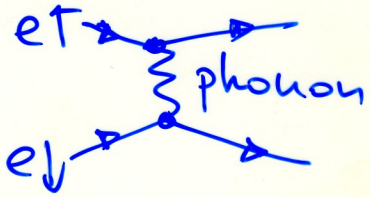
Crystal lattices: Beyond static approximation

lattice vibrations → phonons

Specific heat (low-T: $\sim T^3$)

Thermal expansion (anharmonic effects..)
Melting of crystals

Transport properties:
electron-phonon scattering ⇒ resistivity
superconductivity



Cooperons

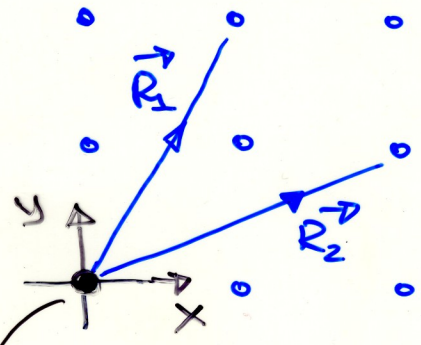
thermal conductivity

Interaction with radiation
FIR absorption
Inelastic light scattering

...
...

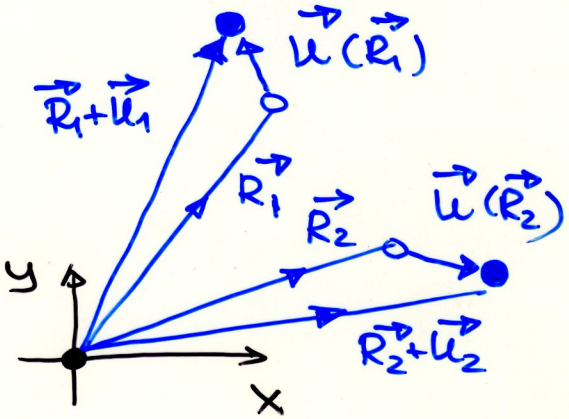
I. Harmonic approximation

① Lattice displacement $\vec{u}(\vec{R})$



"ideal" BL

positions counted from some fixed point (origin)



$\vec{R} \to \vec{r}(\vec{R}) = \vec{R} + \vec{u}(\vec{R})$

when $\vec{u}(\vec{R}) = \vec{u} = \text{const}$

the crystal is moved as a whole

$\Rightarrow$ no deformation $\Rightarrow$ no effects

Energy of deformation

$$U = U(\vec{u}(\vec{R}))$$?

Eg. Long-wavelength description

$\vec{R}$ - continuous variable, $\vec{u}(\vec{R})$ - vector field

$\phi(\vec{R}-\vec{R}')$ interatomic interaction potential

Static lattice

$$U = \frac{1}{2}\sum_{\vec{R}'\neq\vec{R}} \phi(\vec{R}-\vec{R}') = \frac{N}{2}\sum_{\vec{R}\neq 0}\phi(\vec{R})$$

N, number of atoms

Lattice with displacements

$$U = \frac{1}{2}\sum_{\vec{R}'\neq\vec{R}} \phi\left(\vec{R}+\vec{u}(\vec{R}) - \vec{R}'-\vec{u}(\vec{R}')\right)$$

N dynamical variables

velocities of atoms

$$\vec{V}(\vec{R}) = \dot{\vec{R}}+\dot{\vec{u}}(\vec{R}) = \dot{\vec{u}}(\vec{R}) = \frac{d\vec{u}}{dt}$$

Momenta

$$\vec{P}(\vec{R}) = M\vec{V}(\vec{R}) = M\dot{\vec{u}}(\vec{R})$$

M, atoms mass

Hamiltonian

$$H = \sum_{\vec{R}} \frac{\vec{P}^2}{2M} + U(\vec{u})$$

classical

quantum description

quantization

$$\left[\hat{P}_i, \hat{u}_j\right] = -i\hbar\delta_{ij}$$

$U(\vec{u})$ contains high powers of $\vec{u}$

$\vec{u}$ small compared to lattice constant

$\Rightarrow$ expansion in $\vec{u}$!

$$\phi\big(\underbrace{\vec{R}-\vec{R}'}_{\vec{r}} + \underbrace{\vec{u}(\vec{R})-\vec{u}(\vec{R}')}_{\vec{a}}\big) \qquad \vec{\nabla} = \frac{\partial}{\partial \vec{r}}$$

$$f(\vec{r}+\vec{a}) = f(\vec{r}) + (\vec{a}\cdot\vec{\nabla})f(r) + \frac{1}{2!}(\vec{a}\cdot\vec{\nabla})^2 f(r) + \dots$$

$$U = \frac{1}{2}\sum_{\vec{R}'\neq\vec{R}} \Big\{ \phi(\vec{R}-\vec{R}') + \big(\vec{u}(\vec{R})-\vec{u}(\vec{R}')\big)\cdot\vec{\nabla}\phi(\vec{R}-\vec{R}') + \frac{1}{2}\Big[\big(\vec{u}(\vec{R})-\vec{u}(\vec{R}')\big)\cdot\vec{\nabla}\Big]^2 \phi(\vec{R}-\vec{R}') + \dots \Big\}$$

static energy

equilibrium: $\not\phi$

$$\sum_{\vec{R}'} \vec{\nabla}\phi(\vec{R}-\vec{R}') = \vec{F}(\vec{R}) = 0$$

first non-vanishing contribution in $\vec{u}$

keeping this term $\equiv$ Harmonic approx.

$$U^{harm} = \frac{1}{4}\sum_{\vec{R}'\neq\vec{R}} \big[u_\mu(\vec{R})-u_\mu(\vec{R}')\big]\cdot\phi_{\mu\nu}(\vec{R}-\vec{R}')\cdot \big[u_\nu(\vec{R})-u_\nu(\vec{R}')\big]$$

$$\phi_{\mu\nu} \equiv \frac{\partial^2\Phi}{\partial R_\mu \partial R_\nu} = \phi_{\nu\mu}$$ second derivative

Rewrite more simply: $\mu, \nu = x, y, z$

$$U^{harm} = \frac{1}{2} \sum_{\vec{R}' \neq \vec{R}} D_{\mu\nu}(\vec{R}-\vec{R}')\, u_\mu(\vec{R})\, u_\nu(\vec{R}')$$

$$D_{\mu\nu} = \delta_{\vec{R},\vec{R}'} \sum_{\vec{R}''} \Phi_{\mu\nu}(\vec{R}-\vec{R}'') - \Phi_{\mu\nu}(\vec{R}-\vec{R}')$$

Quite a general expression.
Range of validity is wider than used in derivation // pair-wise interaction between atoms //

example: covalent crystals

atom cores (ions) displace $\Rightarrow$ valence electron redistribution... a lot of complicated microscopic physics

Calculation of atomic force constants $D_{\mu\nu}$: adiabatic approximation can be used

electrons move much faster than ions

$v_e \sim v_F \simeq 10^8 \frac{cm}{sec}$ $\quad v_{ion} \simeq 10^5 \frac{cm}{sec}$

Specific heat of a classical crystal

Some recipes of statistical physics

$$W(E) \sim \exp\left(-\frac{E}{k_B T}\right)$$ (J.W. Gibbs 1901)

probability that a system at <u>equilibrium</u> and at temperature T occupies a state with energy E

Boltzmann constant $k_B = 1.36 \times 10^{-16}$ erg/K

T in Kelvins $\longrightarrow$ $k_B T$ temperature in erg

Convenient to measure T in energy units

$k_B T \equiv T$ (formally $k_B = 1$)

How to distinguish different states that system can occupy ? How to measure them?

Phase Space Γ

$$d\Gamma = \frac{d^3P\, d^3R}{(2\pi\hbar)^3} \Longleftrightarrow H(P,R)$$

Hamiltonian

$\downarrow$

energy E

Calculating mean values of any functions $\Psi(R,P)$

$$\langle \Psi(R,P) \rangle = \frac{\int d\Gamma\, e^{-H/T}\, \Psi(R,P)}{\int d\Gamma\, e^{-H/T}}$$

statistical averaging

Back to our problem:

$\vec{u}(\vec{R})$, $\vec{P}(\vec{R})$

3N variables

3N variables

N lattice points $\vec{R}$ * 3 cartesian component of vectors

In fact should exclude some:

3 - displacement of a crystal as a whole

3 - rotations of a crystal

$$6N - 6 = 6N$$

$6N \ggg 6$ macroscopic crystals

relevant for molecules!

$$d\Gamma = \frac{(d\vec{u}_1 \cdot \ldots \cdot d\vec{u}_N)(d\vec{P}_1 \cdot \ldots \cdot d\vec{P}_N)}{(2\pi\hbar)^{3N}} = \prod_{i=1}^{N} \frac{(d\vec{u}_i\, d\vec{P}_i)}{(2\pi\hbar)^3}$$

$$\vec{u}_i = \vec{u}(\vec{R}_i) \qquad \vec{P}_i = \vec{P}(\vec{R}_i)$$

$$H = \sum_{i=1}^{N} \frac{\vec{P}_i^{\,2}}{2M} + \frac{1}{2}\sum_{i\neq j}^{N} D_{\mu\nu}(\vec{R}_i - \vec{R}_j)\, u_{i\mu} u_{j\nu}$$

Let is calculate mean energy U

$$U = U(T) = \frac{\int d\Gamma\, e^{-\frac{H}{T}} H}{\int d\Gamma\, e^{-\frac{H}{T}}} \qquad e^{-\frac{H}{T}} \equiv e^{-\beta H}$$

$$\beta = \frac{1}{T}$$

energy density $u = U/V$ ← crystal volume

$$u = -\frac{1}{V}\frac{\partial}{\partial\beta} \ln\left(\int d\Gamma\, e^{-\beta H}\right)$$

↑ a usual trick.

and another trick to extract T-dependence of u:

$$\vec{u}_i \to \vec{\tilde{u}}_i = \sqrt{\beta}\,\vec{u}_i \qquad \vec{P}_i \to \vec{\tilde{P}}_i = \sqrt{\beta}\,\vec{P}_i$$

change of variables

$$d\vec{u}_i = du_{ix}\, du_{iy}\, du_{iz} = \beta^{-3/2}\, d\vec{\bar{u}}_i$$

$$u_{ix} = \bar{u}_{ix}/\sqrt{\beta} \qquad du_{ix} = \frac{1}{\sqrt{\beta}}\, d\bar{u}_{ix}$$

$$d\vec{p}_i = \beta^{-3/2}\, d\vec{\bar{p}}_i$$

$$d\Gamma = \prod_{i=1}^{N} \frac{d\vec{u}_i\, d\vec{p}_i}{(2\pi\hbar)^3} = \beta^{-3N} \prod_{i=1}^{N} \frac{d\vec{\bar{u}}_i\, d\vec{\bar{p}}_i}{(2\pi\hbar)^3}$$

$$\beta H(\vec{u}_i, \vec{p}_i) = \sum_{i=1}^{N} \frac{\vec{\bar{p}}_i^{\,2}}{2M} + \frac{1}{2} \sum_{i \neq j} D_{\mu\nu}(\vec{R}_i - \vec{R}_j)\, \bar{u}_{i\mu}\, \bar{u}_{j\nu}$$

$$\int d\Gamma\, e^{-\beta H} = \beta^{-3N} \cdot \int \prod_{i=1}^{N} \frac{d\vec{\bar{u}}_i\, d\vec{\bar{p}}_i}{(2\pi\hbar)^3}\, e^{-\beta H}$$

const: does not depend on β!

$$u = -\frac{1}{V} \frac{\partial}{\partial \beta} \ln\left(\beta^{-3N} \cdot \text{const}\right)$$

$$u = -\frac{1}{V} \cdot (-3N) \cdot \frac{\partial}{\partial \beta} \ln\beta = 3\frac{N}{V}\, \frac{1}{\beta} = 3\frac{N}{V}\, kT$$

$$\frac{N}{V} = n \qquad T \to k_B T$$

$$\boxed{u = 3n k_B T}$$

Interpretation

Total thermal energy of lattice vibrations:

$$U = V \cdot u = 3NK_BT$$

N - number of lattice points

6N degrees of freedom

3N independent oscillator modes

$$h = \frac{m\dot{x}^2}{2} + \frac{kx^2}{2}$$

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \left\langle \frac{mv_x^2}{2} \right\rangle = \frac{1}{2}K_BT$$

$$\left\langle \frac{kx^2}{2} \right\rangle = \frac{1}{2}K_BT$$

each oscillator degree of freedom brings in $\frac{1}{2}K_BT$ at thermal equilibrium

(statistical classical mechanics only!)

equipartition

$u = u(T)$ energy

$\Downarrow$

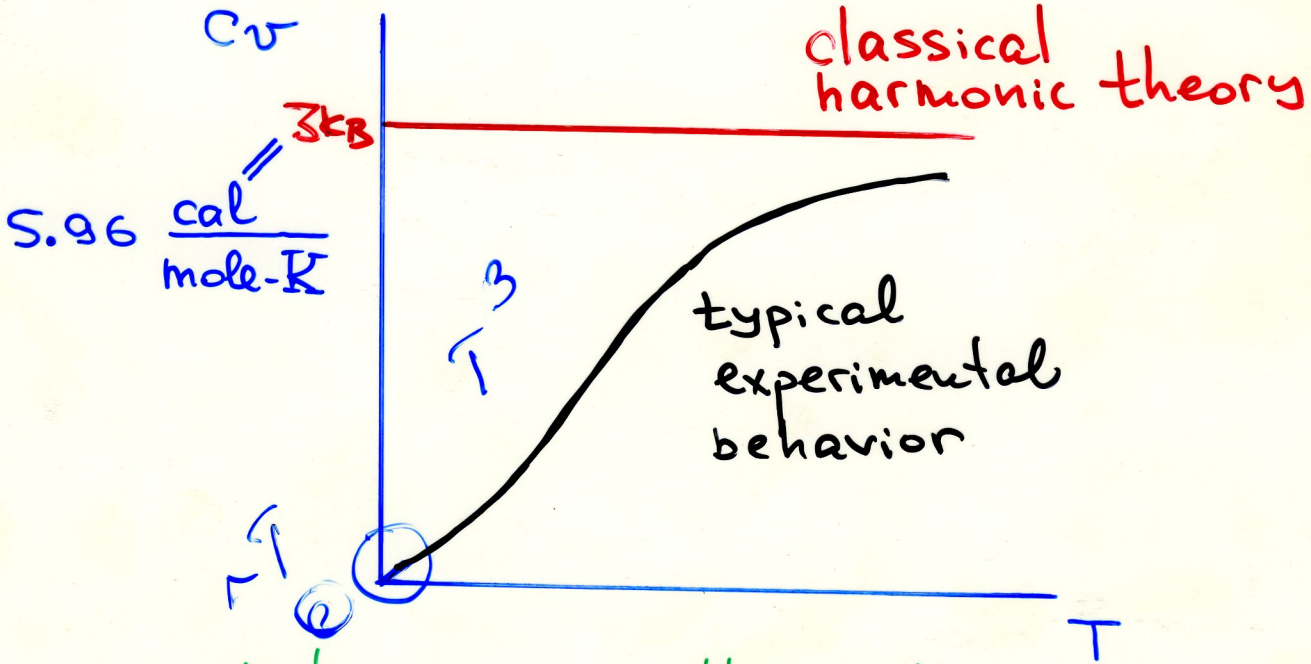
exctract specific heat C_v

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = 3nk_B$$

at constant volume

The law of Dulong and Petit

$C_v = 3k_B$ per atom



What is wrong with the theory at low T ??

$C_v = 3 k_B$ per atom

$$C_v^{molar} = 5.96 \frac{cal}{mole\text{-}K}$$

$$1\,cal = 4.2 \times 10^7\ erg$$

$$1\,mole = 6.02 \times 10^{23}\ atoms$$

$$k_B = 1.38 \times 10^{-16} \frac{erg}{K}$$

$$\frac{C_v^{molar}}{C_v} = \frac{5.96 \cdot 4.2 \times 10^7 \frac{erg}{6.02 \times 10^{23}\ K}}{3 \cdot 1.38 \times 10^{-16} \frac{erg}{K}} = 1.$$