4) Phonons

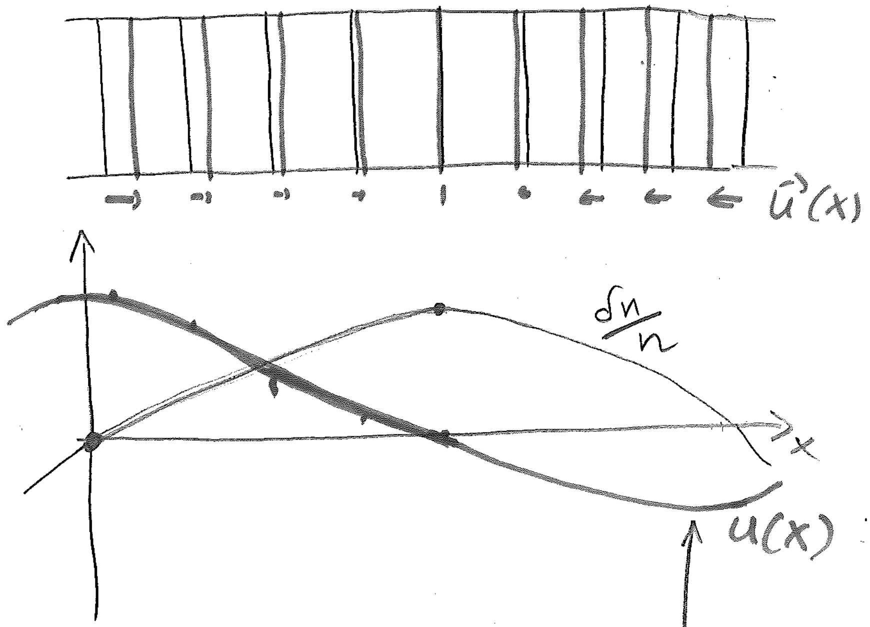
Phonons: elementary lattice vibrations

Microscopic: $3N-3$ normal modes of N atoms

Macroscopic: transverse/longitudinal sound waves

"Quantum sound"

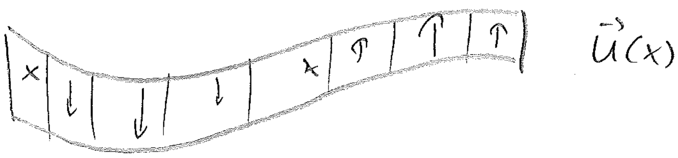
- longitudinal
  "compression wave"



displacement field

$$\frac{\delta n}{n} = -\vec{\nabla} \cdot \vec{u}(\vec{r})$$

- transverse
  "shear wave"



For simplicity we only consider longitudinal waves in isotropic medium.

- elastic energy: $$E_{el} = \overset{\text{compressibility}}{\frac{\lambda}{2}} \int d^3r \, \underbrace{\left(\frac{\delta n}{n}\right)}_{\substack{\text{relative} \\ \text{compression}}}^2$$

$$\frac{\delta n}{n} = -\vec{\nabla}\cdot\vec{u}(\vec{r})$$ (e.g., from Gauss theorem)

- kinetic energy: $$E_{kin} = \underbrace{\frac{\rho_0}{2}}_{\text{density}} \int d^3r \, \dot{\vec{u}}(\vec{r})^2$$

⇒ equation of motion (EOM): $$\boxed{\rho_0 \frac{\partial^2 \vec{u}}{\partial t^2} = \lambda \vec{\nabla}(\vec{\nabla}\cdot\vec{u})}$$
from $L[u,\dot{u}] = E_{kin} - E_{el}$

⇒ plane wave solution
$$\vec{u}(\vec{r},t) = \vec{u}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

in EOM:
$$\rho_0 \ddot{\vec{u}}_{\vec{k}} = -\lambda \vec{k}\cdot(\vec{k}\cdot\vec{u}_{\vec{k}})$$

longitudinal solutions $\vec{k} \parallel \vec{u}_{\vec{k}}$:
$$\boxed{\ddot{\vec{u}}_{\vec{k}} = -c^2k^2\vec{u}_{\vec{k}} \quad , \quad c = \sqrt{\frac{\lambda}{\rho_0}}}$$

⇒ independent harmonic oscillator modes with $\omega_{\vec{k}} = c|\vec{k}|$
(linear dispersion → sound)

⇒ each mode corresponds to plane wave
$$\vec{u}(\vec{r},t) = u_{\vec{k}}^{(0)} e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

• quantization of normal modes:

$$m\ddot{u} = -m\omega_0^2 u \xrightarrow{\text{quantum}} E_n|n\rangle = \hat{H}|n\rangle$$

$$E_n = \hbar\omega_0 (n + \tfrac{1}{2})$$

$$n \in \mathbb{N}_0$$

$$\hat{=} \quad \hat{H} = \hbar\omega_0 \left(a^\dagger a + \tfrac{1}{2}\right)$$

$a, a^\dagger$: annihilate/create oscillator quantum

$$x = \sqrt{\frac{\hbar}{2m\omega_0}}\,(a + a^\dagger)$$

• Normal modes in solid:

$$\boxed{\begin{aligned} \hat{H} &= \sum_k \hbar\omega_k \left(b_k^\dagger b_k + \tfrac{1}{2}\right) \\ \vec{u}(\vec{r}) &= \sqrt{\frac{1}{\text{vol}}} \sum_k \hat{\varepsilon}_k \sqrt{\frac{\hbar}{2\rho_0\omega_k}} \left(b_k e^{i\vec{k}\cdot\vec{r}} + b_k^\dagger e^{-i\vec{k}\cdot\vec{r}}\right) \end{aligned}} \quad (*)$$

polarization vector $\sim \hat{k}$

shear waves: analogous with $\hat{\varepsilon}_k \perp \hat{k}$

total: $$\hat{H} = \sum_{k\,s} \hbar\omega_{ks} \left(b_{ks}^\dagger b_{ks} + \tfrac{1}{2}\right)$$

s: polarizations

- Representation in normal coordinates and momenta: (harmonic oscillator)

$$\boxed{\hat{H} = \frac{1}{2} \sum_k \left(P_k^2 + \omega_k^2 Q_k^2\right)}$$

$$(**) \begin{cases} Q_k = \sqrt{\rho_0}\,(q_k + i q_k^*) \\ P_k = \sqrt{\rho_0}\, i\omega_k (q_k - i q_k^*) \end{cases}$$

$$(***)\ u(\vec{r}) = \frac{1}{\sqrt{vol}} \sum_k \left(q_k(t) e^{ikr} + q_k(t)^* e^{-ikr}\right) \hat{\varepsilon}_k$$

- Quantum theory of sound waves:

$$P_k \to \hat{P}_k \qquad [\hat{Q}_k, \hat{P}_k] = i\hbar$$
$$Q_k \to \hat{Q}_k$$

or: $$b_k = \frac{1}{\sqrt{2\hbar\omega_k}} \left(\omega_k \hat{Q}_k - i\hat{P}_k\right) \qquad (****)$$

$$b_k^+ = \frac{1}{\sqrt{2\hbar\omega_k}} \left(\omega_k \hat{Q}_k + i\hat{P}_k\right)$$

$$\boxed{[b_k, b_{k'}^+] = \delta_{kk'} \qquad \hat{H} = \sum_k \hbar\omega_k \left(b_k^+ b_k + \frac{1}{2}\right)}$$

check: $$u(\vec{r}) \overset{(*)}{=} \frac{1}{\sqrt{vol}} \sum_k \hat{\varepsilon}_k \sqrt{\frac{\hbar}{2\rho_0\omega_k}} \left(b_k e^{ikr} + b_k^+ e^{-ikr}\right)$$

$$\overset{(****)}{=} \frac{1}{\sqrt{vol}} \sum_k \hat{\varepsilon}_k \frac{1}{2\omega_k} \frac{1}{\sqrt{\rho_0}} \left((\omega_k \hat{Q}_k + i\hat{P}_k) e^{ikr} + c.c.\right)$$

$$\overset{(**)}{=} \frac{1}{\sqrt{vol}} \sum_k \hat{\varepsilon}_k \frac{1}{2} \left(\underbrace{\left((q_k + q_k^*) - i\left(i(q_k - i q_k^*)\right)\right)}_{q_k + i q_k^* + q_k - i q_k^*} e^{ikr} + c.c.\right)$$

$= (***)$ ✓

$\Rightarrow$ phonons = independent (for harmonic potential!) quasiparticles with linear dispersion

$$\omega_k = c|\vec{k}|:$$

"longitudinal acoustic phonons"

- Is quantum description important?

  - one can see phonon quanta, e.g., in neutron scattering, inelastic light scattering

  - specific heat:

    – total energy of classical oscillators: $U = k_B T \times N_{modes}$ (? equipartition theorem)

$$C_V = \frac{\partial U}{\partial T} = k_B \times N_{modes}$$

T-independent: valid only for large T

– total energy of quantum oscillators:

$$U = \sum_k U_k \qquad U_k = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n} E_n}{\sum_n e^{-\beta E_n}} \qquad E_n = n\hbar\omega_k + \tfrac{1}{2}$$

$$\Rightarrow U = \sum_k \frac{\hbar\omega_k}{-1+e^{+\beta\hbar\omega_k}}$$

Bose-Einstein statistics $\frac{1}{e^{\beta x}-1}$

- simple estimate:

$$\sum_k \longrightarrow \sum_{|k|<k_D} \quad \text{with} \quad \sum_{|k|<k_D} = N_{modes} = N_{atoms} \equiv N$$

(longitud. modes; k_D: Debye wave vector)

$$\sum_k \rightarrow \left(\frac{L}{2\pi}\right)^3 \int d^3k \Rightarrow N = \frac{L^3}{(2\pi)^3} \frac{4\pi}{3} k_D^3$$

(volume of sphere)

$$\boxed{k_D = \left(\frac{N}{L^3} 6\pi^2\right)^{1/3}}$$

"upper cutoff"

$x = \beta\hbar c|k|$

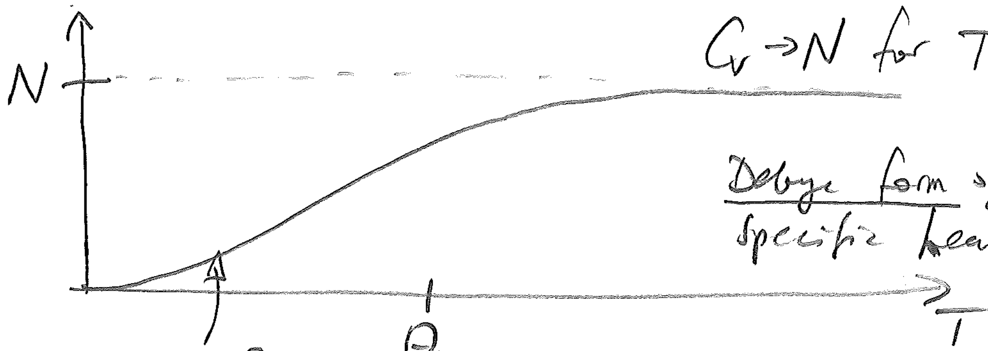
$$U = \left(\frac{L}{2\pi}\right)^3 \underbrace{\int_{|k|<k_D} d^3k}_{4\pi\int_0^{k_D} dk\, k^2} \frac{\hbar c|k|}{e^{\beta\hbar c|k|}-1} \overset{!}{=} \frac{L^3}{2\pi^2}\frac{T^4}{(\hbar c)^3}\int_0^{\beta\hbar c k_D} \frac{dx\, x^3}{e^x-1}$$

$$= 3N\frac{T^4}{(\hbar c k_D)^3}\underbrace{\int_0^{\beta\hbar c k_D}\frac{dx\, x^3}{e^x-1}}_{\substack{\to \text{ const for } \beta\to\infty \\ \text{such that } U\propto T^4}} \xrightarrow{T\to\infty} NT \checkmark$$

$$\boxed{C_V = \frac{\partial U}{\partial T} = \dots = 3\frac{N}{L^3}\left(\frac{T}{\Theta_D}\right)^3\int_0^{T/\Theta_D} dx\,\frac{x^4 e^x}{e^x-1}\,,\quad \Theta_D \equiv \hbar c k_D}$$

for one acoustic branch

$C_V \to N$ for $T\to\infty$



Debye form of phonon specific heat

$C_V \propto T^3$ for $T\to 0$

- <u>Remark:</u> analogy to black-body radiation

  $U \propto T^4$ (Stefan-Boltzmann law)

  Planck's quantum hypothesis ... ☺

Debye temperatures (Wikipedia "Debye model"):

- Aluminum 428 K
- Carbon 2230 K
- Copper 343.5 K ...

typically few hundred kelvin

$\Rightarrow$ quantum effects already visible @ room T !

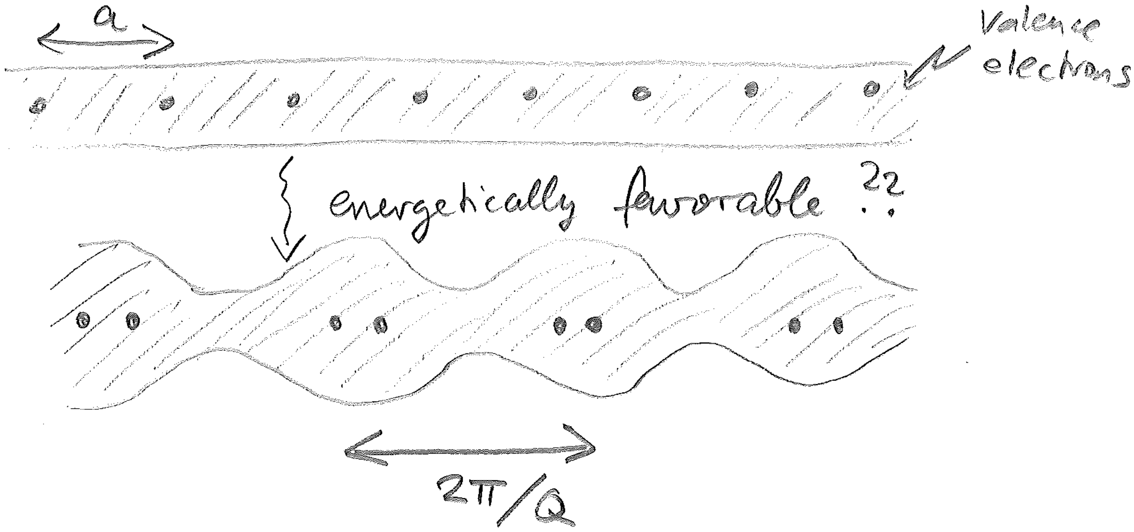
especially in light elements

5) Peierls transition

Usually: Lattice distortion increases energy

Sometimes: Electron-phonon interaction can lead to energy lowering of lattice distortion — the phonon frequency ω_q becomes negative at a wavevector $q = Q$ ($\hat{=}$ ordering wave vector)

$\Rightarrow$ spontaneous formation of a charge-density wave



We discuss this phenomenon in the continuum limit (large wavelength, small $Q \ll \frac{\pi}{a}$) — for the discrete limit the arguments are very similar.

- potential energy:

$$E_{pot} = \underbrace{E_{electron}}_{①} + \underbrace{E_{elastic}}_{②}$$

②: assume distortion

$$u(x) = |u_0| \cos(Qx + \varphi)$$
$$= \frac{1}{2}\left(u_0 e^{iQx} + h.c.\right)$$
$$u_0 = |u_0| e^{i\varphi}$$

elastic energy $= \frac{\lambda}{2}\int dx \left(\frac{du}{dx}\right)^2 = |u_0|^2 L \frac{\lambda Q^2}{4}$

Note: Discussion for 1D where instability is most prominent (see below)

(1) for electronic energy use Born-Oppenheimer approximation:

e^- react instantaneously to lattice distortions, remain in ground state of static potential $V(x)$ due to ions

- $V(x)$ periodic ; ionic density $\frac{\delta n}{n_0} = \frac{du}{dx}$

n_0: eq. density

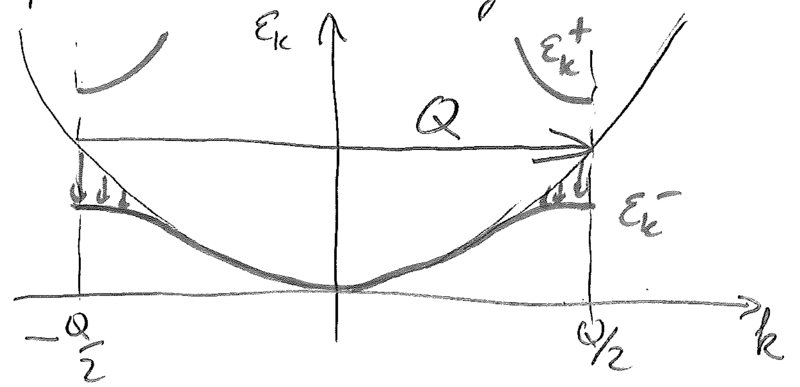
+ Poisson equation

$$\phi_q = \underbrace{\frac{4\pi}{q^2 \varepsilon_q}}_{V_q} \rho_q = V_q n_0 u_0$$

$$\Rightarrow \boxed{V(x) = \Delta_Q e^{iQx} + h.c.}$$

$$\Delta_Q = \alpha u_0 \quad , \quad \alpha \equiv iQ V_Q n_0$$

$\Rightarrow$ periodic potential opens a gap at $k = \frac{Q}{2}$ (compare to discussion of band structure of almost free e^-)



$\Rightarrow$ if filling is such that $k_F < \frac{Q}{2}$

$\Rightarrow$ lowering of electronic energy:

<u>maximum gain for $Q = 2k_F$</u>

$\rightarrow$ can gain overcome cost of $|u_0|^2 L \frac{\lambda Q^2}{4}$?

Schrödinger equation for k, $k-Q$ $\Rightarrow$ diagonalize

$$\begin{pmatrix} \varepsilon_k & \Delta_Q \\ \Delta_Q^* & \varepsilon_{k-Q} \end{pmatrix} \qquad \varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$\Delta_Q = u_0 \underbrace{i n_0 V_Q Q}_{\alpha} = \alpha u_0$$

$$\boxed{\varepsilon_k^{\pm} = \frac{1}{2}\left[(\varepsilon_{k-Q} - \varepsilon_k) \pm \sqrt{(\varepsilon_{k-Q} - \varepsilon_k)^2 + 4|\Delta_Q|^2}\right]}$$

$$E[u_0] = \underbrace{2 \sum_{|k|<k_F} \varepsilon_k^-}_{\substack{\text{energy of occupied} \\ \text{states} \\ \underline{\text{gain}}}} + \underbrace{\frac{L\lambda Q^2}{4} |u_0|^2}_{\substack{\text{elastic energy} \\ \underline{\text{cost}}}}$$

$\Rightarrow$ find minimum $\frac{dE}{du_0} = 0$

Solution:

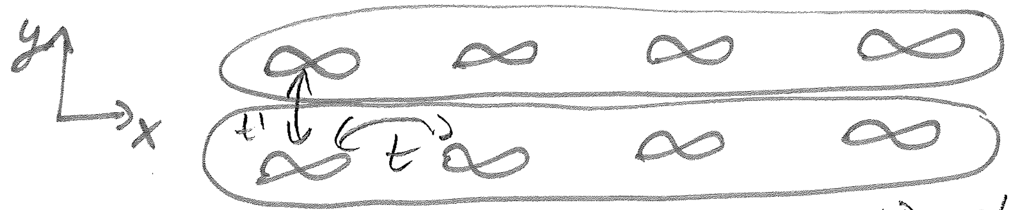
$$\boxed{\Delta_Q = |\alpha u_0| = 4 E_F \, e^{-\frac{1}{N(\varepsilon_F)\cdot g}} \qquad g = \frac{4|\alpha|^2}{\lambda Q^2}}$$

$\Rightarrow$ <u>for arbitrarily small interaction α, a gap is opened at the Fermi surface</u>

$\Rightarrow$ instability occurs for "half-filled" system

Peierls instability in 1D systems

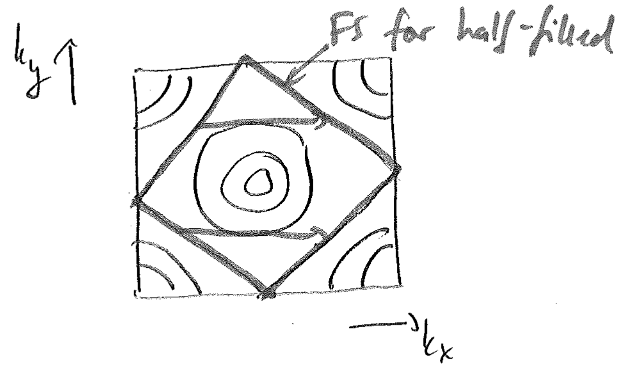
- real materials are not 1D !?



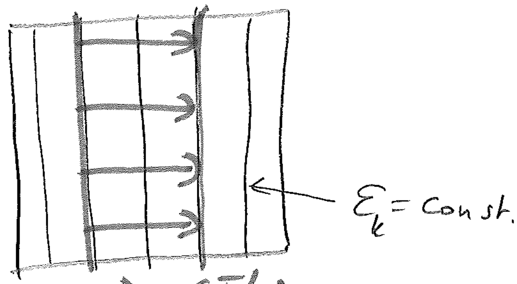
stack of weakly coupled 1D chains

$$\varepsilon_k = \varepsilon(k_x, k_y) \overset{\text{tight-binding}}{\stackrel{\downarrow}{=}} -2t \cos k_x a - 2t' \cos k_y a$$

"almost one-dim."



$t = t'$
(2D)

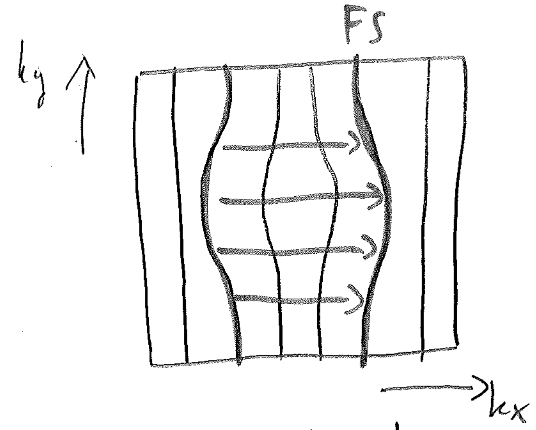


$\vec{q} = \begin{pmatrix} \pi/a \\ 0 \end{pmatrix}$
$t' = 0$
(1D)

- $q = \begin{pmatrix} \pi/a \\ 0 \end{pmatrix}$ only connects single points along FS

(but: $q = \begin{pmatrix} \pi/a \\ \pi/a \end{pmatrix}$ nesting, i.e. checkerboard ordering – special for nearest-neighbor hopping only)

- gap opened at <u>whole</u> Fermi surface
- Fermi surface is <u>nested</u> at nesting vector q



realistic: $t \gg t' \neq 0$

FS almost nested

$\Rightarrow$ instability when t' is small enough

Final remark: The same "Fermi surface nesting instability" underlies other ordering phenomena, e.g., spin-density wave formation.

Transition at finite temperature: $E \to$ free energy

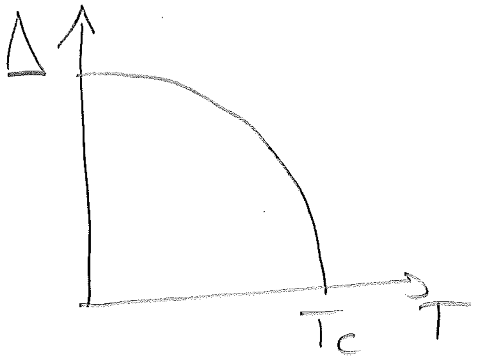
$$F[u_0] = \alpha |u_0|^2 + F_{electron}[u_0]$$

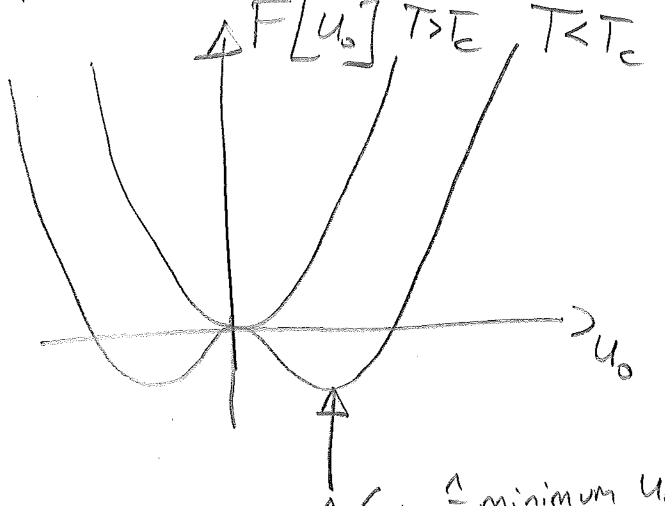
$$F_{electron} = U - TS$$

$$U = \frac{1}{2\pi} \int_{-Q/2}^{Q/2} dk \sum_{s=\pm} \frac{\varepsilon_k^\pm}{e^{\beta \varepsilon_k^\pm} + 1}$$

$k_B T \gg \Delta_{T=0}$ (gap at $T=0$) $\Rightarrow$

energy gain becomes small compared to energy cost for deformation





$\Delta(T) \hat{=}$ minimum $u_0[T]$

6) Ginzburg-Landau theory

- phenomenological theory for phase transitions with spontaneous symmetry breaking
- for superconductivity: 1950
  relation to BCS theory (1957) clarified by Gor'kov ~1960

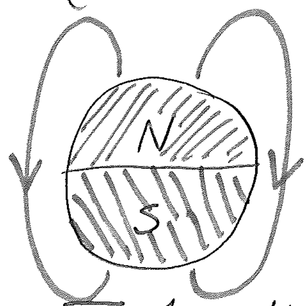
The order parameter

The order parameter $\mathcal{O}$ is a macroscopic quantity which is nonzero below the transition temperature ($T<T_c$) and zero above ($T>T_c$)

Examples:

- Ferromagnet $\qquad \mathcal{O} \mathrel{\hat{=}} M$ (magnetization density) ($\hat{=}$ vector in $\mathbb{R}^3$)

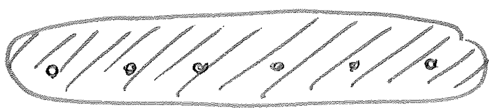
(paramagnet)



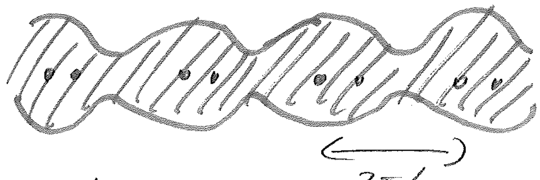
$T < 1040$ K

- Charge-density wave (Peierls)

$T>T_c$



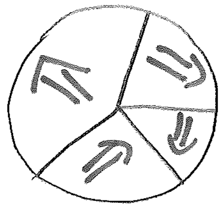
$T<T_c$



$\mathcal{O} \mathrel{\hat{=}}$ Fourier component of charge density ρ_Q

Note 1) The order parameter can be position-dependent

Example: magnetic domains

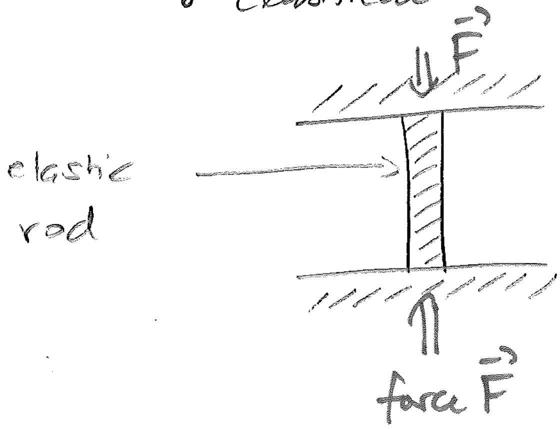


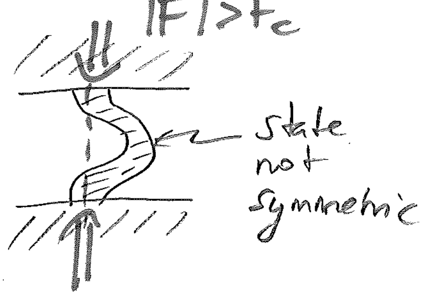
$\vec{M}(\vec{r})$

Note 2) Nonzero $\mathcal{O}$ $\longleftrightarrow$ spontaneous symmetry breaking,

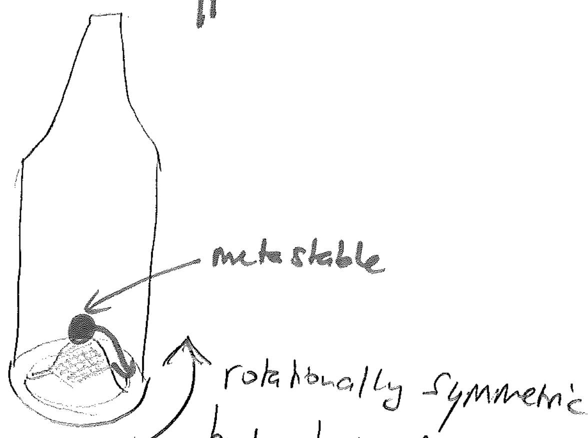
i.e. the symmetry of the state is lower than the symmetry of the underlying (microscopic) description

- classical example: (of course not a thermal transition)





- wine bottle example



- general phenomenological description of 2nd order (continuous) phase transitions:

Landau ~ 1930

(GL)

- Ginzburg & Landau (1950): observed effects in SC (Meissner effect) $\longleftrightarrow$ $\Theta = \psi(\vec{r})$ a complex order parameter

macroscopic, classical field

- GL theory: Θ determined by minimizing a free energy function(al) $F[\Theta(x), T]$

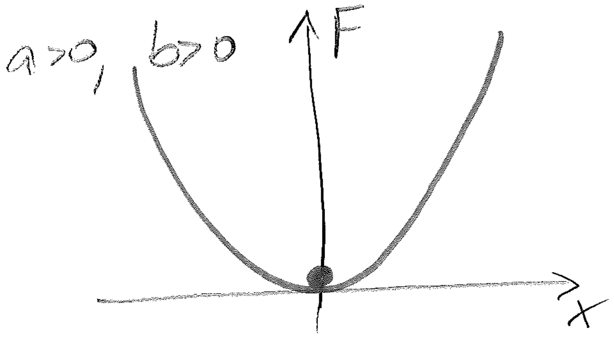
- $F[\Theta]$ is unknown in general, but many general features of the phase transition follow from very few assumptions

1) $\Theta = 0$ for $T > T_c$
2) $F[\Theta]$ must be invariant under all symmetry operations of high-T phase
3) $T \to T_c$, Θ vanishes continuously
$\longrightarrow$ expansion $F[\Theta]$ in Θ-powers possible

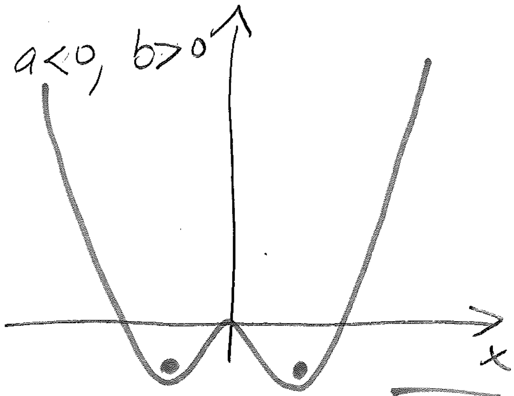
Example: charge-density wave

- scalar $\Theta = X$
- inversion symmetry $X \to -X$

$$F[X,T] = \underbrace{F_n(T)}_{\text{normal phase}} + \underbrace{a(T)\,X^2 + \frac{b(T)}{2}X^4 + \dots}_{\text{expansion around } X=0,\ \text{no odd terms because of inversion symmetry}}$$



$X_{min} = 0$

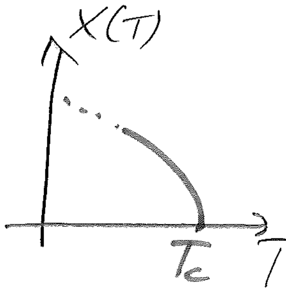


$X_{min} = \pm\sqrt{-\frac{a}{b}}$

⇝ phase transition $\hat{=}$ $a = 0 \Rightarrow a(T_c) = 0$

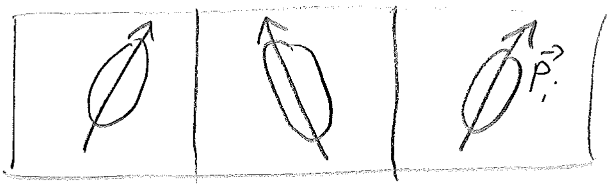
⇝ expand $a(T) \approx \underbrace{\left.\frac{da}{dT}\right|_{T_c}}_{>0} (T - T_c)$

⇝ $X(T) \underset{T \lesssim T_c}{=} \sqrt{\frac{da/dT|_{T_c}}{b(T_c)}} \sqrt{T_c - T}$



- <u>Vector order parameter</u>

polar molecules in cubic crystal



$\mathcal{O}$ $\hat{=}$ <u>macroscopic</u> polarization $\vec{P} = \frac{1}{N} \sum_i \vec{P}_i$

$F[\vec{P}]$: invariant under all point group operations of cubic symmetry

Taylor: $F[\vec{P}] = \alpha \vec{P}^2 + \beta \vec{P}^4 + \gamma \underbrace{(P_x^4 + P_y^4 + P_z^4)}_{\text{not possible in isotropic medium}} + \dots$

⇝ additional phenomenological parameter γ $\hat{=}$ crystalline anisotropy

⇝ depending on β or γ, the transition <u>can only occur in two possible ways</u>:

1) $\vec{P}$ along crystal axis

2) $\vec{P}$ along body diagonal

$\Rightarrow$ nontrivial prediction from GL theory based on symmetry alone

- <u>Coherence length</u>

Spatially dependent $\vec{\mathcal{O}}(\vec{r})$ (e.g., domains)

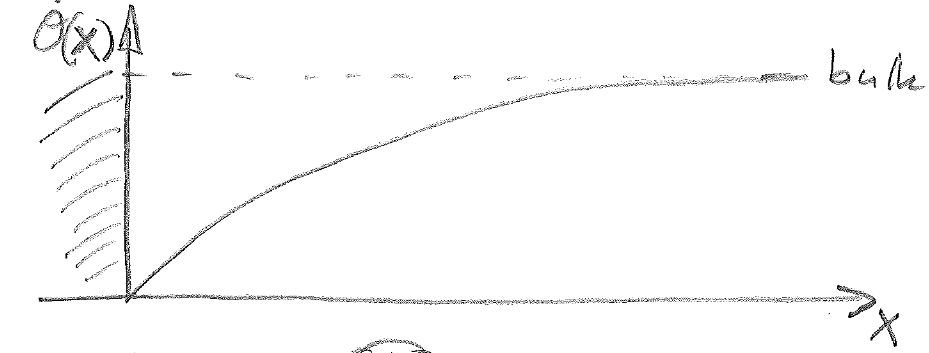
$\Rightarrow$ free energy (scalar)

$$F[\mathcal{O}(\vec{r})] = \int d^3r \left\{ a|\mathcal{O}|^2 + \frac{b}{2}|\mathcal{O}|^4 + \xi_0^2 |\vec{\nabla}\mathcal{O}|^2 \right\} \quad (*)$$

free energy cost for deformation

Consequence: $\mathcal{O}$ cannot change abruptly but only on certain correlation length

e.g., surface



minimization of $(*)$

$\hat{=}$ diff. eqn. $\xi_0^2 \vec{\nabla}^2 \mathcal{O} = a\mathcal{O} + b|\mathcal{O}|^2\mathcal{O}$

asymptotically $\mathcal{O}(x) = \underbrace{\mathcal{O}_\infty}_{\sqrt{-\frac{a}{b}}} + \text{const.}\, e^{-x/\xi}$

$a = a(T-T_c)$

divergent correlation length at transition

$$\xi(T) = \frac{\xi_0}{\sqrt{-2a(T)}} \sim \frac{1}{\sqrt{T_c - T}}$$