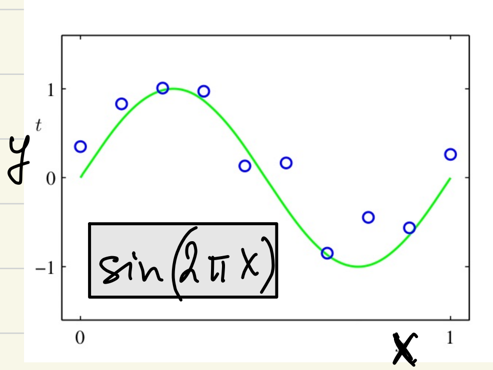
- Machine learning can be used to create the force field using results of expensive DFT calculations as a training set.

$\boxed{\text{Curve fitting problem}}$ as an example



$$y(x,\vec{w}) = w_0 + w_1 x + w_2 x^2 + \dots + w_M x^M = \sum_{\alpha=0}^{M} w_\alpha x^\alpha \quad (13)$$

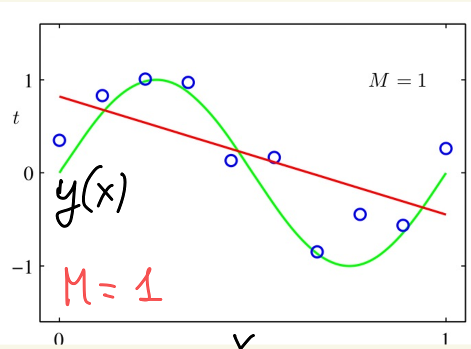
We would like to obtain the "best" set of $\vec{w}$ given our training set (x_n, y_n), $n = 1, \dots, N$

- Naive approach   min error $E[\vec{w}] = \frac{1}{2}\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w})\right)^2$ (14)

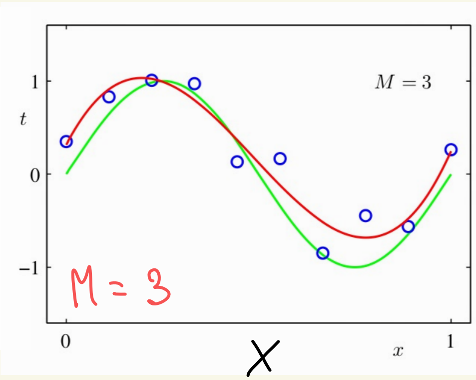
$$\frac{\partial E}{\partial w_\alpha} = \sum_n \left(y_n - y(x_n,\vec{w})\right)\left(-\alpha w_\alpha x_n^{\alpha-1}\right) = 0$$

$\boxed{\text{Very large } w_\alpha \text{ !!!}}$

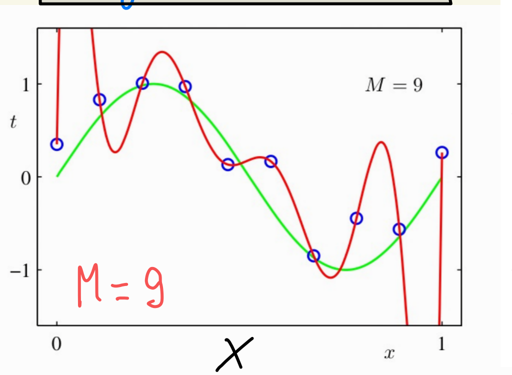
Bigger data set!



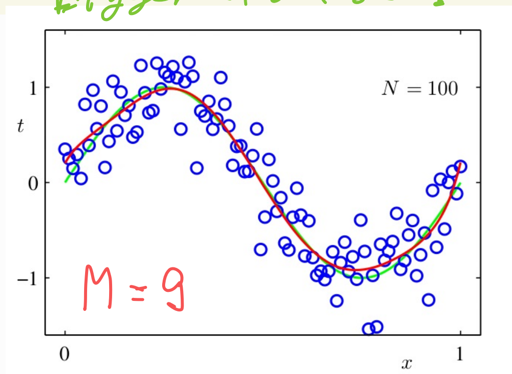
bad fit



good fit

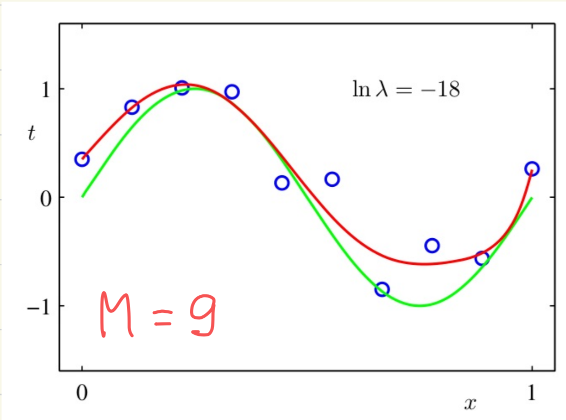


overfitting
(exact match at x_n)



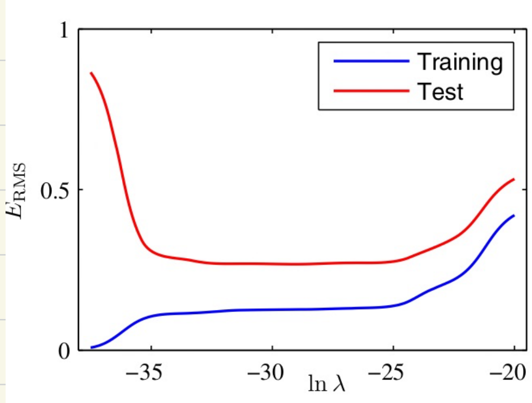
perfect fit

- **Regularisation to eliminate the overfitting problem**



$$E[\vec{w}] = \frac{1}{2}\sum_n \left(y_n - y(x_n,\vec{w})\right)^2 + \frac{\lambda}{2}\vec{w}^2 \qquad (15)$$

a penalty for large w_α



- **Probabilistic approach** We want to make predictions based on the info we have (the training set).

Introduce the likelihood function:

$$p_{LH}(\vec{w},\sigma) = \prod_{n=1}^{N} \mathcal{N}\left(y_n \mid y(x_n,\vec{w}),\sigma\right) = \prod_{n=1}^{N}\frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{1}{2\sigma^2}\left(y_n - y(x_n,\vec{w})\right)^2\right] \qquad (16)$$

- **Maximise the likelihood** to get the "best" $\vec{w}$ and σ^2:

$$\max \ln\left[p_{LH}(\vec{w},\sigma)\right] \Rightarrow \max\left\{-N\ln\sqrt{2\pi\sigma^2} - \frac{1}{2\sigma^2}\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w})\right)^2\right\} \qquad (17)$$

$\boxed{\vec{w}}$ $\quad \min\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w})\right)^2 \Rightarrow \vec{w}_{ML}$ $\qquad$ $\boxed{\sigma^2}$ $\quad \sigma^2_{ML} = \frac{1}{N}\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w}_{ML})\right)^2 \qquad (18)$

Prediction: $p(y|x) = \mathcal{N}\left(y \mid y(x,\vec{w}_{ML}),\sigma_{ML}\right)$ gives y for a new x $\qquad (19)$

Overfitting is not avoided, however!

- **Maximising posterior distribution** (Bayesian approach)

$$\text{posterior} \sim \underbrace{\text{likelihood}}_{\substack{\text{conditional}\\ \text{probability of}\\ \text{the training set}\\ \text{given parameters } \vec{w}}} \times \underbrace{\text{prior}}_{\substack{\text{probability}\\ \text{to have the}\\ \text{parameters } \vec{w}\\ P(\vec{w},\alpha)}} \tag{20}$$

$$P(\vec{w},\alpha) = \left(\frac{\alpha}{2\pi}\right)^{\frac{M+1}{2}} \exp\left(-\frac{\alpha}{2}\vec{w}^{\,2}\right), \quad \alpha \text{ – another parameter} \tag{21}$$

Hence, the posterior:

$$\boxed{P_{PD}(\vec{w}\,|\,\{x_n,y_n\},\sigma,\alpha) \sim P_{LH}(\vec{w},\sigma)\,P(\vec{w},\alpha)} \tag{22}$$

Maximise its logarithm with respect to $\vec{w}$:

$$\ln P_{PD} \sim -N\ln\sqrt{2\pi\sigma^2} - \frac{1}{2\sigma^2}\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w})\right)^2 + \frac{M+1}{2}\ln\frac{\alpha}{2\pi} - \frac{\alpha}{2}\vec{w}^{\,2} \tag{23}$$

$$\frac{\partial}{\partial w_\alpha}\text{"} = 0 \Rightarrow \min\left\{+\frac{1}{2\sigma^2}\sum_{n=1}^{N}\left(y_n - y(x_n,\vec{w})\right)^2 + \frac{\alpha}{2}\vec{w}^{\,2}\right\} \tag{24}$$

which is basically the regularisation method!

Prediction:

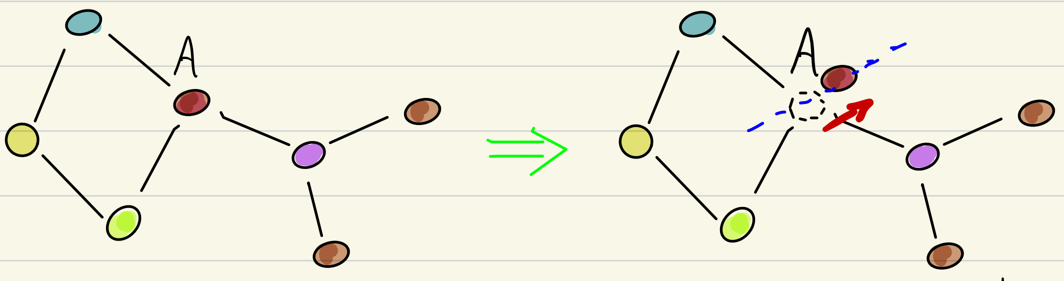
$$\boxed{P(y|x) = \int d\vec{w}\,\mathcal{N}(y|x,\vec{w})\,P_{PD}(\vec{w})} \tag{25}$$

$\Rightarrow$ Gaussian as well

Using ab initio methods

- Frozen phonon approximation

$U_\xi(R)$ – ground state property, can differentiate numerically

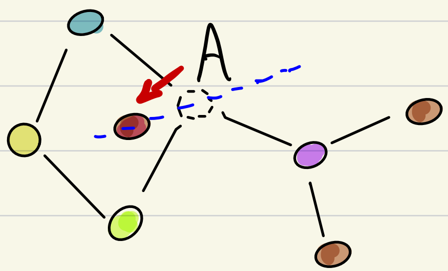


$u_{A\alpha} \neq 0$ only!

$$F^{(+)}_{B\beta} = -\sum_{A'\alpha'} \Phi_{B\beta, A'\alpha'} u_{A'\alpha'} = -\Phi_{B\beta, A\alpha} u_{A\alpha}$$

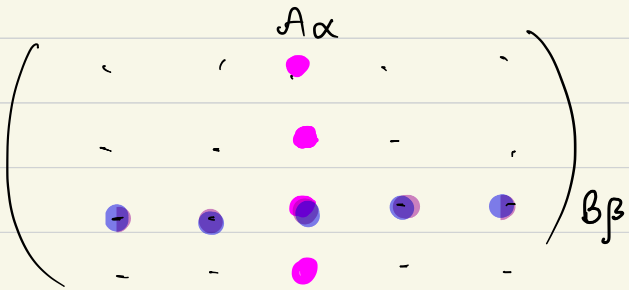
$$\boxed{\Phi_{B\beta, A\alpha} = -F^{(+)}_{B\beta} / u_{A\alpha}}$$

Better precision:
– $u_{A\alpha}$ as well



$$\boxed{\Phi_{B\beta, A\alpha} \simeq -\left(F^{(+)}_{B\beta} - F^{(-)}_{B\beta}\right) / u_{A\alpha}}$$

$\Phi_{B\beta, A\alpha} =$

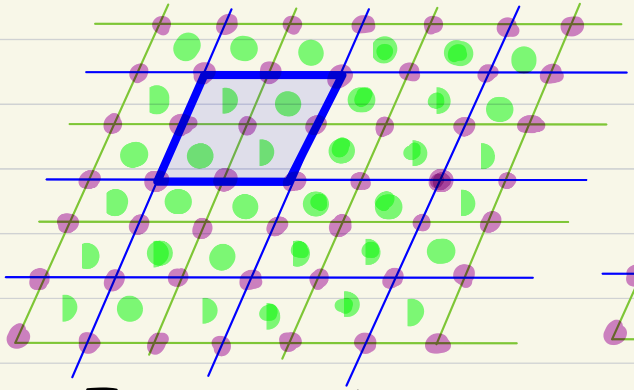


It won't be symmetric. Need to impose the symmetrisation posteriori by either accepting

or averaging over two.

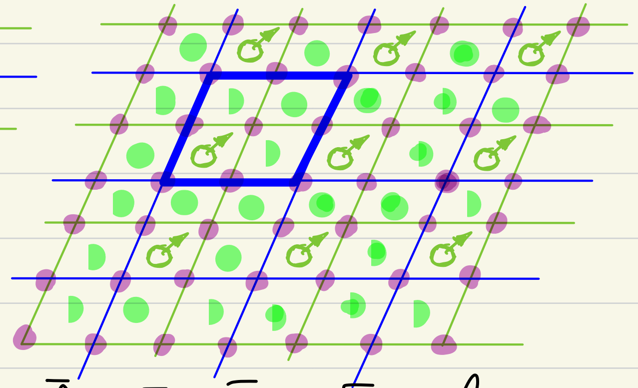
Symmetry: the number of calculations can be reduced.

Periodic boundary conditions (crystal phonons)



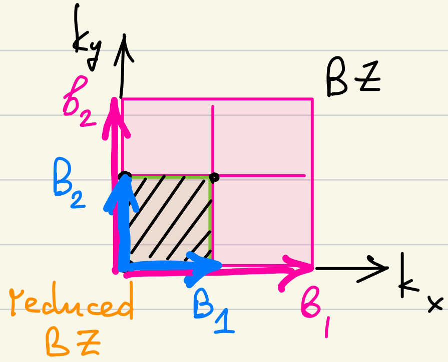
$\bar{a}_1, \bar{a}_2$ – primitive

$\bar{b}_1, \bar{b}_2$ – reciprocal



$\bar{A}_1 = 2\bar{a}_1,\ \bar{A}_2 = 2\bar{a}_2$ – large

$\bar{B}_1 = \bar{b}_1/2,\ \bar{B}_2 = \bar{b}_2/2$



$$\underset{\text{all}}{\vec{L}} = \underset{\text{large}}{\vec{N}} + \underset{\text{internal}}{\vec{n}}$$

- $$D_{s\alpha,s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_L \Phi^{L,0}_{s\alpha,s'\alpha'} e^{-ikL} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_N \sum_n \Phi^{N+n,0}_{s\alpha,s'\alpha'} e^{-ik(N+n)}$$

$$= \frac{1}{\sqrt{M_s M_{s'}}} \sum_n \left[\sum_N \Phi^{N+n,0}_{s\alpha,s'\alpha'} e^{-ikN} \right] e^{-ikn} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_n f^{n}_{s\alpha,s'\alpha'}(k)\, e^{-ikn}$$

- Displace $u_{0s_1\alpha_1}$ from $\vec{n}=0$: $\quad F_{ns\alpha} = -\left[\sum_N \Phi^{N+n,0}_{s\alpha,s_1\alpha_1} \right] u_{0s_1\alpha_1}$

For those $k \in BZ$, for which $\exp(i\vec{k}\vec{N}) = 1$, this gives $f^{n}_{s\alpha,s_1\alpha_1}$ exactly.

These are $k \in BZ$, which become $\sum_j m_j \vec{B}_j$ in the reduced BZ:

$$\exp\Big[-i \sum_j m_j \vec{B}_j \cdot \underbrace{\vec{N}}_{\sum_k p_k \vec{A}_k}\Big] = \exp\Big[-i \sum_{jk} m_j p_k \underbrace{\vec{B}_j \cdot \vec{A}_k}_{2\pi\,\delta_{jk}}\Big] = \exp(-2\pi i(\text{integer})) = 1$$

For crystals with PBC this method would only give vibrations for certain $\vec{k} \in BZ$. Larger UC are needed to have more $\vec{k}$ points reproduced.

The method is EXACT!

- Practical steps:

  1. given extension $\vec{A}_i = \sum_j T_{ij} \vec{a}_j$, determine all internal translations $\vec{n}$
  2. determine all $\vec{k} \in BZ$ that satisfy $e^{i\vec{k}\vec{N}} = 1$ for this extension — equivalent to $\vec{k}=0$ from rBZ
  3. displace atoms in the primitive unit cell $\Rightarrow f^{n}_{s\alpha, s'\alpha'}$
  4. calculate $\mathcal{D}_{s\alpha, s'\alpha'}(k) = \sum_{\vec{n}} f^{n}_{s\alpha, s'\alpha'} e^{-i\vec{k}\vec{n}}$ for $\forall\, \vec{k} \in BZ$ equiv. to $\vec{k}=0$ from rBZ

- Playing with supercells:
  - one cell → many $\vec{k}$ points (it will then be large)
  - many small cells designed for specific $\vec{k}$ points

  TETR

- Small $\vec{k}$ vectors require VERY LARGE extensions
- Numerical problems: "small" displacements; symmetrisation required.
- Problem: the smallest supercell to give a particular $\vec{k} \in BZ$?

Calculating phonons at other k-points (Interpolation) $\Downarrow$

$$D_{s\alpha,s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_L \Phi^{L,0}_{s\alpha,s'\alpha'} e^{-ikL}$$

$$\Phi^{n,0}_{s\alpha,s'\alpha'} = \sqrt{M_s M_{s'}} \frac{1}{N} \sum_k D_{s\alpha,s'\alpha'}(k) e^{ikn}$$

$$\simeq \sqrt{M_s M_{s'}} \frac{1}{N_r} \sum_{k \in rBZ} D_{s\alpha,s'\alpha'}(k) e^{ikn}.$$

$$\Phi^{N+n,0}_{s\alpha,s'\alpha'} = 0 \text{ for any } N \neq 0$$

Once Φ is known in the direct space, then for any other $k \in BZ$:

$$D_{s\alpha,s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_N \sum_n \Phi^{N+n,0}_{s\alpha,s'\alpha'} e^{-ik(N+n)}$$

$$\simeq \frac{1}{\sqrt{M_s M_{s'}}} \sum_n \Phi^{n,0}_{s\alpha,s'\alpha'} e^{-ikn}$$

$$= \frac{1}{N_r} \sum_{k_r \in rBZ} D_{s\alpha,s'\alpha'}(k_r) \left[\sum_n e^{i(k_r - k)n} \right]$$

Density Functional Perturbation Theory (DFPT)

PRL 58 1861 (1987)

KS equations: $[\hat{t} + \hat{G}(r)]\varphi_\lambda = \varepsilon_\lambda \varphi_\lambda$,

$$\hat{G}(r) = -eV_H(r) + V(r) + V_{xc}(r) = \frac{\delta}{\delta\rho(r)}\left[E_H + E_{xc} + E_{e\text{-}n}\right]$$

Total energy: $E = \sum_\lambda \langle \varphi_\lambda | \hat{t} | \varphi_\lambda \rangle + E_H + E_{xc} + E_{e\text{-}n} + E_{nn}$

Electron density: $\rho(r) = \sum_\lambda^{occ} \varphi_\lambda^*(r)\varphi_\lambda(r)$

Hellmann-Feynman theorem (the 1st energy derivative):

$$\frac{\partial E}{\partial R_{A\alpha}} = \sum_\lambda \langle \varphi_\lambda | \frac{\partial V}{\partial R_{A\alpha}} | \varphi_\lambda \rangle + \frac{\partial E_{nn}}{\partial R_{A\alpha}} = \int \rho(r) \frac{\partial V}{\partial R_{A\alpha}} dr + \frac{\partial E_{nn}}{\partial R_{A\alpha}}$$

2nd energy derivative (Hessian) $[\xi \equiv R_{A\alpha}]$:

$$\frac{\partial^2 E}{\partial\xi\partial\xi'} = \frac{\partial^2 E_{nn}}{\partial\xi\partial\xi'} + \int \rho(r) \frac{\tilde{\partial} V}{\partial\xi\partial\xi'} dr + \int \frac{\partial V}{\partial\xi} \frac{\partial\rho(r)}{\partial\xi'} dr$$

Consider $\hat{G}(r)$ caused by a change $\xi \to \xi + \Delta\xi$ of ξ:

$$\Delta\hat{G}(r) = \Delta V(r) + \int dr' \frac{\delta}{\delta\rho(r')}\left[-eV_H(r) + V_{xc}(r)\right]\Delta\rho(r') = \Delta V(r) + \int dr' \left[\frac{-e}{|r-r'|} + \underbrace{\frac{\delta V_{xc}(r)}{\delta\rho(r')}}_{(LDA)\ \delta(r-r')\left(\frac{dV_{xc}}{d\rho}\right)(r)}\right]\Delta\rho(r')$$

$$\frac{\partial\hat{G}(r)}{\partial\xi'} = \frac{\partial V}{\partial\xi'} + \int \frac{-e}{|r-r'|}\frac{\partial\rho(r')}{\partial\xi'} dr' + \left(\frac{dV_{xc}}{d\rho}\right)(r)\frac{\partial\rho(r)}{\partial\xi'}$$

On the other hand,

$$\Delta\rho(r) = \sum_{\lambda}^{occ} \left[\varphi_\lambda^*(r)\,\Delta\varphi_\lambda(r) + \Delta\varphi_\lambda^*(r)\,\varphi_\lambda(r) \right]$$

where, to the 1st order of perturbation theory:

$$\Delta\varphi_\lambda(r) = \underbrace{\sum_{\lambda'}^{all}{}'}_{v+c\ (\text{all!})} \frac{\langle \varphi_{\lambda'} | \Delta\hat{G} | \varphi_\lambda \rangle}{\varepsilon_\lambda - \varepsilon_{\lambda'}} \varphi_{\lambda'} \,, \quad (\hat{t} + \hat{G})\varphi_\lambda = \varepsilon_\lambda \varphi_\lambda$$

$\boxed{\begin{array}{l} v - \text{occ} \\ c - \text{unocc} \end{array}}$

We finally obtain a <u>self-consistent scheme</u>:

$$\left\{ \begin{array}{l} \dfrac{\partial\rho(r)}{\partial\xi'} = \sum_c \sum_v \dfrac{1}{\varepsilon_v - \varepsilon_c} \left[\langle \varphi_c | \dfrac{\partial\hat{G}(r)}{\partial\xi'} | \varphi_v \rangle \varphi_v^*(r)\,\varphi_c(r) + c.c. \right] \\ \dfrac{\partial\hat{G}(r)}{\partial\xi'} = \dfrac{\partial V}{\partial\xi'} + \displaystyle\int \dfrac{-e}{|r - r'|} \dfrac{\partial\rho(r')}{\partial\xi'}\,dr' + \left(\dfrac{dV_{xc}}{d\rho}\right)(r)\,\dfrac{\partial\rho(r)}{\partial\xi'} \end{array} \right. \Rightarrow \boxed{\text{SCF}}$$

Advantages

- Primitive unit cell $\Rightarrow$ any $\vec{k}$-point accessible
- Symmetry can be used
- Efficient implementation exist in many codes (QE, VASP, etc.)

Dynamic properties via MD: normal modes representation.

$$H = \sum_i \frac{p_i^2}{2M_i} + \frac{1}{2}\sum_{ij} \Phi_{ij} u_i u_j \quad (103), \qquad \mathcal{L} = \sum_i \frac{M_i \dot{u}_i^2}{2} - \frac{1}{2}\sum_{ij} \Phi_{ij} u_i u_j \quad (104)$$

$$PE = \frac{1}{2} u^T \Phi u = \sum_\lambda \frac{1}{2}\omega_\lambda^2 y_\lambda^2(t), \quad (105)$$ **where** $$\boxed{y_\lambda(t) = M^{1/2} \Upsilon_\lambda^T u = \sum_i \sqrt{M_i}\, \Upsilon_{\lambda i} u_i} \quad (106)$$

Hence, $\dot{y}_\lambda = \sum_i \sqrt{M_i}\, \Upsilon_{\lambda i} \dot{u}_i \quad \Big| \times \sum_\lambda \Upsilon_{\lambda j}$ (107)

$$(108) \Rightarrow \sum_\lambda \Upsilon_{\lambda j} \dot{y}_\lambda = \sum_i \sqrt{M_i} \underbrace{\left(\sum_\lambda \Upsilon_{\lambda j} \Upsilon_{\lambda i}\right)}_{\delta_{ij}} \dot{u}_i = \sqrt{M_j}\, \dot{u}_j \Rightarrow \dot{u}_j = \frac{1}{\sqrt{M_j}} \sum_\lambda \Upsilon_{\lambda j} \dot{y}_\lambda \quad (109)$$

Substitute into the KE:

$$KE = \frac{1}{2}\sum_j M_j \dot{u}_j^2 = \frac{1}{2}\sum_{\lambda\lambda'} \underbrace{\left(\sum_j \Upsilon_{\lambda j} \Upsilon_{\lambda' j}\right)}_{\delta_{\lambda\lambda'}} \dot{y}_\lambda \dot{y}_{\lambda'} = \frac{1}{2}\sum_\lambda \dot{y}_\lambda^2 \quad (110)$$

The conjugate momentum:

$$(111) \quad p_\lambda = \frac{\partial \mathcal{L}}{\partial \dot{q}_\lambda} = \frac{\partial}{\partial \dot{q}_\lambda}(KE) = \dot{y}_\lambda = \sum_i \sqrt{M_i}\, \Upsilon_{\lambda i} \dot{u}_i \Rightarrow \boxed{p_\lambda = \sum_i \frac{1}{\sqrt{M_i}} \Upsilon_{\lambda i} p_i} \quad (112)$$

Hence, $KE = \frac{1}{2}\sum_\lambda p_\lambda^2$ (113) and $$\boxed{H = \sum_\lambda \left[\frac{1}{2} p_\lambda^2 + \frac{1}{2}\omega_\lambda^2 y_\lambda^2\right] = \sum_\lambda h_\lambda} \quad (114)$$

$\rightarrow$ EOM $\dot{p}_\lambda = -\omega_\lambda^2 y_\lambda \Rightarrow \boxed{\ddot{y}_\lambda + \omega_\lambda^2 y_\lambda = 0}, \ \boxed{y_\lambda = A_\lambda e^{i\omega_\lambda t} + c.c.}$ (115)

Dynamic properties via MD : vibrational spectrum

- $H = \sum_i \frac{p_i^2}{2M} + \frac{1}{2}\sum_{ij} \Phi_{ij} u_i u_j \equiv \sum_\lambda \left(\frac{p_\lambda^2}{2} + \frac{\omega_\lambda^2 y_\lambda^2}{2} \right)$

$y_\lambda = \sum_i \sqrt{M_i}\, Y_{\lambda i} u_i \leftarrow$ normal coordinates

$p_\lambda = \sum_i \frac{1}{\sqrt{M_i}} Y_{\lambda i} p_i \leftarrow$ normal momenta

$\mathcal{D} = M^{-1/2} \Phi M^{-1/2}$

$\mathcal{D} Y_\lambda = \omega_\lambda^2 Y_\lambda$

EoM : $\ddot{y}_\lambda + \omega_\lambda^2 y_\lambda = 0 \Rightarrow y_\lambda(t) = A_\lambda e^{i\omega_\lambda t} + c.c.$

$u_i(t) = \sum_\lambda \frac{1}{\sqrt{M_i}} Y_{\lambda i} y_\lambda = \sum_\lambda \frac{1}{\sqrt{M_i}} Y_{\lambda i} \left(A_\lambda e^{i\omega_\lambda t} + c.c. \right), \quad p_i(t) = i \sum_\lambda \sqrt{M_i}\, Y_{\lambda i} \omega_\lambda A_\lambda e^{i\omega_\lambda t} + c.c.$

A_λ, A_λ^* can be found from initial positions & momenta :

$$\sqrt{M_i}\, u_i^\circ = \sum_\lambda Y_{\lambda i} (A_\lambda + A_\lambda^*) \quad \text{and} \quad \frac{1}{\sqrt{M_i}} p_i^\circ = i \sum_\lambda Y_{\lambda i} (A_\lambda - A_\lambda^*)$$

$$\Rightarrow A_\lambda = \sum_i Y_{\lambda i} \left[\sqrt{M_i}\, u_i^\circ + \frac{1}{i\omega_\lambda \sqrt{M_i}} p_i^\circ \right] \frac{1}{2} .$$

This yields:

$$\boxed{\begin{cases} u_i(t) = \sum_{j\lambda} Y_{i\lambda} Y_{j\lambda} e^{i\omega_\lambda t} \left[u_j^\circ \left(\frac{1}{2}\sqrt{\frac{M_j}{M_i}} \right) + p_j^\circ \left(\frac{1}{2i\sqrt{M_i M_j}\, \omega_\lambda} \right) \right] + c.c. \\ p_i(t) = \sum_{j\lambda} Y_{i\lambda} Y_{j\lambda} e^{i\omega_\lambda t} \left[u_j^\circ \left(\frac{i}{2} \sqrt{M_i M_j}\, \omega_\lambda \right) + p_j^\circ \left(\frac{1}{2}\sqrt{\frac{M_i}{M_j}} \right) \right] + c.c. \end{cases}}$$

- **Statistical averages:** $H = \sum_\lambda h_\lambda$, $h_\lambda = (p_\lambda^2 + \omega_\lambda^2 y_\lambda^2)/2$

Jacobian: $\prod_i du_i dp_i = J \prod_\lambda dy_\lambda dp_\lambda$, $J = \left|\frac{\partial(u_i p_j)}{\partial(y_\lambda p_{\lambda'})}\right| = \left|\frac{\partial u_i}{\partial y_\lambda}\right| \cdot \left|\frac{\partial p_j}{\partial p_{\lambda'}}\right| = |M^{-\frac{1}{2}} e| \cdot |M^{1/2} e| = 1$

$$\langle A_\lambda \rangle = \prod_{\lambda'} \frac{1}{Z_{\lambda'}} \int dy_{\lambda'} dp_{\lambda'}\, e^{-\beta h_{\lambda'}} A_\lambda = \frac{1}{Z_\lambda} \int dy_\lambda dp_\lambda\, e^{-\beta h_\lambda} A_\lambda \,, \quad Z_\lambda = \frac{2\pi}{\beta \omega_\lambda}$$

$$\langle y_\lambda^o \rangle = \langle p_\lambda^o \rangle = \langle y_\lambda^o p_{\lambda'}^o \rangle = 0 \,, \quad \langle y_\lambda^o y_{\lambda'}^o \rangle = \delta_{\lambda\lambda'} \frac{1}{\beta \omega_\lambda^2} \,, \quad \langle p_\lambda^o p_{\lambda'}^o \rangle = \delta_{\lambda\lambda'} \frac{1}{\beta}$$

$$\Rightarrow \begin{cases} \langle u_i^o u_j^o \rangle = \dfrac{1}{\sqrt{M_i M_j}} \sum_{\lambda\lambda'} Y_{\lambda i} Y_{\lambda' j} \langle y_\lambda^o y_{\lambda'}^o \rangle = \dfrac{1}{\beta} \dfrac{1}{\sqrt{M_i M_j}} \sum_\lambda \dfrac{Y_{\lambda i} Y_{\lambda j}}{\omega_\lambda} \\ \langle p_i^o p_j^o \rangle = \sqrt{M_i M_j} \sum_{\lambda\lambda'} Y_{\lambda i} Y_{\lambda' j} \langle p_\lambda^o p_{\lambda'}^o \rangle = \dfrac{1}{\beta} M_i \delta_{ij} \end{cases} \quad \Bigg\| \quad \langle u_i^o p_j^o \rangle = 0$$

Consider now the correlation function:

$$\Rightarrow \sum_i \frac{1}{M_i} \langle p_i(t) p_i(t') \rangle = \frac{1}{\beta} \sum_\lambda \cos\omega_\lambda (t-t') \qquad \text{(after some (!) algebra)}$$

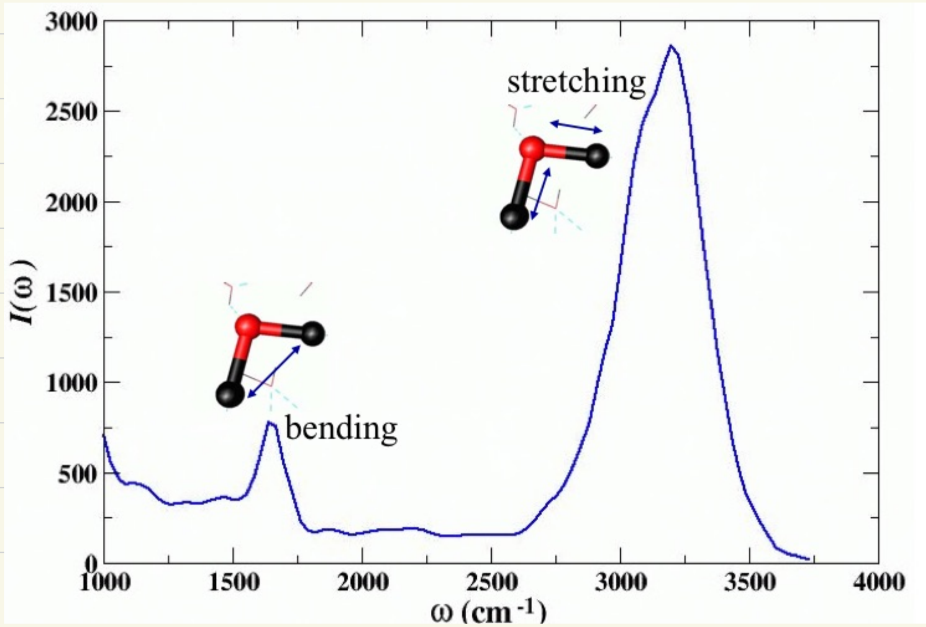
since $\sum_j Y_{\lambda j} Y_{\lambda' j} = \delta_{\lambda\lambda'}$ and $\sum_\lambda Y_{\lambda i} Y_{\lambda j} = \delta_{ij}$.

Take the FT:

$$\mathcal{F}[\dots] = \frac{1}{\beta} \sum_\lambda \int_{-\infty}^{\infty} e^{i\omega\tau} \cos\omega_\lambda \tau \, d\tau$$

$$= \frac{2\pi}{\beta} \sum_\lambda \delta(\omega^2 - \omega_\lambda^2)$$

$\boxed{\text{phonon DOS}}$



Quantum consideration

$$PE = \frac{1}{2}\sum_{ij}\Phi_{ij}u_i u_j \Rightarrow \left[\sum_i \frac{p_i^2}{2M_i} + \frac{1}{2}\sum_{ij}\Phi_{ij}u_i u_j\right]\Psi = E\Psi$$

This can be diagonalised to "classical" normal modes: $\mathcal{D} = M^{-1/2}\Phi M^{-1/2}$, classical dynamical matrix

$$PE = \frac{1}{2}u^T\Phi u = \frac{1}{2}u^T\left(M^{1/2}\mathcal{D}M^{1/2}\right)u = \frac{1}{2}u^T M^{1/2}\left(\sum_\lambda \omega_\lambda^2 Y_\lambda Y_\lambda^T\right)M^{1/2}u = \frac{1}{2}\sum_\lambda \omega_\lambda^2 y_\lambda^2$$

where $y_\lambda = M^{1/2}Y_\lambda^T u \equiv \sum_i \sqrt{M_i}\,Y_{\lambda i}u_i$ are normal modes (classical)

Momentum: $p_i = -i\hbar\frac{\partial}{\partial u_i} = -i\hbar\sum_\lambda \frac{\partial y_\lambda}{\partial u_i}\frac{\partial}{\partial y_\lambda} = -i\hbar\sum_\lambda \sqrt{M_i}\,Y_{\lambda i}\frac{\partial}{\partial y_\lambda} = \sum_\lambda \sqrt{M_i}\,Y_{\lambda i}\,p_\lambda$

Hence,

$$KE = \frac{1}{2}\sum_i \frac{1}{M_i}p_i^2 = \frac{1}{2}\sum_i \frac{1}{M_i}\sum_{\lambda\lambda'} M_i Y_{\lambda i}Y_{\lambda' i}\,p_\lambda p_{\lambda'} = \frac{1}{2}\sum_{\lambda\lambda'}\underbrace{\left(\sum_i Y_{\lambda i}Y_{\lambda' i}\right)}_{\delta_{\lambda\lambda'}}p_\lambda p_{\lambda'} = \frac{1}{2}\sum_\lambda p_\lambda^2$$

The Hamiltonian

$$\boxed{H = \sum_\lambda\left(\frac{1}{2}p_\lambda^2 + \frac{1}{2}\omega_\lambda^2 y_\lambda^2\right)} \Rightarrow \text{sum of independent harmonic oscillators}$$

$$\boxed{E_\lambda = \sum_\lambda \hbar\omega_\lambda\left(n_\lambda + \frac{1}{2}\right)}, \quad \boxed{\Psi = \prod_\lambda \psi_\lambda^{(n_\lambda)}}$$

$n_\lambda \to 0, 1, 2, \dots$

Phonon's statistics

$$H=\sum_\lambda h_\lambda, \quad h_\lambda=\hbar\omega_\lambda\left(n_\lambda+\tfrac{1}{2}\right)$$

The free energy (Helmholtz) $\boxed{F=U-TS=-k_BT\ln Z}$

$\boxed{\beta=1/k_BT}$

Z – statistical sum: $Z=\mathrm{Tr}\left(e^{-\beta H}\right)=\prod_\lambda Z_\lambda, \quad Z_\lambda=\mathrm{Tr}\left(e^{-\beta h_\lambda}\right)$

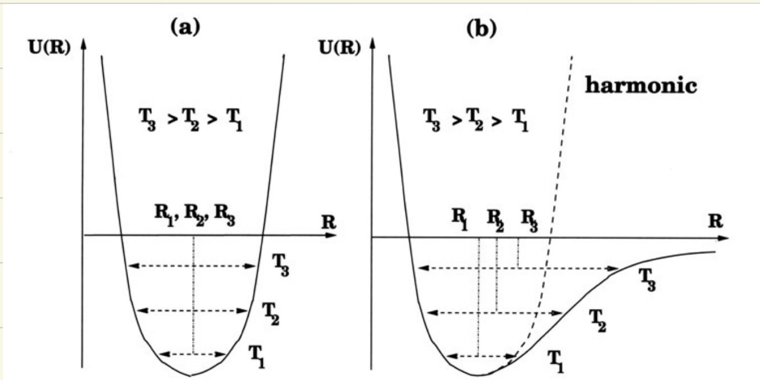
$\mathrm{Tr} \to \sum_n \langle n|\,..\,|n\rangle$

For one oscillator

$$Z_\lambda=\sum_{n_\lambda=0}^{\infty}\langle n_\lambda|e^{-\beta h_\lambda}|n_\lambda\rangle=\sum_{n_\lambda=0}^{\infty}e^{-\beta\hbar\omega_\lambda(n_\lambda+\frac{1}{2})}=\frac{e^{-\beta\hbar\omega_\lambda/2}}{1-e^{-\beta\hbar\omega_\lambda}}$$

The free energy $F=-k_BT\ln\left(\prod_\lambda Z_\lambda\right) \Rightarrow \boxed{F=\sum_\lambda\left[\underbrace{\frac{\hbar\omega_\lambda}{2}}_{\text{zero point energy}}+k_BT\ln\left(1-e^{-\beta\hbar\omega_\lambda}\right)\right]}\equiv F(T)$

Quasiharmonic approximation



harmonic anharmonic

At $T>0$ crystals expand. Approximately:

$$F=U_{DFT}(V)+F_{vibr}(V,T)$$

$\min_V F \to$ structure for the given T

At $P>0$ one has to use $G=F+PV$

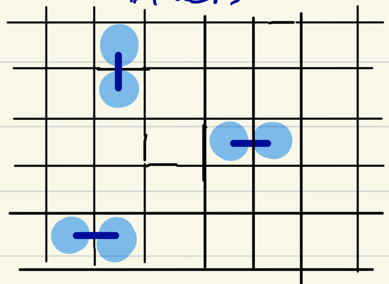
$\min_V G \to$ structure for the given T

$\boxed{\left(\frac{\partial F}{\partial V}\right)_T=-P}$

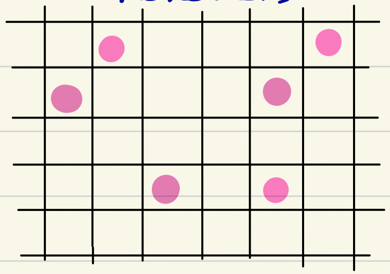
● Configuration entropy

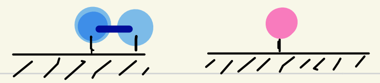
Which structure is more energetically favourable?

Dimers



Monomers





dimer monomer

$N \ll M$

but still $\gg 1$

M – total number of sites available; N – number of species.

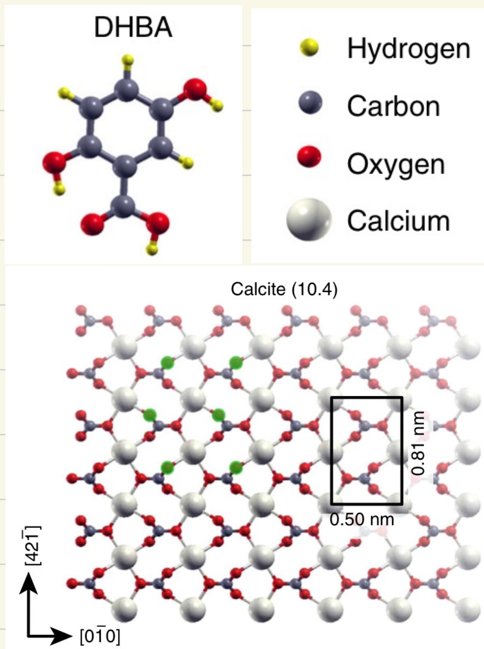
$$\boxed{\ln N! \simeq N \ln N - N}$$

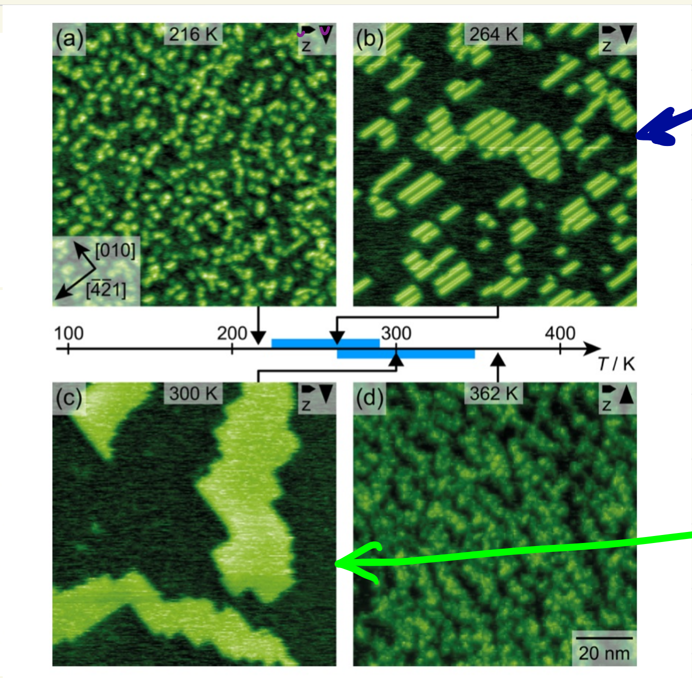
$$\Delta S = k_B \ln \frac{M!}{N!(M-N)!} = N k_B \left[\ln \frac{1-\theta}{\theta} - \frac{1}{\theta} \ln(1-\theta) \right],\ \text{where } \theta = \frac{N}{M} \text{ coverage.}$$

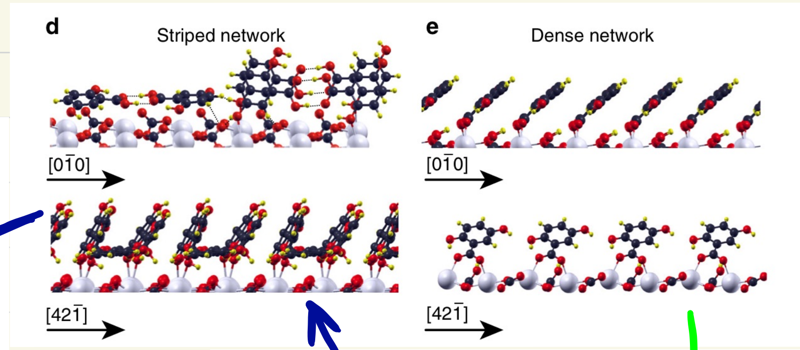
$\theta_D = \theta_M / 2$

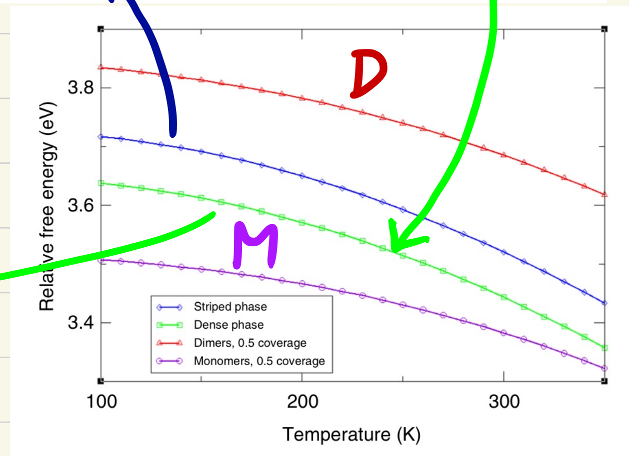
Free energy per species:

$$F = \Delta U_{DFT} + \Delta F_{vibr} - k_B T \left[\ln \frac{1-\theta}{\theta} - \frac{1}{\theta} \ln(1-\theta) \right]$$

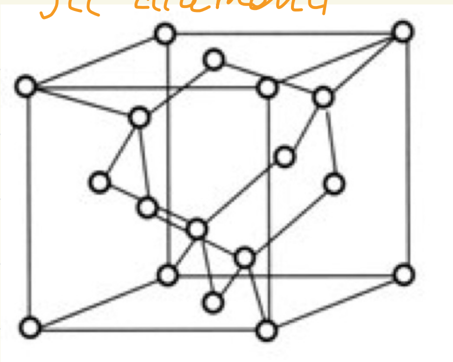








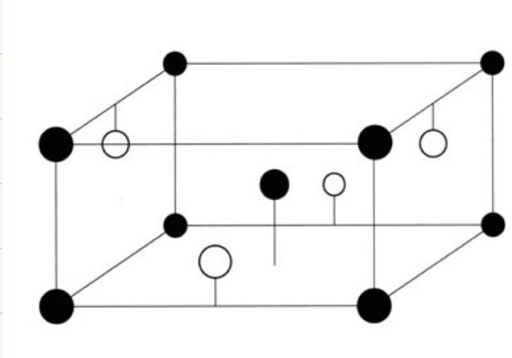
C. Paris et al. – Comm. Chem. 1 66 (2018) fcc diamond



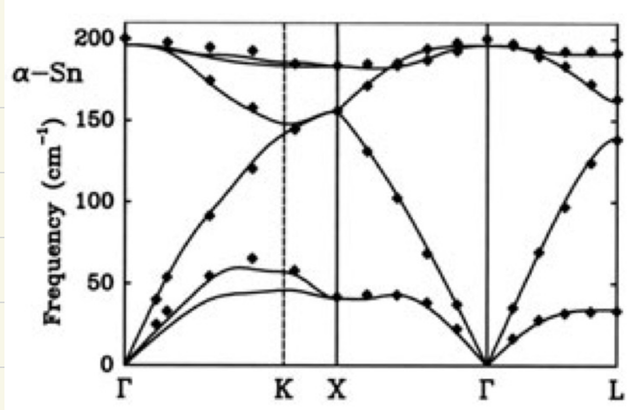
α - Sn (gray tin)
($T < T_c$)

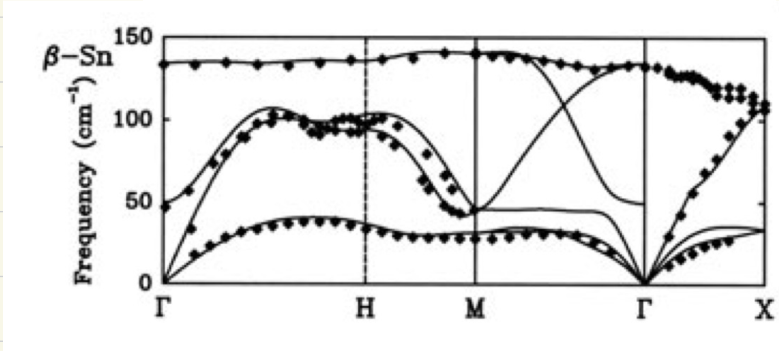
$\xrightarrow{13°C}$

body-centred tetragonal (bct)

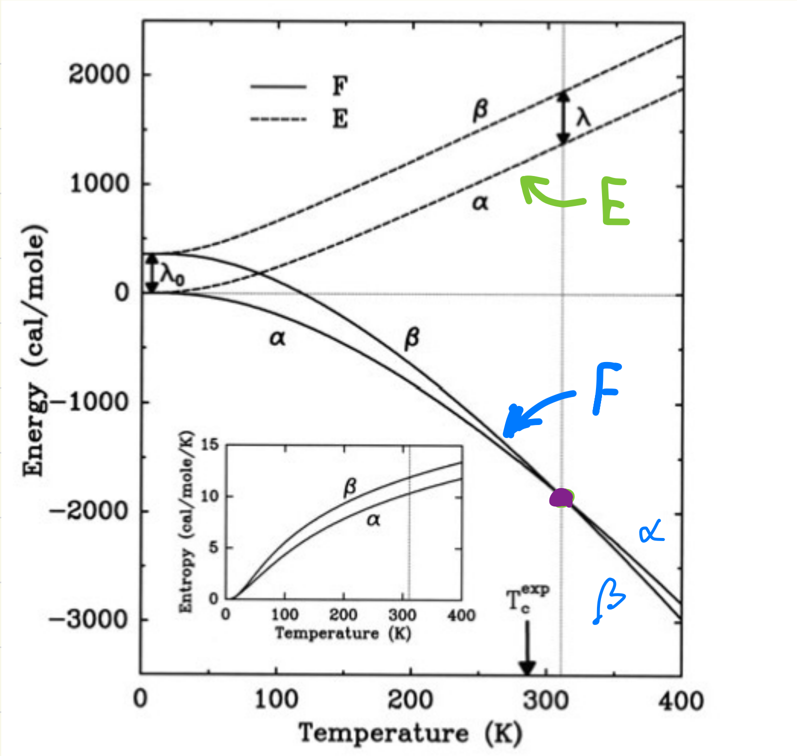


β - Sn (white tin)
($T > T_c$)



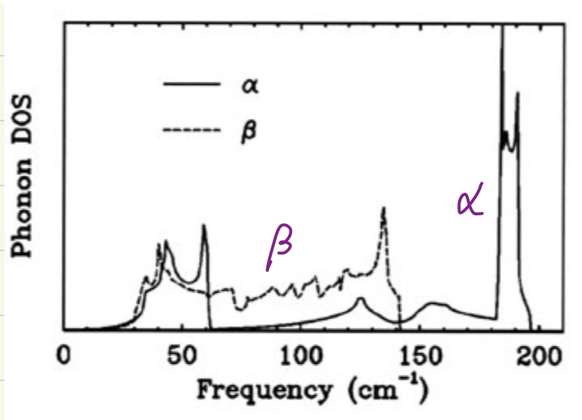


$F = E - TS$ (naive QH approximation)



The phase transition is driven by phonons

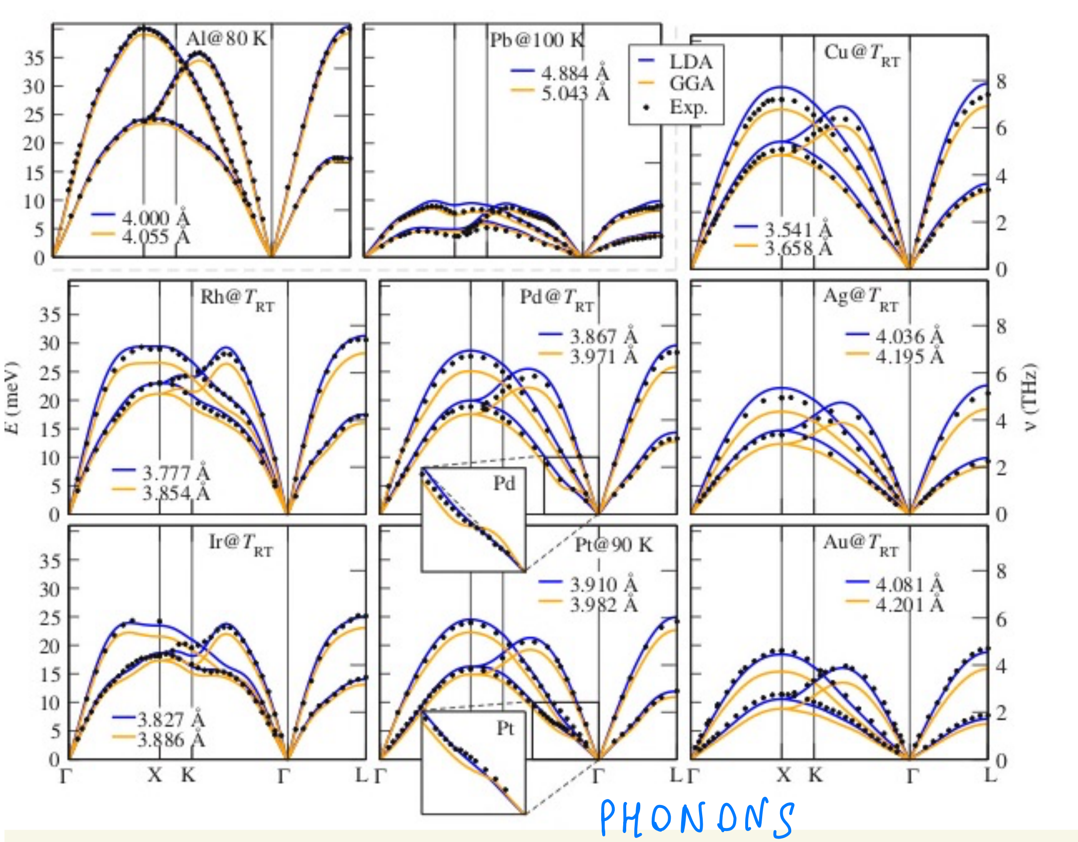
$S_\beta - S_\alpha \simeq k_B \ln \frac{\omega_\alpha}{\omega_\beta}$
(Einstein model)
$\omega_\alpha >> \omega_\beta \Rightarrow S_\beta - S_\alpha > 0$



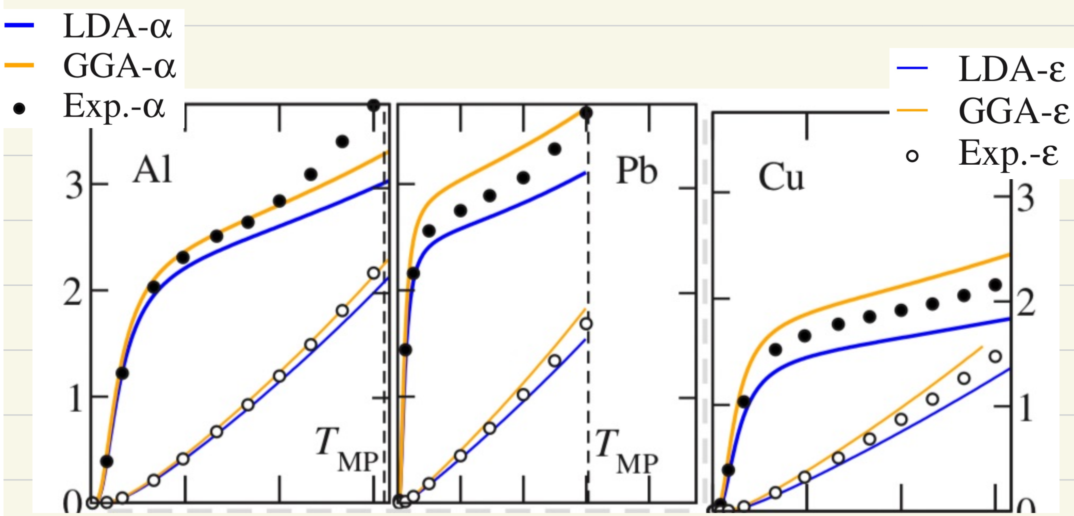
[193] P. Pavone. Old and new aspects in lattice-dynamical theory. *J. Phys.: Condens. Matter*, 13:7593–7610, 2001.

Thermal expansion of simple metals

$F = F_{el} + F_{QH} \; (+F_{AH} + F_{defects})$



PHONONS



EXPANSION

- Large cutoffs
- Large k-points meshes (up to $4\times4\times4$)
- Large supercells (up to $5\times5\times5$)
- LDA vs. GGA compared

- DFT first used for various values of the volume V.
- For each V phonons were calculated
- Frequences ω_{kj} for non-exact k points were interpolated across the BZ using a Fourier method (?)
- Free energy $f(V,T)$ calculated
- $P = -\left(\frac{\partial f}{\partial V}\right)_T$ solved to get $V_{eq}(P,T)$

$$\alpha(T) = \frac{a(T) - a(T_{ref})}{a(T_{ref})}$$

$$\varepsilon(T) = \frac{1}{a(T)}\frac{da(T)}{dT}$$

B. Grabowski et al. – PRB 76 024309 (2007)

Ab initio methods for predicting phase equilibria & transitions

- DFT + quasiharmonic approximation. ⇒ free energy
  - practical only for cubic systems
  - difficult to include anharmonicity
  - fails near phase transitions as unstable structures need to be sampled.
- Self-consistent phonons: difficult in practice
- Velocity-velocity autocorrelation function from MD:
  - works at finite T
  - difficult ab initio: long times + large cell sizes needed
  - combine with thermodynamic integration to include anharmonicity; however, if the system is harmonically unstable, the methods cannot start from this.
- T-dependent effective potential (TDEP) method:
  - ab initio
  - includes anharmonicity
  - finite T
  - can be extended to any lattices (e.g. non cubic)

PHYSICAL REVIEW B **84**, 180301(R) (2011)

Lattice dynamics of anharmonic solids from first principles

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(Received 10 August 2011; revised manuscript received 25 October 2011; published 14 November 2011)

PHYSICAL REVIEW B **87**, 104111 (2013)

Temperature dependent effective potential method for accurate free energy calculations of solids

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(Received 10 December 2012; published 25 March 2013)

- $U(t) = U_0(T) + \frac{1}{2} u_t^T \Phi u_t$ ← a model PE

u_t → displacements

Φ → force constant matrix

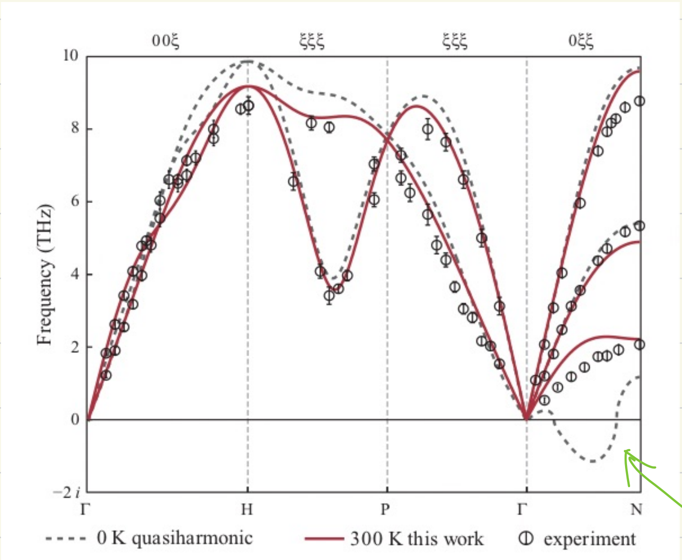
MD (NVT): U_t and forces f_t $\Rightarrow$ $f_t = -\Phi u_t$

- The "best" least square fit to Φ: $\boxed{\min \Delta F = \frac{1}{N_t} \sum_t \left| F_t^{MD} - \left(-\Phi u_t^{MD}\right) \right|^2}$

The force constant matrix is obtained via a Moore-Penrose pseudoinverse.

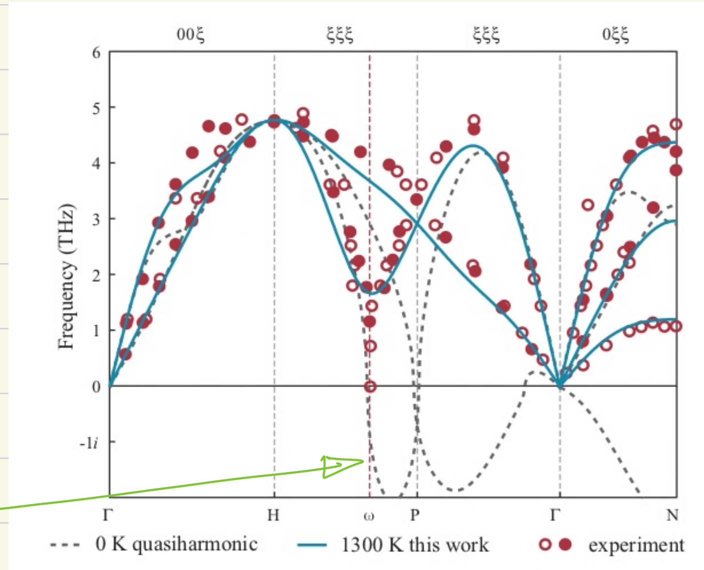
- free energy follows from vibrational frequences due to Φ:

$$\underbrace{\boxed{\mathcal{F} = U_0 + \mathcal{F}_{vib}}}_{\text{free energy}} \quad \text{with} \quad \underbrace{\boxed{U_0 = \left\langle U_{MD}(t) - \frac{1}{2} \sum_{ij} \Phi_{ij} u_i(t) u_j(t) \right\rangle}}_{T \text{ dependent!}}$$



bcc Li

instability

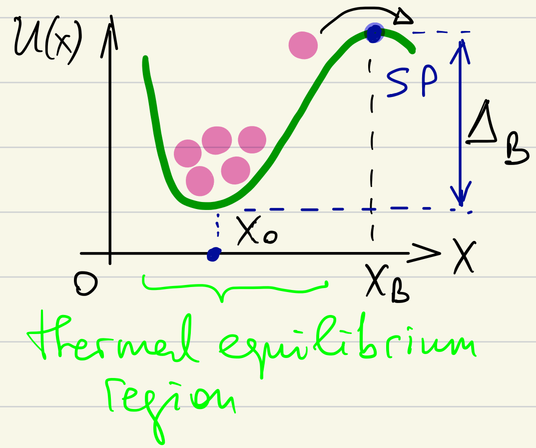


bcc Zr

Calculation of rates (an elementary event)

Transition State Theory $\boxed{TST}$

- **1D model** $\quad H = \frac{mv^2}{2} + \mathcal{U}(x) \quad (75)$



- Probability to find the particle in the ground state basin:

$$\rho(x,v) = \rho(x)\underbrace{\rho(v)}_{\text{Maxwell}}, \quad \rho(x) = \frac{1}{z_x} e^{-\beta\mathcal{U}(x)}, \quad z_x = \int_0^{x_B} dx\, e^{-\beta\mathcal{U}(x)} \quad (76)$$

- Probability to find it at the saddle point: $\rho(x_B, v)$

- The total flux over the barrier to the right ($\dot{x} = v > 0$):

$$k_{TST} = \int_0^{\infty} v\,\rho(v)\rho(x_B)\,dv = \rho(x_B)\bar{v}_{\to}, \quad \bar{v}_{\to} = \int_0^{\infty} v \frac{1}{z_v} e^{-\frac{mv^2}{2k_BT}} dv \quad (77)$$

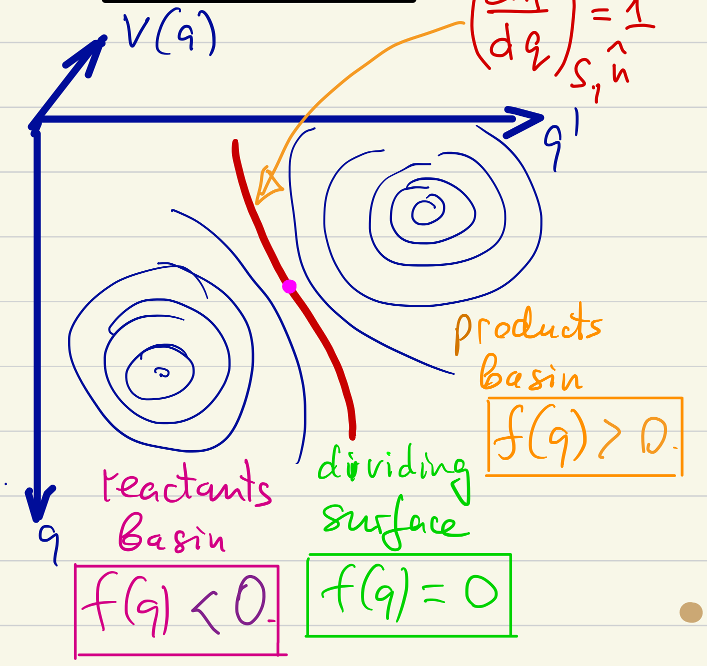
$$z_v = \int_{-\infty}^{\infty} e^{-\beta\frac{mv^2}{2}} dv = \sqrt{\frac{2\pi}{\beta m}}, \quad \text{so} \quad \bar{v}_{\to} = \frac{1}{\sqrt{2\pi m\beta}} \quad (78)$$

- In the harmonic model: $\mathcal{U}(x) = \mathcal{U}(x_0) + \frac{1}{2}m\omega_0^2 x^2, \quad \mathcal{U}(x_B) = \mathcal{U}(x_0) + \underbrace{\Delta_B}_{\text{barrier}} \quad (79)$

$$z_x = \int_0^{x_B} dx\, e^{-\beta\mathcal{U}(x_0)} e^{-\beta\frac{1}{2}m\omega_0^2 x^2} \simeq \int_{-\infty}^{+\infty} dx \ldots = e^{-\beta\mathcal{U}(x_0)}\sqrt{\frac{2\pi}{\beta m\omega_0^2}} \quad (80)$$

$$\Rightarrow k_{TST} = \frac{1}{\sqrt{2\pi m\beta}}\sqrt{\frac{\beta m\omega_0^2}{2\pi}}\, e^{-\beta\mathcal{U}(x_B)} e^{+\beta\mathcal{U}(x_0)} \quad (81) \quad \Rightarrow \boxed{k_{TST} = \frac{\omega_0}{2\pi} e^{-\beta\Delta_B}} \quad (82)$$

3N-D model



- Flux through dS on the dividing surface:

$$dJ = dS(v \cdot \hat{n})\,dt \,, \quad \hat{n} = \nabla f(q) \tag{83}$$

- The total flux to the right ($\rightarrow$ products):

$$dJ = dt \int dv \iint_S dS \; v \cdot \nabla f(q) \, P(q_s, v) \, \theta(v \cdot \nabla f(q)) \tag{84}$$

- Probability to be on the dividing surface:

$$P(q_s, V) = \frac{1}{Z_R} e^{-\beta H(q_s, v)} \,, \quad Z_R = \int dv \int dq \, \theta(-f(q)) \, e^{-\beta H} \tag{85}$$

- The surface integral can be worked into the volume:

$$\iint_S dS \ldots = \int dq \, \delta(f(q)) \ldots \quad \text{as } \delta(f(q)) \neq 0 \text{ only when } q \in S \tag{86}$$

- This allows writing the transition rate as:

$$\boxed{K_{TST} = \frac{dJ}{dt} = \frac{\int dv \int dq \, \delta(f(q)) \, [v \cdot \nabla f(q)] \, e^{-\beta H} \, \theta(v \cdot \nabla f(q))}{\int dv \int dq \, \theta(-f(q)) \, e^{-\beta H}}} \tag{87}$$

TST

- Bennett-Chandler correction In TST trajectories going over the S always fall into the products, never return. It is an approximation. A correction is needed,

- The momenta integrals can be calculated exactly:

Numerator: $$I_n = \int dv\, (v\cdot\nabla f(q))\,\theta(v\cdot\nabla f(q))\, e^{-\beta K(v)} \quad (88), \qquad K(v) = \frac{1}{2}\sum_i m_i v_i^2 \quad (89)$$

Denominator: $$I_d = \int dv\, e^{-\beta K(v)} \quad (90)$$

Massless velocities: $$v = M^{-1/2}\tilde{v} \Rightarrow K(v) = \frac{1}{2}\tilde{v}^T\tilde{v}, \quad \left|\frac{\delta v}{\delta \tilde{v}}\right| = \frac{1}{\sqrt{\det M}} \quad (91)$$

$$\Rightarrow I_n = \int \frac{d\tilde{v}}{\sqrt{\det M}}\, e^{-\beta\frac{\tilde{v}^T\tilde{v}}{2}}(\tilde{v}\cdot e_q)\,\theta(\tilde{v}\cdot e_q), \quad \boxed{e_q = M^{-1/2}\nabla f(q)}. \quad (92)$$

Rotate the coordinate system, that the 1st component $\tilde{v}_1$ of $\tilde{v}$ be $\parallel e_q$, others $\perp$:

$$I_n = \frac{|e_q|}{\sqrt{\det M}}\int d\tilde{v}\,\tilde{v}_1 e^{-\beta/2\,\tilde{v}^T\tilde{v}}\,\theta(\tilde{v}_1) = \frac{|e_q|}{\sqrt{\det M}}\int_0^\infty d\tilde{v}_1\tilde{v}_1 e^{-\frac{\beta}{2}\tilde{v}_1^2}\prod_{i\neq 1}\int_{-\infty}^{+\infty} d\tilde{v}_i\, e^{-\frac{\beta}{2}\tilde{v}_i^2} = \frac{|e_q|\,(2\pi/\beta)^{3N/2}}{\sqrt{2\pi\beta}\sqrt{\det M}} \quad (93)$$

$$\Rightarrow I_d = \frac{1}{\sqrt{\det M}}\prod_{i=1}\int_{-\infty}^{\infty} d\tilde{v}_i\, e^{-\frac{\beta}{2}\tilde{v}_i^2} = \frac{1}{\sqrt{\det M}}\left(\frac{2\pi}{\beta}\right)^{3N/2} \quad (94), \quad \text{hence} \quad \frac{I_d}{I_n} = \frac{|e_q|}{\sqrt{2\pi\beta}} = \frac{|M^{-1/2}\nabla f(q)|}{\sqrt{2\pi\beta}} \quad (95)$$

- Finally, we obtain:

over reactive surface

$$\boxed{K_{TST} = \frac{1}{\sqrt{2\pi\beta}}\frac{\int dq\,\delta(f(q))\,e^{-\beta U(q)}\,|M^{-1/2}\nabla f(q)|}{\int dq\, e^{-\beta U(q)}\theta(-f(q))} = \frac{1}{\sqrt{2\pi\beta}}\frac{\iint_S dS\, e^{-\beta U(q)}\,|M^{-1/2}\nabla f(q)|}{\int dq\, e^{-\beta U(q)}\theta(-f(q))}} \quad (96)$$

over reactants basin

3N-D model: Harmonic TST

- $\mathcal{U}(q) = \mathcal{U}(q_0) + \frac{1}{2}(q-q_0)^T \Phi (q-q_0)$ (97)

Φ – Hessian at q_0, $\Phi = M^{1/2} \underbrace{D}_{\text{dynamical matrix}} M^{1/2}$ Using: $\boxed{y = M^{1/2}(q-q_0)}$:

$$\mathcal{U}(q) = \mathcal{U}(q_0) + \frac{1}{2} y^T D y$$

We can integrate the denominator of K_{TST} changing $q \to y$ via $\left|\frac{\partial y}{\partial q}\right| = \sqrt{\det M}$:

$$\mathcal{J}_d = \int e^{-\beta \mathcal{U}(q)} \theta(-f(q))\, dq \cong e^{-\beta \mathcal{U}(q_0)} \int_{\text{all space}} e^{-\frac{\beta}{2} y^T D y}\, dy \cdot \frac{1}{\sqrt{\det M}} \qquad (98)$$

as the basin is centred around $q = 0$.

Since $D = \sum_\lambda \omega_\lambda^2 e_\lambda e_\lambda^T$, the quadratic form in the exponential becomes

$$\frac{\beta}{2} y^T D y = \frac{\beta}{2} \sum_\lambda \omega_\lambda^2 (e_\lambda^T y)^T (e_\lambda^T y) = \frac{\beta}{2} \sum_\lambda \omega_\lambda^2 y_\lambda^2 \qquad (99)$$

where $\boxed{y_\lambda = e_\lambda^T y}$ are scalars. Consequently,

$$\Rightarrow \mathcal{J}_d = \frac{1}{\sqrt{\det M}} e^{-\beta \mathcal{U}(q_0)} \prod_{\lambda=1}^{3N} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2}\omega_\lambda^2 y_\lambda^2} dy_\lambda = \frac{1}{\sqrt{\det M}} e^{-\beta \mathcal{U}(q_0)} \prod_{\lambda=1}^{3N} \sqrt{\frac{2\pi}{\beta \omega_\lambda^2}} \qquad (100)$$

- Now we calculate the numerator $\iint_S dS\, e^{-\beta\mathcal{U}(q)} \, |\underbrace{M^{-1/2}\nabla f(q)}_{e_q}|$

All of the contribution there comes from the dividing surface. Therefore, we shall expand the energy there around the SP.

$$\mathcal{U}(q_s) = \mathcal{U}(q_{SP}) + \frac{1}{2}\underbrace{\sum_\lambda{}' (\omega_\lambda^{SP})^2 y_\lambda^2}_{3N-1\ \omega\text{'s}} \underbrace{- \frac{1}{2}\omega_{im}^2 y_{im}^2}_{1\ \text{imaginary}\ \omega}, \text{ where: } \boxed{y_\lambda = \sum_i \sqrt{m_i}\,(q_i^s - q_i^{SP})\, e_{i\lambda}^{SP}} \quad (101)$$

Dividing surface – a plane $\perp e_q$. On S: $y_{im} = 0$

- $|e_q| = |M^{-1/2}\nabla f(q)|^2 = \sum_i \left(\frac{1}{\sqrt{m_i}}\frac{\partial f}{\partial q_i}\right)^2 = \sum_i \frac{1}{m_i}\left(\sum_\lambda \frac{\partial f}{\partial y_\lambda}\frac{\partial y_\lambda}{\partial q_i}\right)^2$. Since $\frac{\partial y_\lambda}{\partial q_i} = \sqrt{m_i}\, e_{i\lambda}^{SP}$, we have:

$$|e_q| = \sum_i \frac{1}{m_i}\left(\sum_\lambda \frac{\partial f}{\partial y_\lambda}\sqrt{m_i}\, e_{i\lambda}^{SP}\right)^2 = \sum_{\lambda\lambda'} \frac{\partial f}{\partial y_\lambda}\frac{\partial f}{\partial y_{\lambda'}}\underbrace{\left(\sum_i e_{i\lambda}^{SP} e_{i\lambda'}^{SP}\right)}_{\delta_{\lambda\lambda'}} = \sum_\lambda \left(\frac{\partial f}{\partial y_\lambda}\right)^2 = 1 \quad (102)$$

This is because $\partial f/\partial y_{im} = 1$, $\partial f/\partial y_\lambda = 0$ for any $\lambda \neq im$.

- $$I_n = \iint_S dS\, e^{-\beta\mathcal{U}(q)} = \frac{1}{\sqrt{\det M}} \int \underbrace{dy'}_{\text{on } S \text{ only}}\, e^{-\beta\sum_\lambda{}'(\omega_\lambda^{SP})^2 y_\lambda^2/2} \cdot e^{-\beta \mathcal{U}(q_{SP})} \quad (103)$$

($y_{im} = 0$ on S, so y_{im} contribution) (104)

$$= \frac{1}{\sqrt{\det M}}\, e^{-\beta\mathcal{U}(q_{SP})} \prod_\lambda{}' \sqrt{\frac{2\pi}{\beta(\omega_\lambda^{SP})^2}} \Rightarrow \boxed{K_{HTST} = \left(\frac{1}{2\pi}\frac{\prod_\lambda \omega_\lambda}{\prod_\lambda{}' \omega_\lambda^{SP}}\right) e^{-\beta(\mathcal{U}(q_{SP}) - \mathcal{U}(q_0))}} \quad (105)$$