

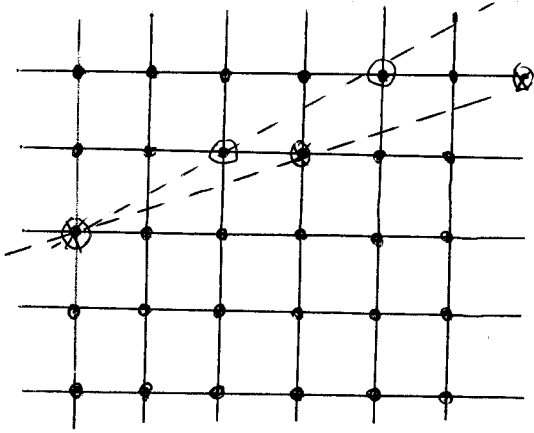
## Worked example

\* square lattice in 2D

→ described by lattice vectors  $\vec{a}_1 = a\hat{e}_x$ ,  $\vec{a}_2 = a\hat{e}_y$

→ trivial basis

→ lattice consists of all points  $\vec{R} \in \mathbb{Z}\vec{a}_1 + \mathbb{Z}\vec{a}_2$  (infinite set)



→ lines connecting nearest neighbor sites are just guides to the eye (not part of the lattice per se)

→ actually an infinite number of planes (through an infinite subset of lattice points) we could draw with slope

$$\frac{1}{\infty}, \dots, \frac{1}{3}, \frac{1}{2}, \frac{1}{1}, 1, 2, 3, \dots, \infty$$

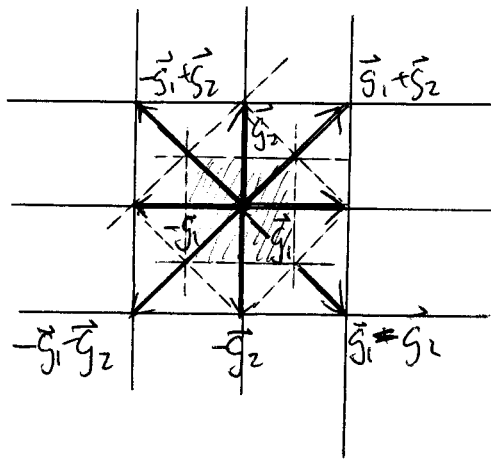
→ in 2D we can include a dummy vector  $\vec{a}_3 = \hat{e}_z$  so that all the 3D formulas hold: e.g. vol. unit cell  $\Omega_0 = (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3 = a^2$

→ reciprocal lattice vectors

$$\vec{g}_1 = \frac{2\pi}{\Omega_0} \vec{a}_2 \times \vec{a}_3 = \frac{2\pi}{a^2} a\hat{e}_y \times \hat{e}_z = \frac{2\pi}{a} \hat{e}_x$$

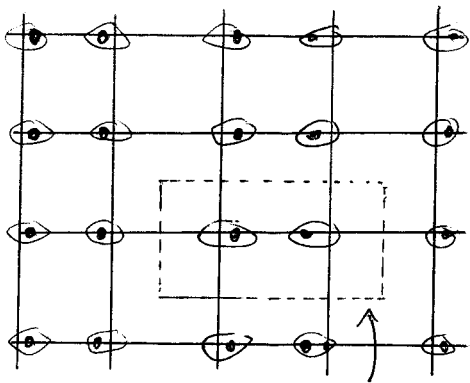
$$\vec{g}_2 = \frac{2\pi}{\Omega_0} \vec{a}_3 \times \vec{a}_1 = \frac{2\pi}{a^2} \hat{e}_z \times a\hat{e}_x = \frac{2\pi}{a} \hat{e}_y$$

→ in this special case, the reciprocal lattice  $Z\vec{g}_1 + Z\vec{g}_2$  is just a rescaled version of the real-space lattice



→ Wigner-Seitz construction  $\Rightarrow$  BZ =  $[-\frac{\pi}{a}, \frac{\pi}{a}] \times [-\frac{\pi}{a}, \frac{\pi}{a}]$

\* Consider a deformed lattice where atoms have been shifted alternately left and right

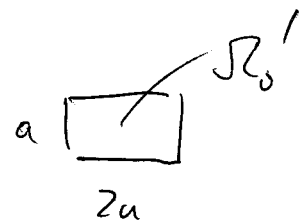


doubled unit cell  
with a nontrivial  
2-site basis

→ new lattice with doubled repeat unit in the  $\hat{e}_x$  direction

$$\vec{a}_1 = 2a\hat{e}_x$$

$$\vec{a}_2 = a\hat{e}_y$$



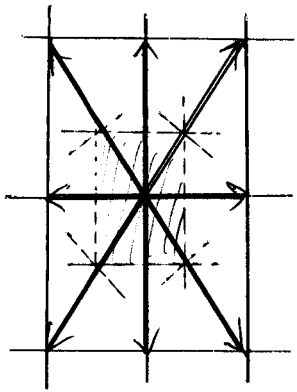
$$\Omega_0' = 2a^2$$

$$\frac{\Omega_0'}{\dim(\text{basis})} = \Omega_0 = a^2$$

→ corresponding reciprocal lattice vectors

$$\vec{g}_1 = \frac{2\pi}{2a^2} a\hat{e}_y \times \hat{e}_z = \frac{\pi}{a}\hat{e}_x$$

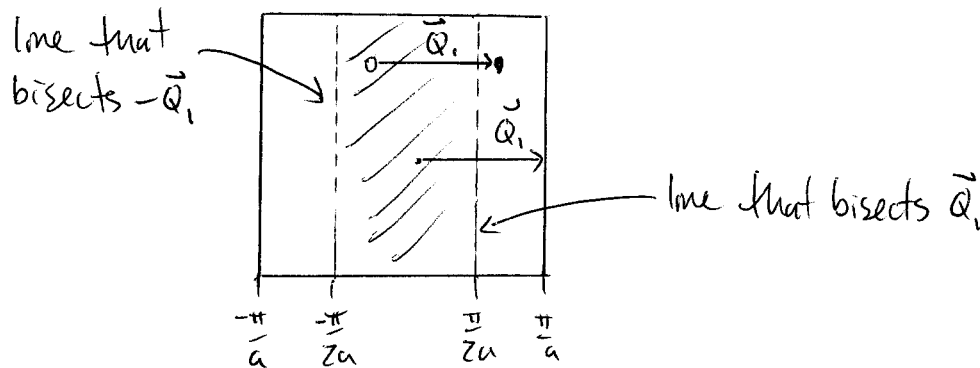
$$\vec{g}_2 = \frac{2\pi}{2a^2} \hat{e}_z \times (2a\hat{e}_x) = \frac{2\pi}{a}\hat{e}_y$$



$$\rightarrow \text{new BZ}' = \left[ \begin{matrix} -\frac{\pi}{2a} & \frac{\pi}{2a} \\ \frac{\pi}{a} & \frac{\pi}{a} \end{matrix} \right] \times \left[ \begin{matrix} -\frac{\pi}{a} & \frac{\pi}{a} \end{matrix} \right]$$

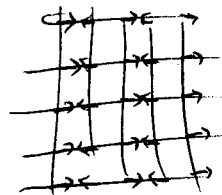
Compressed by a factor of two in the  $\hat{e}_x$  direction

$\rightarrow$  note that the old BZ can be "folded" into the reduced BZ by a vector  $\vec{Q}_1 = \frac{\pi}{a} \hat{e}_x = \frac{\pi}{a} (1, 0)$



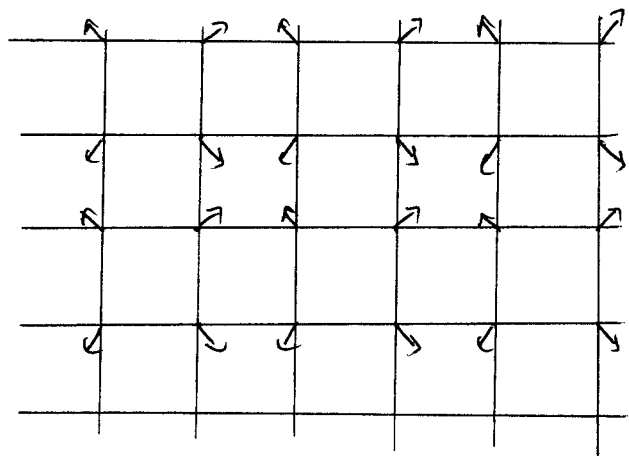
$\rightarrow \vec{Q}_1$  is related to the ordering vector of the atomic displacement:  $\vec{d} = \alpha_1 e^{i\vec{Q}_1 \cdot \vec{R}_j} \hat{e}_x = \alpha_1 (-1)^{R_x/a} \hat{e}_x$

i.e. each atom  $\vec{R}$  in the original lattice was moved to  $\vec{R} + \vec{d}$



\* Consider a more complicated distortion  $\vec{d} = \alpha_1 \hat{e}_x e^{i\vec{Q}_1 \cdot \vec{R}} + \alpha_2 \hat{e}_y e^{i\vec{Q}_2 \cdot \vec{R}}$

with  $\vec{Q}_1 = \frac{\pi}{a} (1, 0)$  and  $\vec{Q}_2 = \frac{\pi}{a} (0, 1)$



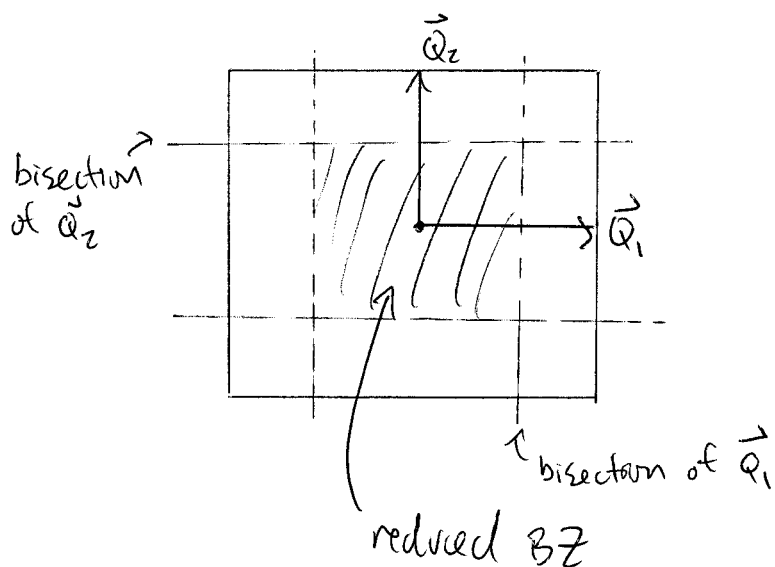
→ real-space  $\hat{e}_x$  and  $\hat{e}_y$  atomic distortions alternating by row and column

→  $\alpha_1 \neq 0, \alpha_2 \neq 0$  leads to unit cell doubling in both directions:

$$\vec{a}_1 = 2a \hat{e}_x$$

$$\vec{a}_2 = 2a \hat{e}_y$$

$\Omega_0 = 4a^2$  and a 4-atom basis



→ pattern is invariant (modulo translations and  $90^\circ$  rotations) under  $\alpha_1 \rightarrow -\alpha_1, \alpha_2 \rightarrow -\alpha_2$  and the swap  $\alpha_1 \leftrightarrow \alpha_2$

→ implies that the most general Ginzburg-Landau functional  $F[\alpha_1, \alpha_2]$  is a mixed powerseries in  $\alpha_1^2$  and  $\alpha_2^2$ :

$$F[\alpha_1, \alpha_2] = v(\alpha_1^2 + \alpha_2^2) + S\alpha_1^2 \alpha_2^2 + u(\alpha_1^4 + \alpha_2^4) + \dots$$

Alternatively, we could parameterize  $\alpha_1 = \alpha \cos \theta$

$$\alpha_2 = \alpha \sin \theta$$

$$F[\alpha, \theta] = r\alpha^2 + s\alpha^4 \cos^2 \theta \sin^2 \theta + u(\alpha^4 \cos^4 \theta + \alpha^4 \sin^4 \theta)$$

$$= r\alpha^2 + \left[ s\left(\frac{1}{4}\sin^2 2\theta\right) + u\left(1 - \frac{1}{2}\sin^2 2\theta\right) \right] \alpha^4$$

$u > 0$  is required for stability; at the special point  $s = 2u$ , the free energy is degenerate in  $\theta$ ; other values of  $s$

tend to favour or penalize solutions along the lines  $\alpha_2 = \pm \alpha_1$ .

→ find the stationary points:

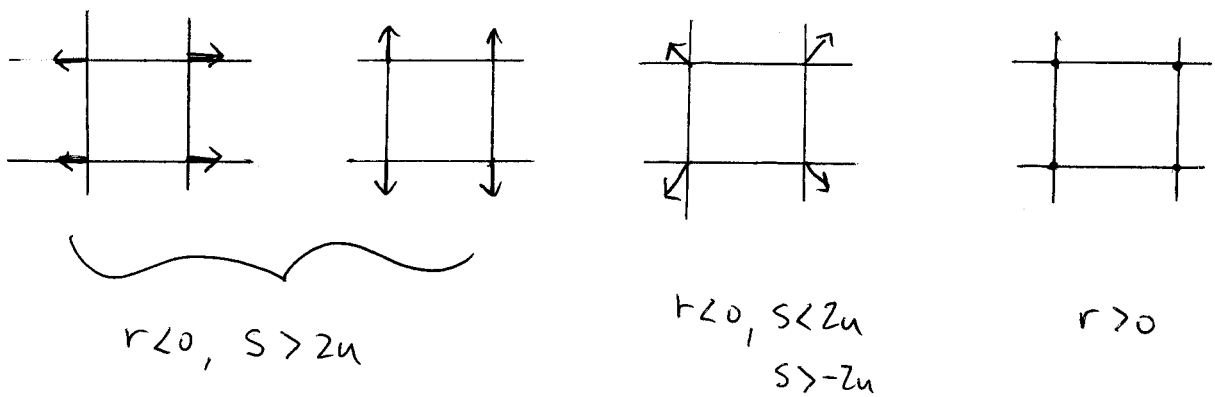
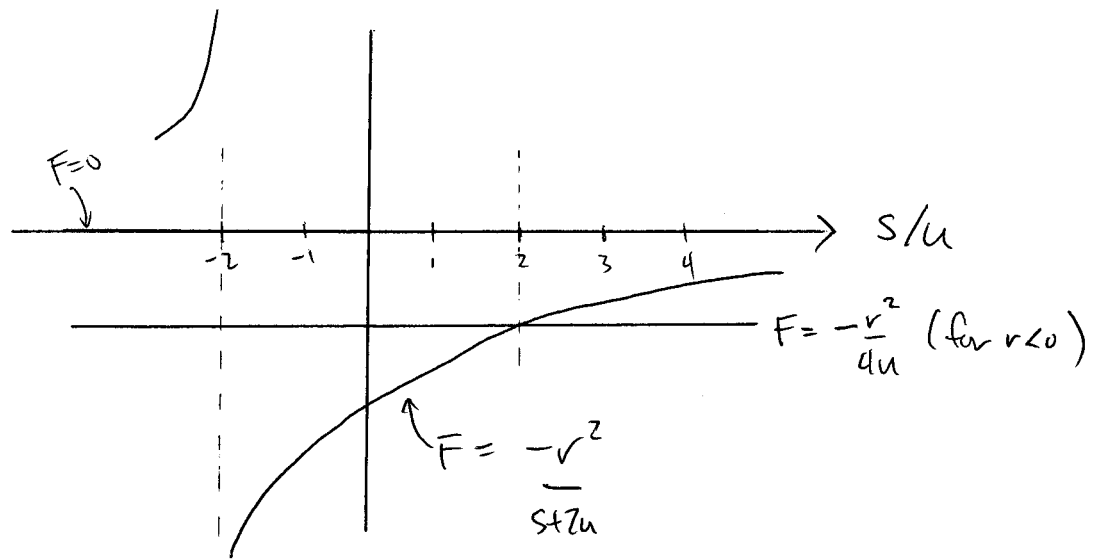
$$\frac{\partial F}{\partial \alpha_1} = 2r\alpha_1 + 2s\alpha_1\alpha_2^2 + 4u\alpha_1^3 = 2\alpha_1(r + s\alpha_2^2 + 2u\alpha_1^2) = 0$$

$$\frac{\partial F}{\partial \alpha_2} = 2r\alpha_2 + 2s\alpha_1^2\alpha_2 + 4u\alpha_2^3 = 2\alpha_2(r + s\alpha_1^2 + 2u\alpha_2^2) = 0$$

→ Solutions  $\alpha_1 = \alpha_2 = 0$  with  $F = 0$

$$\left. \begin{array}{l} \alpha_1 = 0, \alpha_2 = \pm \sqrt{\frac{-r}{2u}} \\ \alpha_2 = 0, \alpha_1 = \pm \sqrt{\frac{-r}{2u}} \end{array} \right\} \text{with } F = -\frac{r^2}{4u} \quad (r < 0 \text{ only})$$

$$\alpha_1 = \alpha_2 = \pm \sqrt{\frac{-r}{s+2u}} \quad \text{with } F = -\frac{r^2}{s+2u}$$



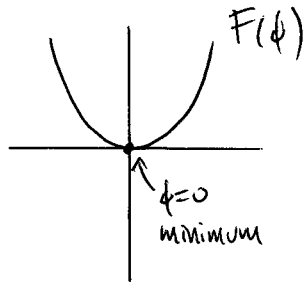
QUESTIONS:

- ① Consider the transition from  $r > 0$  to  $r < 0$  when the crystal initially distorts. Is this first- or second-order?
- ② Consider the transition of the distorted lattice ( $r < 0$ ) from one kind of distortion to another (i.e.  $s - zu$  changes sign). Is this first- or second-order?

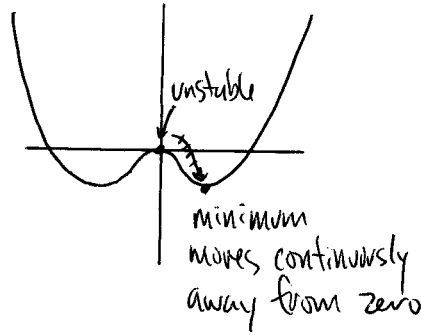
# Crystal Growth

\* the transition from liquid to solid is first order

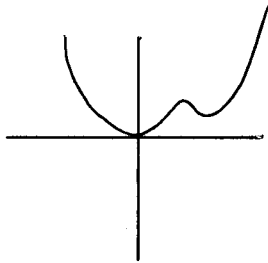
→ recall our classifications



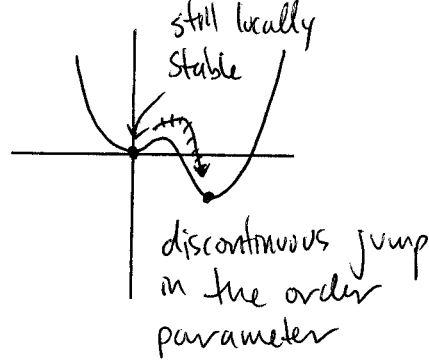
2nd  
→



1st  
↕



→



infinitesimal change in φ  
↓

$$d(\text{Push}) = d(\text{Amplitude}) \times \text{Sample}$$

↑  
across the whole system

$$d(\text{Push}) = \text{Amplitude} \times d(\text{Sample})$$

↑  
finite change in φ

↑  
in a microscopic region

\* crystals grow from a nucleation point

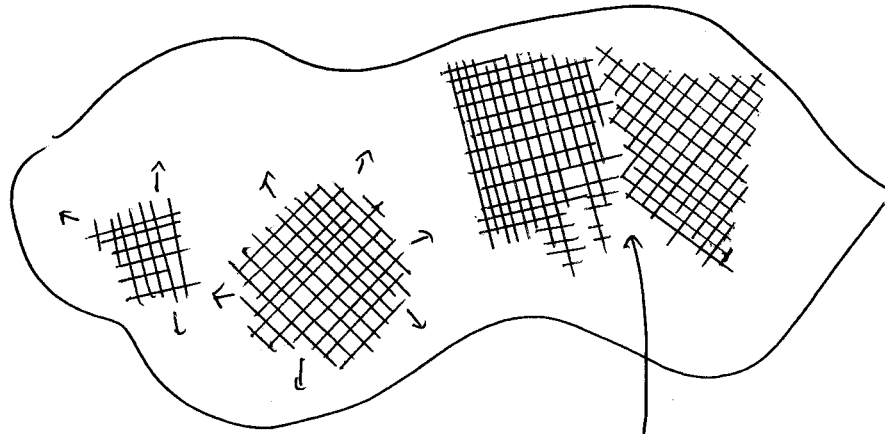
→ jump in the free energy ⇒ latent heat of formation

→ liquid can be supercooled below its solidification temp.

→ may have to wait a very long time for local fluctuations to initiate the crystallization process

→ crystals are most often seeded by a nucleation centre

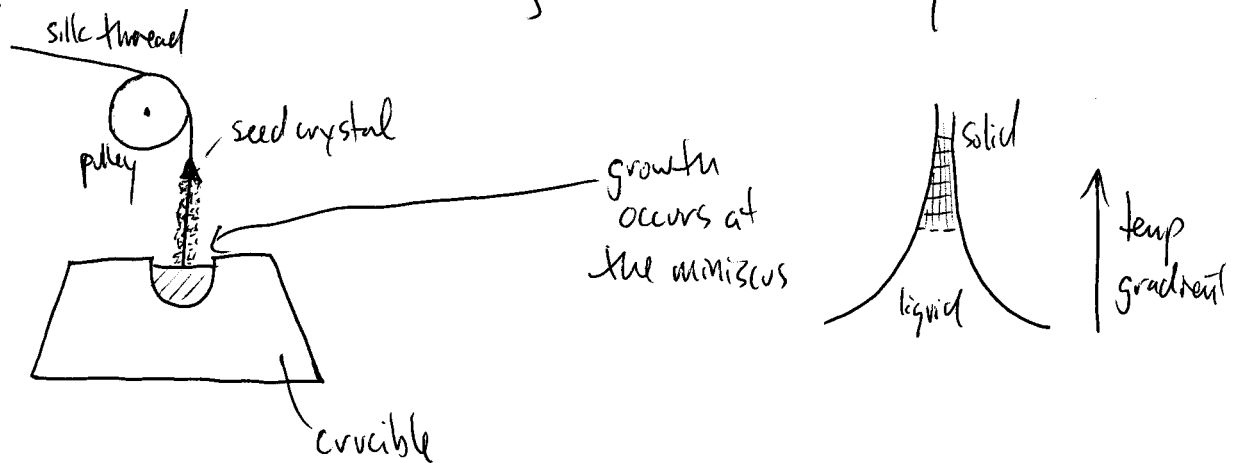
- \* it can be difficult to grow large, single-crystal samples
  - lattice arrangements arising from far separated nucleation centres may be incompatible



grain boundary between differently aligned domains

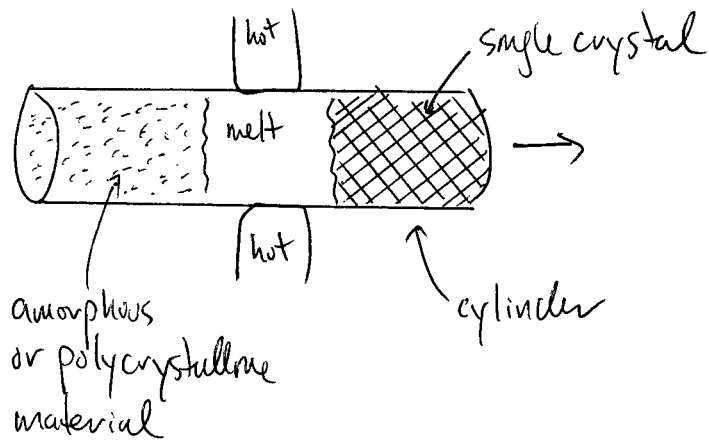
\* growth methods

① Pull crystals from a melt using a small seed crystal





② draw packed powder through a hot zone



→ multiple passes help to eliminate defects, impurities, and mismatched grains (zone refinement)

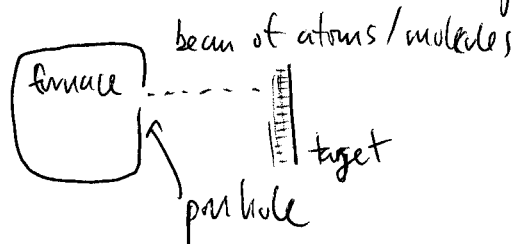
③ nucleated in supersaturated solution (like sugar in syrup)

④ grown in vapour (only good for small single crystals)

Modern techniques lay down material on a surface layer by layer

⑤ Molecular beam epitaxy

⑥ Chemical vapour deposition



# X-ray diffraction

1895 Roentgen discovers x-rays

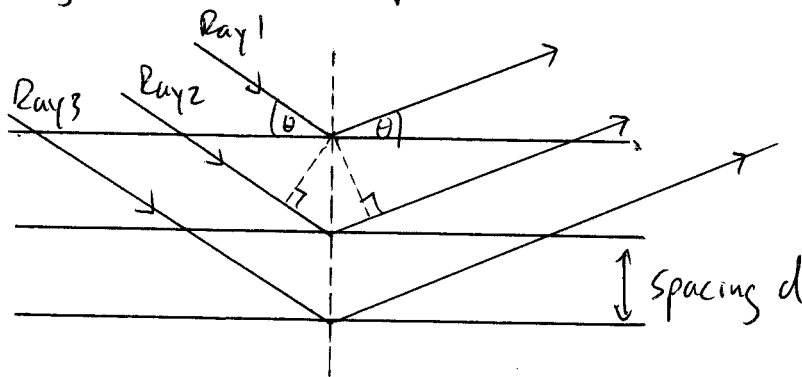
→ unknown emission later understood to be high-energy EM radiation (photons)

→ recall that  $hc = 12400 \text{ eV} \cdot \text{\AA}$ , hence  $E = \frac{hc}{\lambda} \sim 8 \text{ keV}$  corresponds to  $\lambda \sim 1.5 \text{\AA}$  (atomic separation in a solid)

1912 von Laue proposes using x-rays for diffraction in a crystal

→ lattice planes act as a diffraction grating

1913 Bragg picture imagines monochromatic light specularly reflecting off atomic planes

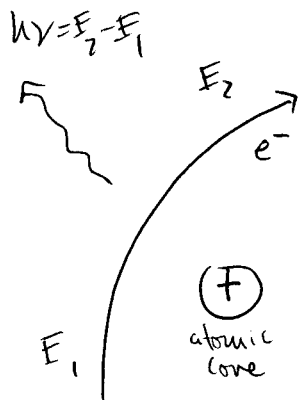
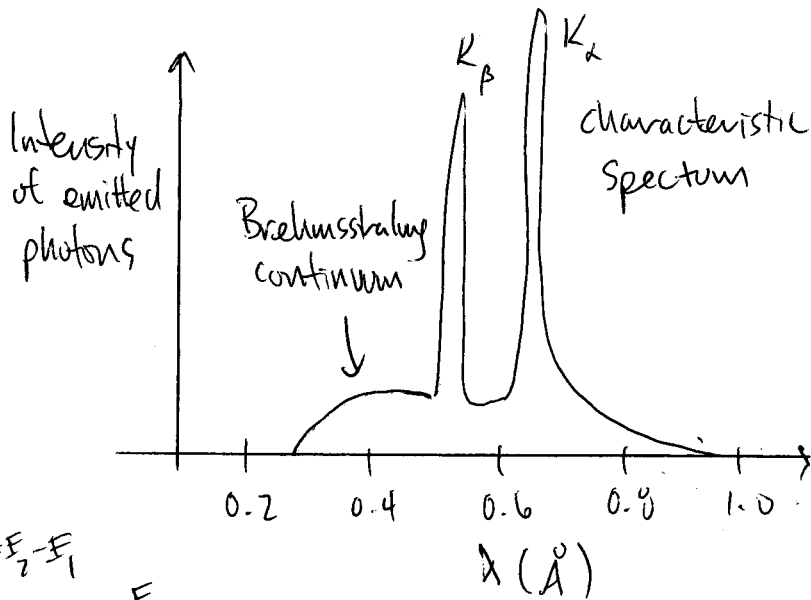
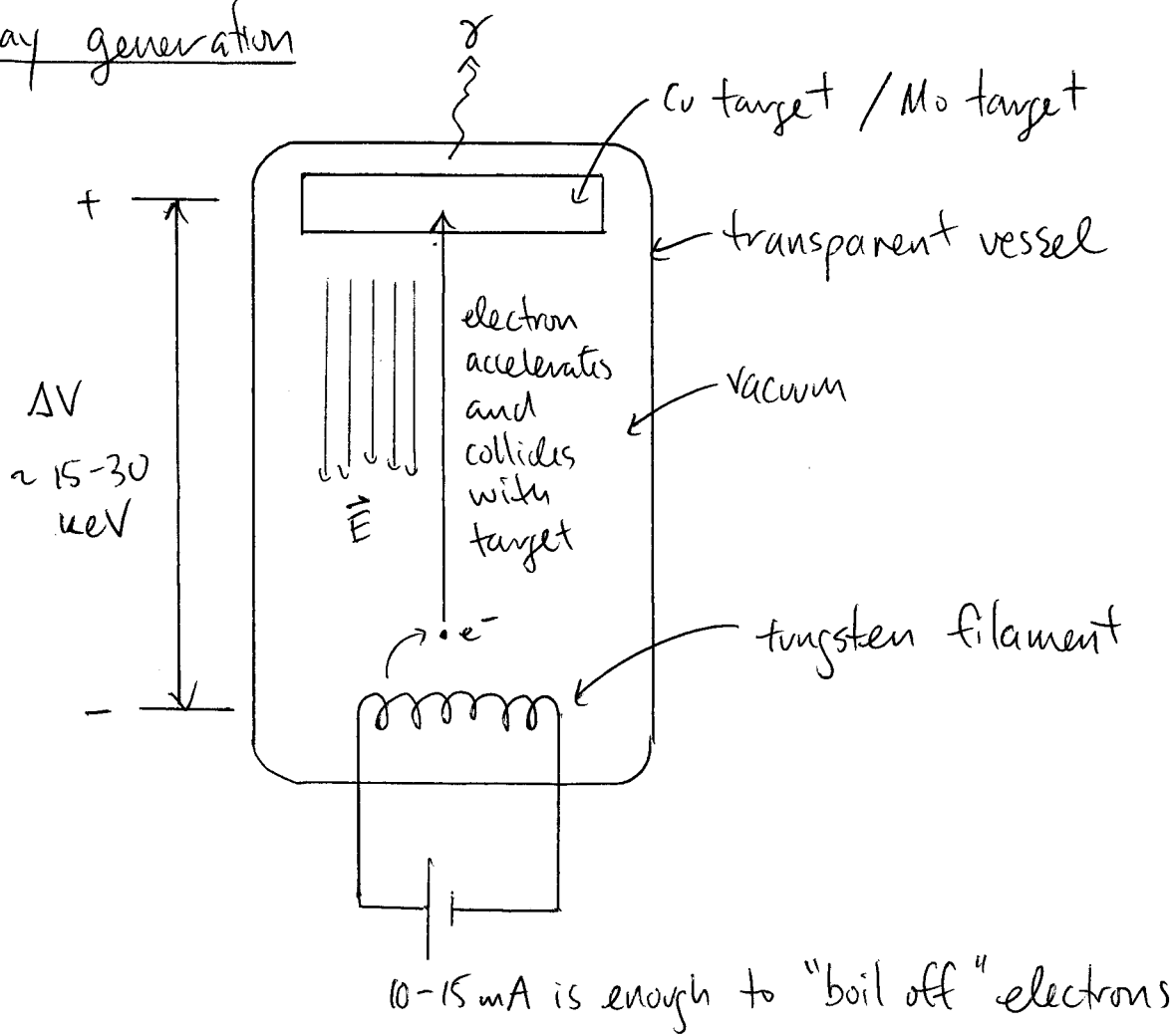


- successive path differences of  $2d \sin \theta$

- if all the phase shifts associated with reflection are constant then there is constructive interference whenever

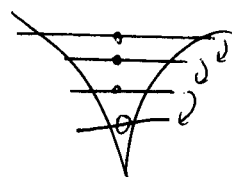
$$2d \sin \theta = \text{integer} \times \lambda$$

# X-ray generation



Bremsstrahlung gives a continuous spectrum of photon energies from deflection

The sharp emission lines are discrete and correspond to the cascade of level changes when an electron is kicked out of a core



## Scattering

Recall: Any function  $f(\vec{r})$  can be expanded in a Fourier series. And if it shares the periodicity of the lattice, i.e.  $f(\vec{r} + \vec{R}) = f(\vec{r})$  for any lattice vector  $\vec{R}$ , then its only nonzero Fourier components are at reciprocal lattice vectors:

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}$$

$$f_{\vec{G}} = \int \frac{d^3r}{\Omega_0} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}}$$

\* minimal coupling of EM field to electrons

$$H = \frac{1}{2m} \sum_i [p_i - eA(r_i)]^2$$

$$= H_0 + \vec{J} \cdot \vec{A} + V$$

$$\text{where } V = \frac{e^2}{2m} \sum_i |A(r_i)|^2 = \frac{e^2}{2m} \int d^3r \underbrace{n(\vec{r})}_{\substack{\text{is the electron} \\ \text{density}}} |A(\vec{r})|^2$$

nonlinear interaction  
of EM field with  
electron density

\* simple scattering event for photon



$$\vec{A}(\vec{r}) = \vec{A}_{in} e^{i\vec{k}\cdot\vec{r}} + \vec{A}_{out} e^{i\vec{k}'\cdot\vec{r}}$$

$$|\vec{A}(\vec{r})|^2 = |\vec{A}_{in}|^2 + |\vec{A}_{out}|^2 + 2\vec{A}_{in}\cdot\vec{A}_{out} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

$$\Rightarrow \frac{e^2}{2m} \int d^3r n(\vec{r}) |\vec{A}(\vec{r})|^2 = \frac{e^2}{2m} \int d^3r n(\vec{r}) \left[ (\text{trivial constant}) + 2\vec{A}_{in}\cdot\vec{A}_{out} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} \right]$$

$$= \text{const} + \frac{e^2}{m} \vec{A}_{in}\cdot\vec{A}_{out} \int d^3r \sum_{\vec{G}} \vec{n}_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

$$= \text{const} + \frac{e^2}{m} \vec{A}_{in}\cdot\vec{A}_{out} \sum_{\vec{G}} \vec{n}_{\vec{G}} \int d^3r e^{i\vec{r}\cdot(\vec{k}+\vec{G}-\vec{k}')}$$

$$\underbrace{\int d^3r e^{i\vec{r}\cdot(\vec{k}+\vec{G}-\vec{k}')}}_{\delta_{\vec{k}+\vec{G}, \vec{k}'}}$$

→ elastic scattering can only change the photon wavevector by a reciprocal lattice vector

→ scattering x-section  $\propto \frac{e^2}{m_e}$ , which is what we expect of classical Rayleigh scattering from a charged particle

→ x-rays only sensitive to the electronic configuration  
 since  $m_p = 2000 \times m_e$

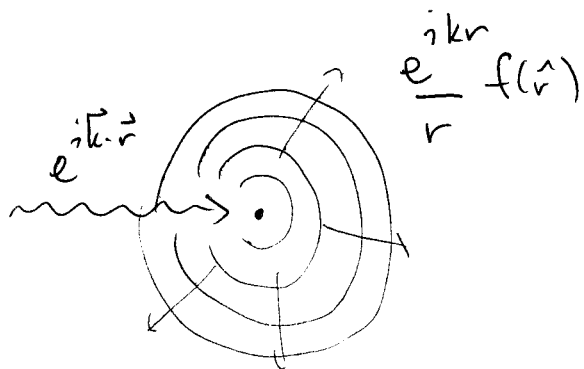
### Array of point scatterers

\* Bragg picture is highly oversimplified (there is not actually specular reflection off planes)

\* We need to consider a lattice of points that absorb and re-emit photons in a circular wavefront

$$\psi \simeq A e^{-i\omega t} \left[ e^{i\vec{k} \cdot \vec{r}} + e^{\frac{ikr}{r}} f(\hat{r}) \right]$$

↑ radial wave with  $k = |\vec{k}|$ ,  $r = |\vec{r}|$ , scattered from a point at the origin



$|\psi_{\text{absorbing}}|^2 \sim \frac{1}{r^2}$  is required

by normalization over spherical shells:

$$\int d^3r |\psi|^2 = \int dr 2\pi r^2 |\psi|^2 \sim 1$$

\* Scatter instead from a lattice site at  $\vec{R}$

$$\psi \sim A e^{-i\omega t} \left[ e^{i\vec{k}\cdot\vec{r}} + e^{i\vec{k}\cdot\vec{R}} f(\widehat{r-\vec{R}}) e^{\frac{i k |\vec{r}-\vec{R}|}{|\vec{r}-\vec{R}|}} \right]$$

→ at distant points  $r \gg R$ ,

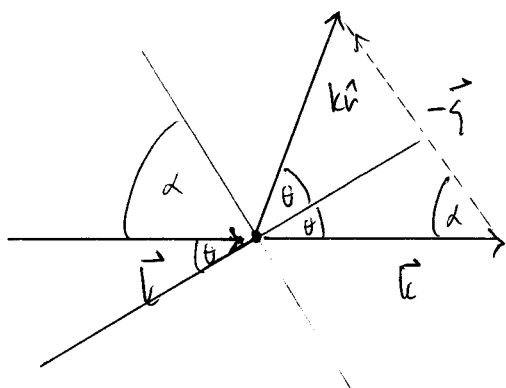
$$\widehat{r-\vec{R}} \simeq \hat{r} \quad (\text{rays become parallel})$$

$$\begin{aligned} \text{and } k|\vec{r}-\vec{R}| &= k\sqrt{r^2 - 2\vec{r}\cdot\vec{R} + R^2} \\ &= kr\sqrt{1 - \frac{2\hat{r}\cdot\vec{R}}{r} + \frac{R^2}{r^2}} \end{aligned}$$

$$\simeq kr - k\hat{r}\cdot\vec{R}$$

→ net phase in the outgoing wave is

$$k|\vec{r}-\vec{R}| + \vec{k}\cdot\vec{R} \simeq kr - \underbrace{(\vec{k} - k\hat{r})\cdot\vec{R}}_{\text{def}^n \vec{q}}$$



$$\text{with } \alpha = \frac{\pi}{2} - \theta$$

→ combine ①  $\vec{k}\cdot\vec{q} = kq \cos \alpha = kq \sin \theta$

②  $\vec{k}\cdot(k\hat{r}) = k^2 \cos 2\theta = \vec{k}\cdot(\vec{k} - \vec{q}) = k^2 - \vec{k}\cdot\vec{q}$

$$\Rightarrow \vec{k}\cdot\vec{q} = k^2(1 - \cos 2\theta) = 2k^2 \sin^2 \theta$$

to get  $q = 2k \sin \theta$

\* Sum over contributions from all lattice points

$$\psi \sim A e^{-i\omega t} \left[ e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{r}} f_{\vec{r}}(\vec{r}) e^{\frac{i\vec{k}\cdot\vec{r} + i\vec{q}\cdot\vec{r}}{r}} \right]$$

→ outgoing intensity is

$$I \propto \frac{1}{r^2} \left| \sum_{\vec{r}} f_{\vec{r}}(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \right|^2$$

→ for identical scatterers

$$I = I_{\text{atom}} \left| \sum_{\vec{r}} e^{i\vec{q}\cdot\vec{r}} \right|^2$$

↑ strong scattering only when  $\vec{q}\cdot\vec{r} = 2\pi \times \text{integer}$ , otherwise, perfect cancellation

i.e. we only see intensity peaks for  $\vec{q} = \vec{G}$  for some  $\vec{G}$  in the reciprocal lattice

### Scattering with a basis

$$I \propto \left| \sum_{\vec{r}} \sum_{\vec{c}} f_{\vec{r}+\vec{c}}(\vec{r}) e^{i\vec{q}\cdot(\vec{r}+\vec{c})} \right|^2$$

↑ ↑  
 Sum over lattice      Sum over basis in each unit cell



\* by translational invariance,  $f_{\vec{D}+\vec{c}} = f_{\vec{c}}$

$$I \propto \left| \sum_{\vec{c}} e^{i\vec{\gamma} \cdot \vec{c}} f_{\vec{c}}(\hat{r}) - \sum_{\vec{R}} e^{i\vec{\gamma} \cdot \vec{R}} \right|^2$$

$$= \left| \sum_{\vec{c}} e^{i\vec{\gamma} \cdot \vec{c}} f_{\vec{c}}(\hat{r}) \right|^2 - \left| \sum_{\vec{R}} e^{i\vec{\gamma} \cdot \vec{R}} \right|^2$$

↑ selects  $\vec{\gamma} = \vec{G}$

↑ "atomic form factors" have arbitrary amplitude and phase (complex numbers)

→ intensity now premultiplied by a "structure factor"

→ possible to have valid  $\vec{\gamma} = \vec{G}$  scattering events with zero amplitude (extinction)