D x e^{-\beta \epsilon(x, p)} \\ &= \left(\frac{2 \pi m}{\beta} \right)^{D/2} \left(\frac{2 \pi}{\beta \kappa} \right)^{D/2}. \end{aligned} \quad (239)$$

- $\beta = k_B T$: k_B - Boltzmann constant, T - temperature.
- D - dimension of space.
- Variance of displacement

$$\begin{aligned} \langle x^2 \rangle &= \int d^D p d^D x x^2 p(x, p) \\ &= -\frac{2}{\beta} \partial_\kappa \ln Z \\ &= \frac{D k_B T}{\kappa}. \end{aligned} \quad (240)$$

- The result is consistent with the **equal partition theorem**, that the average energy stored in each quadratic term of the Hamiltonian is $\frac{1}{2} k_B T$. Thus, for harmonic oscillator the average potential energy should be

$$\left\langle \frac{1}{2} \kappa x^2 \right\rangle = \frac{D}{2} k_B T \quad (241)$$

- Strictly speaking, the variance should be given by $\langle x^2 \rangle - \langle x \rangle^2$, but the first moment $\langle x \rangle = 0$ vanishes due to the inversion symmetry $\epsilon(x, p) = \epsilon(-x, p)$ of the harmonic oscillator.
- **Melting condition:** If the displacement variance exceeds the squared atomic spacing a^2 of the lattice, the solid will melt.

$$\langle x^2 \rangle = \frac{D k_B T}{\kappa} > a^2 \Rightarrow T > \frac{\kappa a^2}{D k_B} = T_*. \quad (242)$$

- The melting temperature T_* is consistent with the rough estimate in Eq. (14) $T_* = E_{\text{bind}} / (N k_B)$, as $E_{\text{bind}} \sim N \kappa a^2$.
- However, this estimation did not takes into account the quantum effect and the collective nature of phonon excitations, and is wrong in low dimensions.

■ Einstein Model

The Einstein model includes the quantum effect of the harmonic oscillator.

- Eigen energies of a D -dimensional harmonic oscillator (labeled by $\mathbf{n} \in \mathbb{N}^D$)

$$\epsilon_n = \hbar \omega \sum_{i=1}^D \left(n_i + \frac{1}{2} \right). \quad (243)$$

- $\omega = \sqrt{\kappa/m}$ - oscillator frequency.

- \hbar - Planck constant.
- Probability to find the oscillator in the ϵ_n energy level

$$p_n = \frac{1}{Z} e^{-\beta \epsilon_n}, \quad (244)$$

where Z is the partition function (quantum, canonical ensemble)

$$\begin{aligned} Z &= \sum_{n \in \mathbb{N}^D} e^{-\beta \epsilon_n} \\ &= (2 \sinh(\beta \hbar \omega / 2))^{-D}. \end{aligned} \quad (245)$$

- Variance of displacement on a particular eigenstate $|n\rangle$

$$\langle n | x^2 | n \rangle = 2 \partial_\kappa \epsilon_n. \quad (246)$$

Variance of displacement in the thermal ensemble

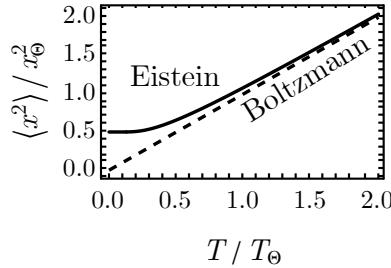
$$\begin{aligned} \langle x^2 \rangle &= \sum_{n \in \mathbb{N}^D} \langle n | x^2 | n \rangle p_n \\ &= \sum_{n \in \mathbb{N}^D} 2 (\partial_\kappa \epsilon_n) p_n \\ &= -\frac{2}{\beta} \partial_\kappa \ln Z \\ &= \frac{D \hbar}{2 m \omega} \coth\left(\frac{\beta \hbar \omega}{2}\right) \\ &= \frac{D \hbar \omega}{\kappa} \left(n_B(\beta \hbar \omega) + \frac{1}{2} \right). \end{aligned} \quad (247)$$

- Introduce the Einstein temperature following Eq. (222)

$$T_\Theta = \frac{\hbar \omega}{k_B}, \quad (248)$$

the variance Eq. (247) can be written as

$$\begin{aligned} \langle x^2 \rangle &= x_\Theta^2 \left(n_B \left(\frac{T_\Theta}{T} \right) + \frac{1}{2} \right), \\ x_\Theta^2 &= \frac{D k_B T_\Theta}{\kappa} = \frac{D \hbar}{m \omega}. \end{aligned} \quad (249)$$



- At high temperature ($T \gg T_\Theta$), the linear temperature behavior is restored,

$$\langle \mathbf{x}^2 \rangle = x_\Theta^2 \left(\frac{T}{T_\Theta} \right) = \frac{D k_B T}{\kappa}, \quad (250)$$

matching the Boltzmann model Eq. (240).

- At low temperature ($T \ll T_\Theta$), the fluctuation saturates to a finite level

$$\langle \mathbf{x}^2 \rangle = \frac{x_\Theta^2}{2} = \frac{D k_B T_\Theta}{2 \kappa} = \frac{D \hbar}{2 m \omega}. \quad (251)$$

This non-vanishing fluctuation at zero temperature is called the **zero-point fluctuation**, or the **quantum fluctuation**, originated from the *uncertainty relation* between position and momentum in quantum mechanics.

■ Debye Model

The Debye model further takes into account the collective nature of the phonon excitation in crystal, that the frequency ω_q vanishes with the momentum \mathbf{q} for acoustic phonons, which leads to diverging fluctuation at long wave-length.

- Define the average displacement variance of an atom in the solid

$$\langle \mathbf{x}^2 \rangle = \frac{1}{N} \sum_i \langle \mathbf{x}_i^2 \rangle. \quad (252)$$

- Fourier transform to the momentum space

$$\mathbf{x}_i = \frac{1}{N^{1/2}} \sum_{\mathbf{q} \in \text{BZ}} \mathbf{x}_{\mathbf{q}} e^{i \mathbf{q} \cdot \mathbf{R}_i} \quad (253)$$

- The fluctuation Eq. (252) can be written as

$$\langle \mathbf{x}^2 \rangle = \frac{1}{N} \sum_{\mathbf{q} \in \text{BZ}} \langle \mathbf{x}_{\mathbf{q}}^\dagger \mathbf{x}_{\mathbf{q}} \rangle. \quad (254)$$

Each momentum \mathbf{q} labels an independent acoustic phonon mode (for each polarization), for which $\mathbf{x}_{\mathbf{q}}$ fluctuates as an independent harmonic oscillator.

- Use the quantum result in Eq. (247), and take the Debye model for density of state in Eq. (227),

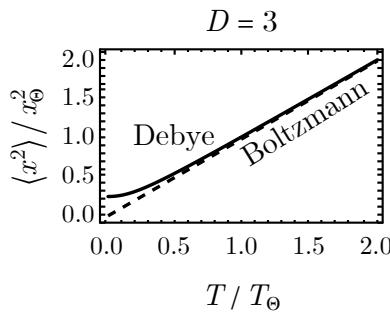
$$\begin{aligned}\langle x^2 \rangle &= \frac{1}{N} \sum_{q \in \text{BZ}} \frac{D \hbar}{2 m \omega_q} \coth\left(\frac{\beta \hbar \omega_q}{2}\right) \\ &= \int_0^{\omega_\Theta} d\omega g(\omega) \frac{\hbar}{2 m \omega} \coth\left(\frac{\beta \hbar \omega}{2}\right),\end{aligned}\quad (255)$$

which can be organized as

$$\begin{aligned}\langle x^2 \rangle &= x_\Theta^2 \left(\frac{T}{T_\Theta} \right)^{D-1} Z\left(\frac{T_\Theta}{T}\right), \\ x_\Theta^2 &= \frac{D^2 \hbar}{(D-2) m \omega_\Theta}, \\ Z\left(\frac{T_\Theta}{T}\right) &= (D-2) \int_0^{T_\Theta/T} dx \frac{x^{D-2}}{2} \coth\left(\frac{x}{2}\right).\end{aligned}\quad (256)$$

- For $D > 2$, at high temperature ($T \gg T_\Theta$), $\langle x^2 \rangle$ approaches to the linear T behavior

$$\langle x^2 \rangle = x_\Theta^2 \left(\frac{T}{T_\Theta} \right) = \frac{D}{(D-2) m \omega_\Theta^2} D k_B T. \quad (257)$$



In the zero temperature limit ($T \rightarrow 0$), the fluctuation saturates to

$$\langle x^2 \rangle = \frac{D-2}{2(D-1)} x_\Theta^2 = \frac{D^2 \hbar}{2(D-1)m\omega_\Theta}. \quad (258)$$

Exc 12

Derive Eq. (257) and Eq. (258).

- For $D = 2$, according to Eq. (257), $\langle x^2 \rangle$ diverges at any *finite* temperature \Rightarrow **2D crystals** are inevitably *melted by thermal fluctuations*.
However, 2D crystals can still be stable at *zero-temperature*, as $\langle x^2 \rangle$ remains finite in the $T \rightarrow 0$ limit for $D = 2$ in Eq. (258).
- For $D = 1$, according to Eq. (258), $\langle x^2 \rangle$ even diverges in the *zero-temperature* limit \Rightarrow **1D crystals** are inevitably *melted by quantum fluctuations*.

- **Quantum-classical duality:** a **quantum system** ($T = 0$) at D dimension has properties similar to a **classical system** ($T > 0$) at $(D + 1)$ dimension. This duality connects quantum mechanics with statistical mechanics in one higher dimension.

HW
7

Suppose the dispersion of phonon is modified to $\omega_q \sim |\mathbf{q}|^z$ with some $z > 0$ in D -dimensional space, determine

- the critical dimension D_T that the crystal will melt by thermal fluctuation,
- the critical dimension D_Q that the crystal will melt by quantum fluctuation.
- Verify that the result is consistent with the generalized quantum-classical duality, that under a generic dynamical exponent z , a quantum system at D dimension will be dual to a classical system at $(D + z)$ dimension.