

Advanced School on  
**QUANTUM MODELLING**  
of Materials with CRYSTAL

# Harmonic and Quasi-Harmonic Thermodynamics of Solids

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Alessandro Erba

Dipartimento di Chimica, Università di Torino (Italy)  
[alessandro.erba@unito.it](mailto:alessandro.erba@unito.it)

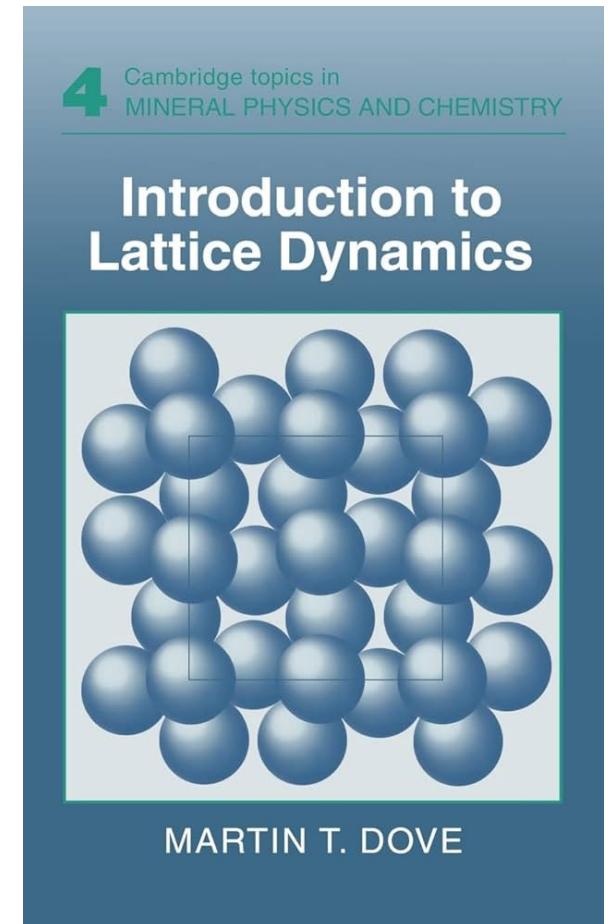
# Temperature and Lattice Dynamics



An effective inclusion of the effect of **temperature** requires a description of the motion of the atomic nuclei within the solid (i.e. **lattice dynamics**).

Indeed, atoms in a lattice are never at rest in their equilibrium positions: they always move of vibrational motion (even at 0 K because of zero-point motion). Such lattice vibrations (**phonons**) are key to understand:

- Thermodynamics (specific heat, free energy, entropy)
- Phase transitions
- Thermal expansion and Thermo-elasticity
- Lattice thermal conductivity and Pyro-electricity
- Debye-Waller factors and ADPs
- Thermal broadening of spectral peaks
- and many other properties of solids





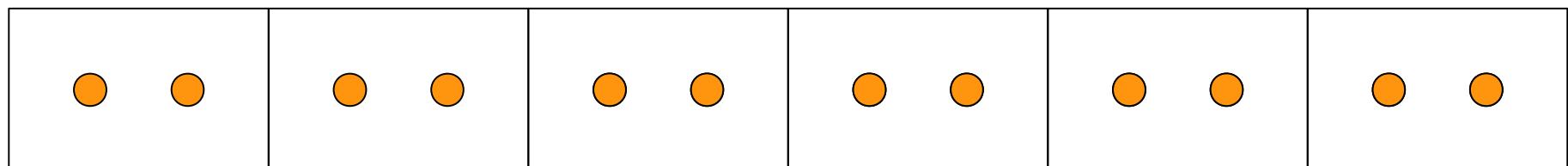
# Vibrations in Solids: Phonon Dispersion

In a molecule, there is a finite number of vibrational degrees of freedom (i.e. distinct ways in which the atoms can vibrate relative to one another), and we know how to count them: it is  $N_{\text{vib}} = 3N - 6(5)$  for a molecule with  $N$  atoms.



For instance, for a linear molecule with  $N = 2$ , we have  $N_{\text{vib}} = 1$ , i.e. just the stretching mode, vibrating at frequency  $\omega$ .

In an infinite periodic lattice, the number of vibrational degrees of freedom becomes infinite,  $N_{\text{vib}} = \infty$ . Indeed atoms in different lattice cells can vibrate with phase modulations, leading to phonon dispersion.





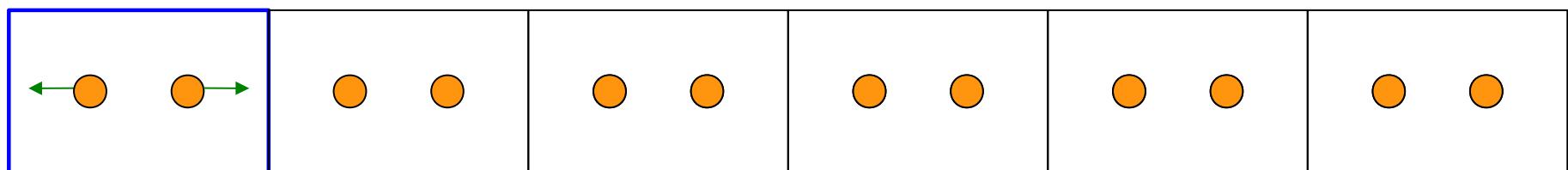
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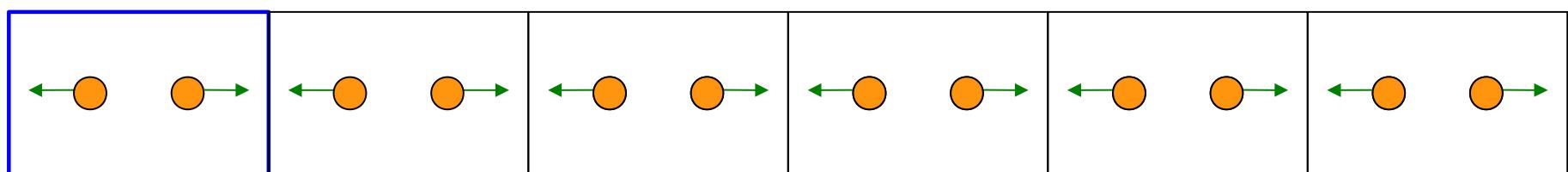
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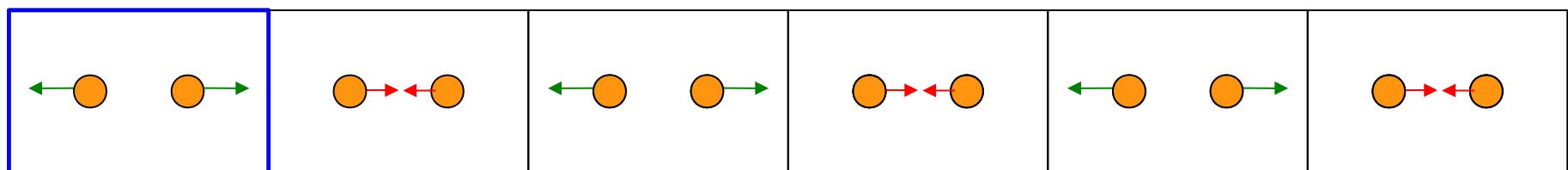
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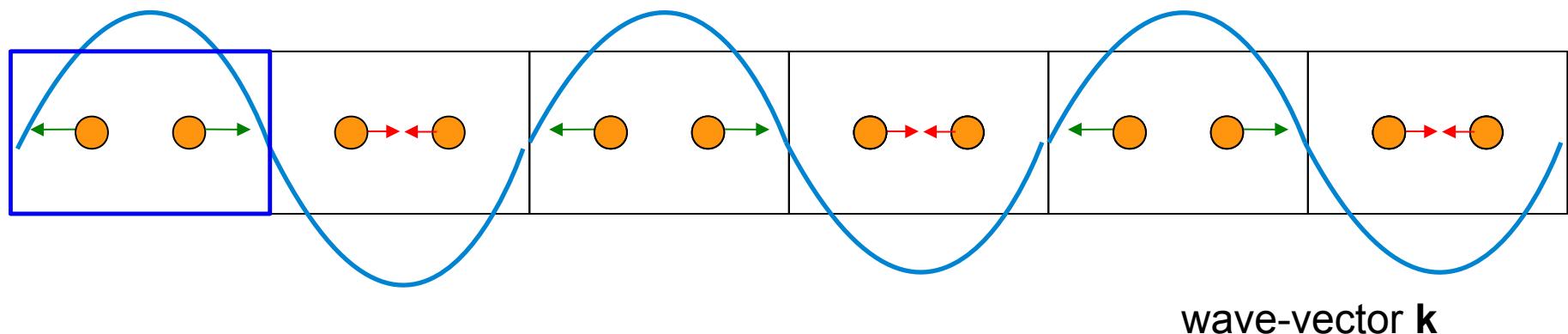
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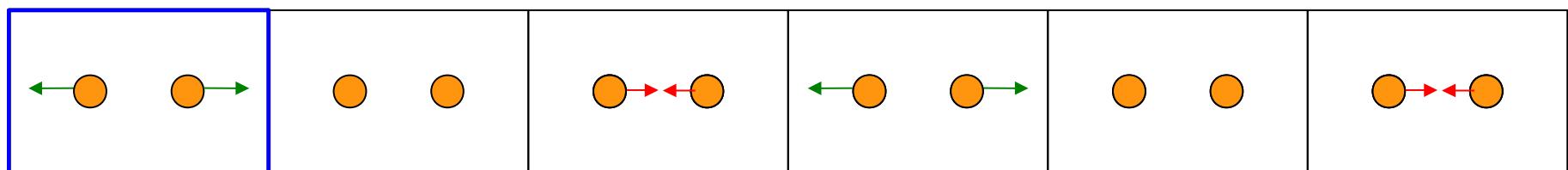
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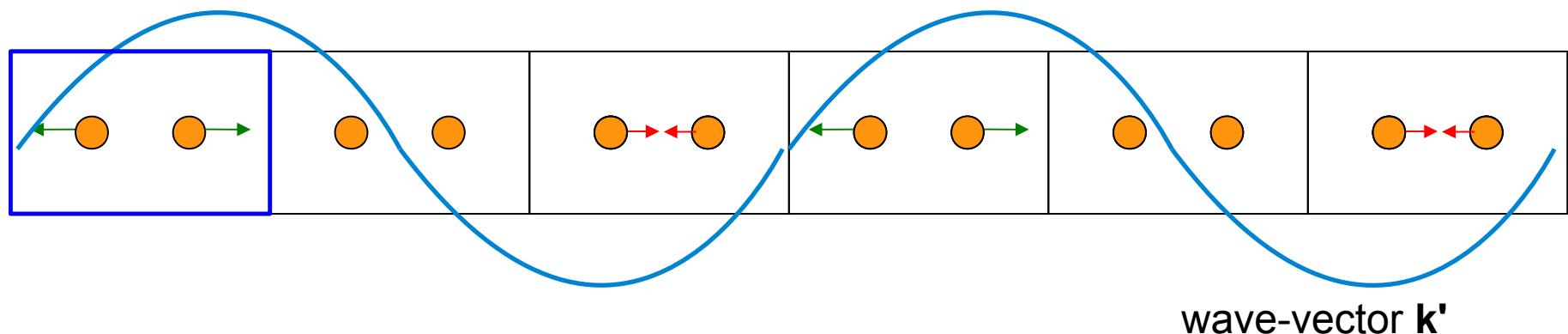
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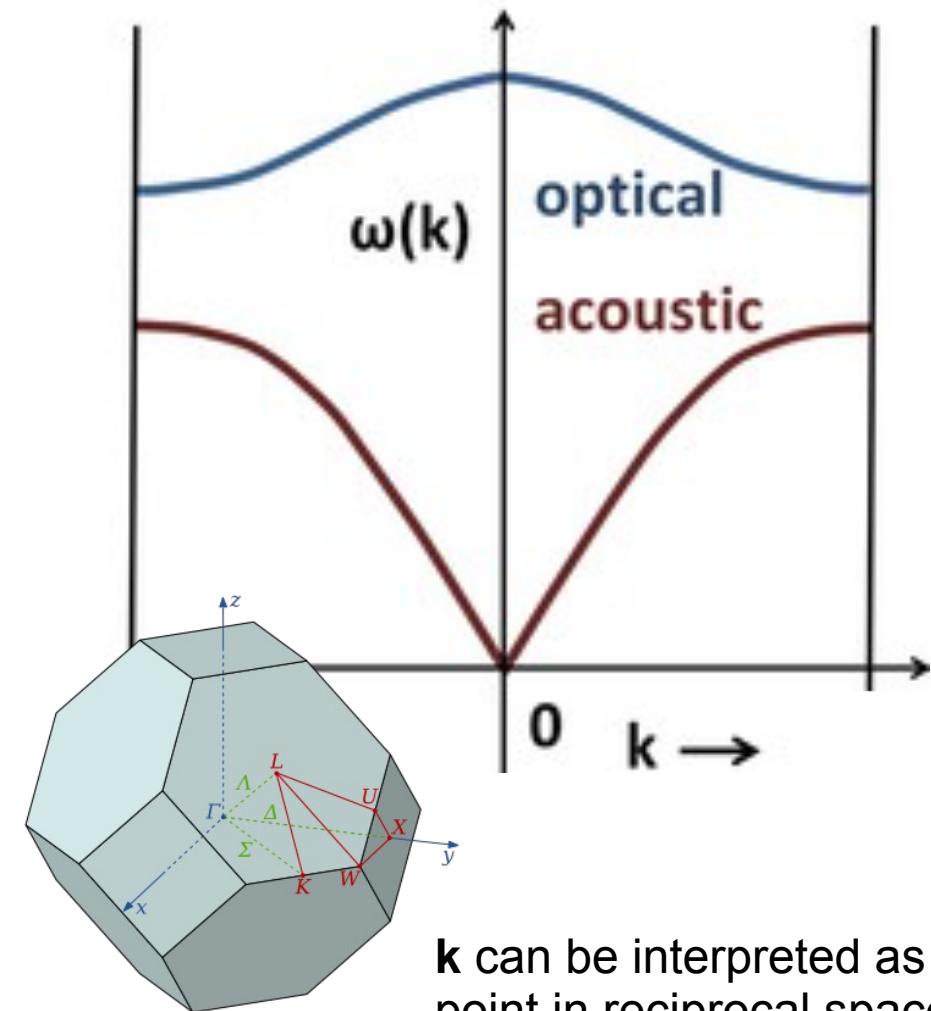
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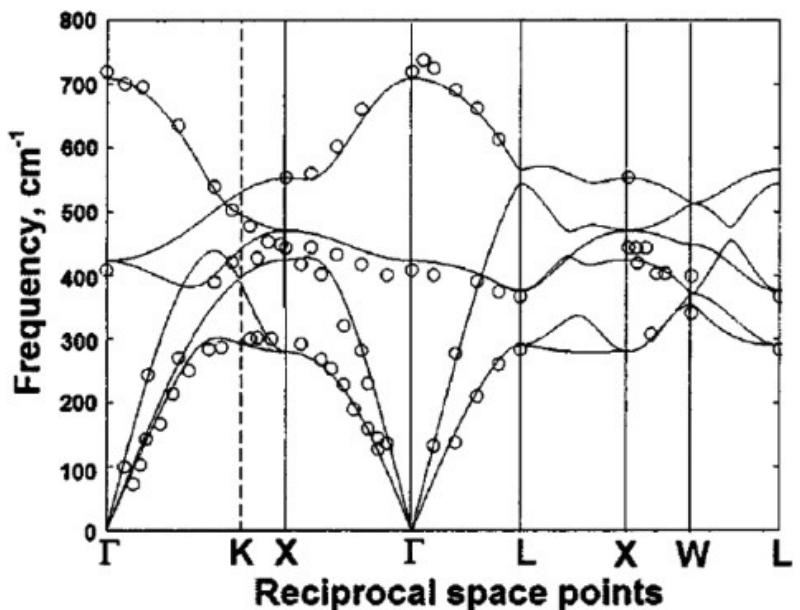
# Vibrations in Solids: Phonon Dispersion

Thus, in a solid, vibration frequencies depend on wavevector  $\mathbf{k}$ , with a typical dispersion pattern, the so-called **phonon dispersion**  $\omega(\mathbf{k})$ .



Lattice vibrations at  $\mathbf{k} = 0$  (i.e. at  $\Gamma$ ) are probed by infrared (IR) and Raman spectroscopies.

Phonon dispersion can be probed by inelastic neutron scattering (INS).





# Dulong-Petit “Law” (1)

In 1819, Dulong and Petit noted that the molar specific heat of all elementary solids is very nearly 6.

In 1831 Neumann extended this law to say that each atom in the solid contributes 6 cal/g mol K to the specific heat of the solid.

Molar $c_v$ for Monatomic Solids			Molar $c_v$ for Diatomic and Triatomic Solids		
Substance	$T, ^\circ\text{C}$	$c_v, \text{cal/g mole}^{-\circ\text{C}}$	Substance	$T, ^\circ\text{C}$	$c_v/2 \text{ or } 3, \text{cal/g mole}^{-\circ\text{C}}$
Ag	0	6.00	AgCl	28	6.27
Au	0	6.07	CuO	22	5.20
Cr	0	5.35	KCl	23	6.20
Fe	0	5.85	CuS	25	5.95
Ni	0	6.05	PbO <sub>2</sub>	24	5.17
Sb	0	6.00	CaF <sub>2</sub>	15–99	5.61
Graphite	0	1.82	ZnO	16–99	5.08
Diamond	0	1.25	PbCl <sub>2</sub>	0–20	6.08

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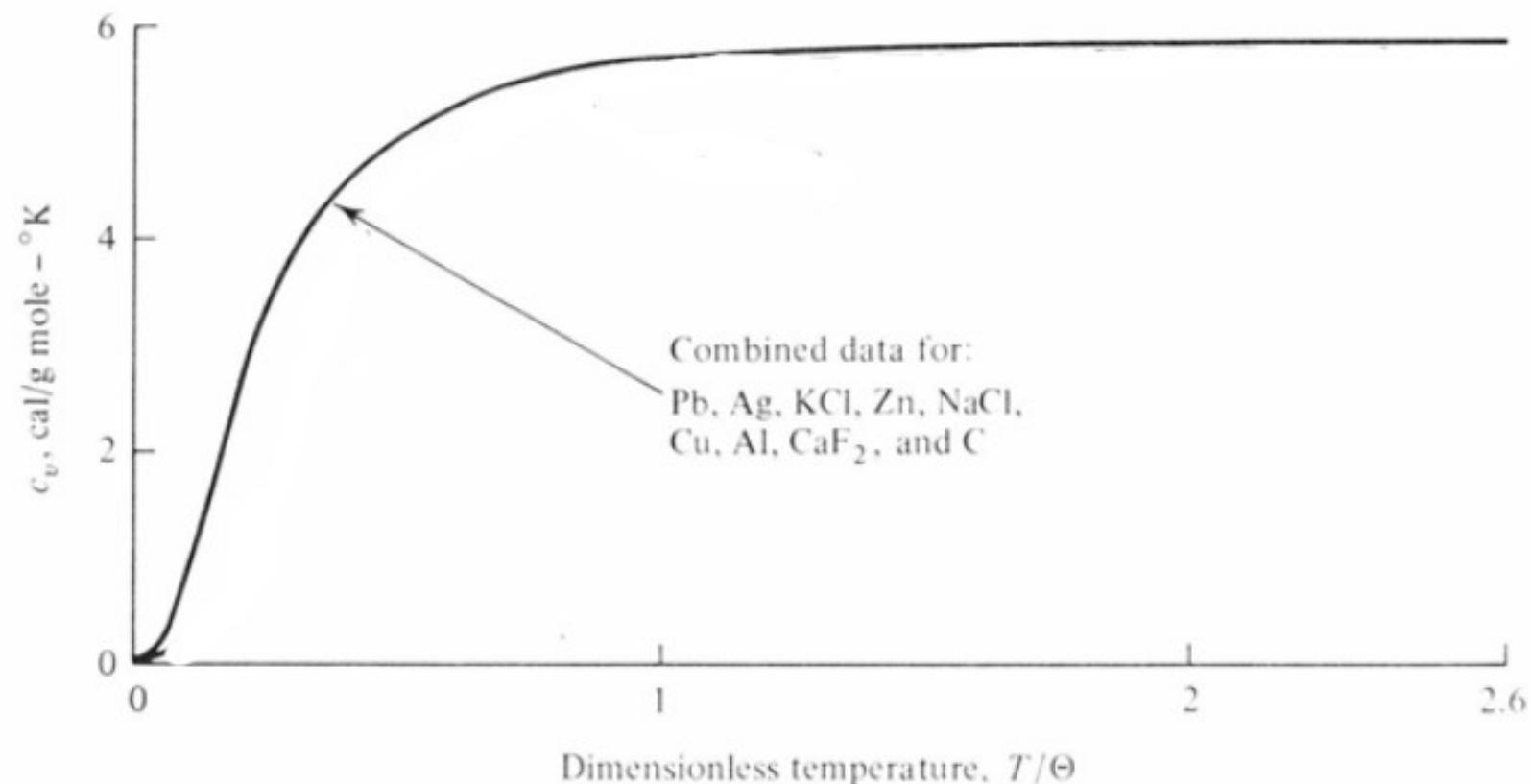
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# Dulong-Petit “Law” (2)

Although these laws are by no means exact, they strongly suggest that some underlying physical principle might be responsible for the degree of success they enjoy.

Fig. 4.5 Temperature dependence of  $c_v$  for many solids.  $\Theta_{\text{Pb}} = 88$ ,  $\Theta_{\text{Ag}} = 215$ ,  $\Theta_{\text{KCl}} = 218$ ,  $\Theta_{\text{Zn}} = 235$ ,  $\Theta_{\text{NaCl}} = 287$ ,  $\Theta_{\text{Cu}} = 315$ ,  $\Theta_{\text{Al}} = 392$ ,  $\Theta_{\text{CaF}_2} = 499$ ,  $\Theta_{\text{C}} = 1860$ .





# Dulong-Petit “Law” (3)

In 1871, Boltzmann showed how a **classical model** for a crystal based on the equipartition of the energy could provide a simple explanation to the Dulong-Petit law.

## Equipartition of the energy:

*The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms.*

*Each degree of freedom contributes with  $\frac{1}{2} k_B T$  to the thermal internal energy of the system.*

For a classical harmonic oscillator, the total energy would be

$$H = H_{\text{kin}} + H_{\text{pot}} = \frac{p^2}{2m} + \frac{1}{2}aq^2.$$

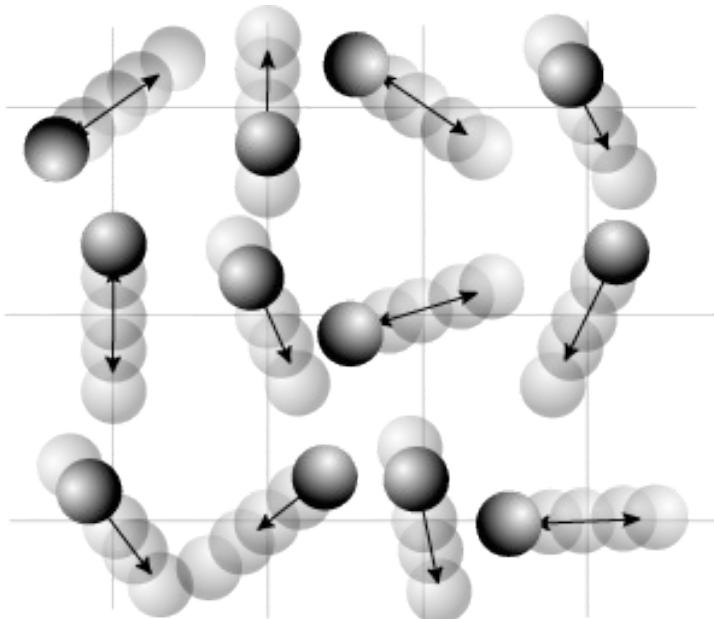
Equipartition therefore implies that in thermal equilibrium, the oscillator has average energy

$$\langle H \rangle = \langle H_{\text{kin}} \rangle + \langle H_{\text{pot}} \rangle = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T.$$



# Dulong-Petit “Law” (4)

In 1871, Boltzmann showed how a **classical model** for a crystal based on the equipartition of the energy could provide a simple explanation to the Dulong-Petit law.



Each atom in the solid can oscillate in three independent directions, so the solid can be viewed as a **system of  $3N$  independent simple harmonic oscillators**, where  $N$  denotes the number of atoms in the lattice. Since each harmonic oscillator has average energy  $k_B T$ , the **average total energy of the solid** is

$$U = 3Nk_B T$$

By taking  $N$  to be the Avogadro number  $N_A$ , and using the relation  $R = N_A k_B$ ,  $U = 3RT$ .

The constant volume specific heat is just the temperature derivative of the internal energy:

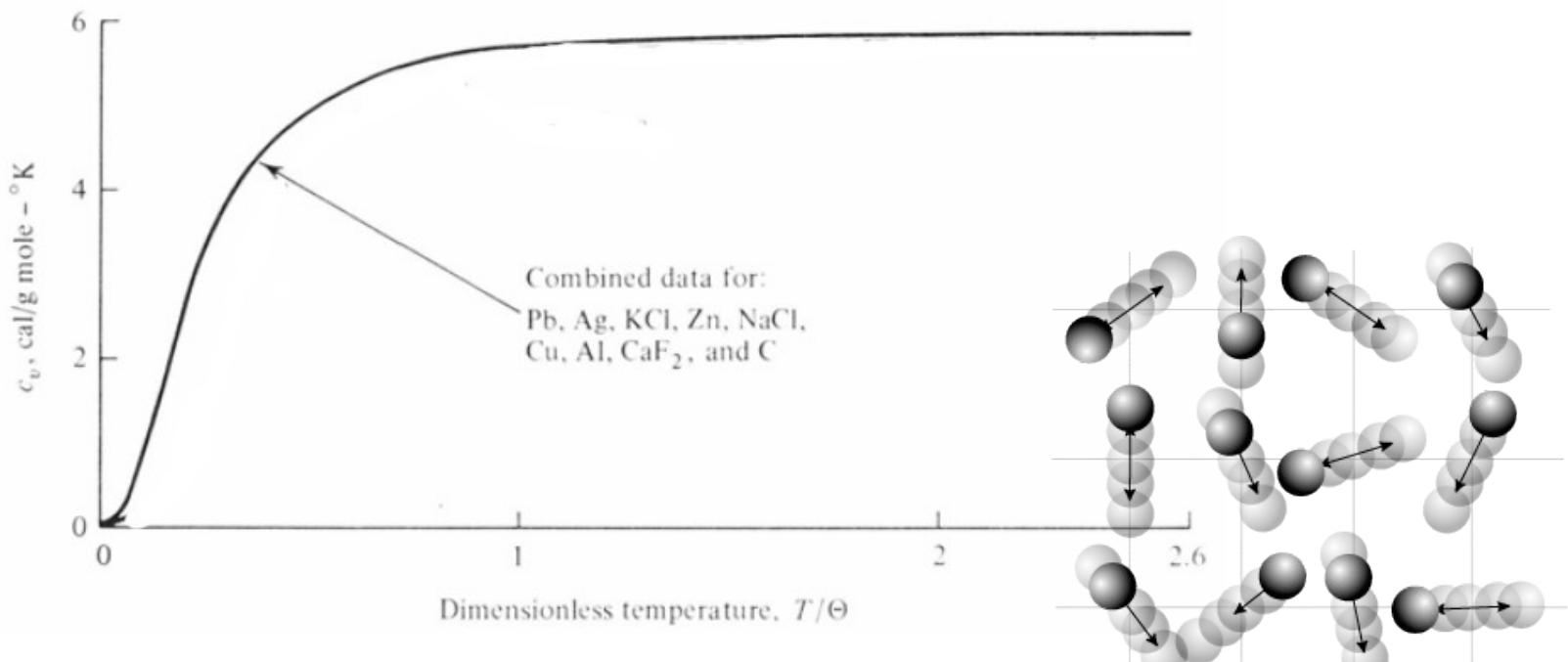
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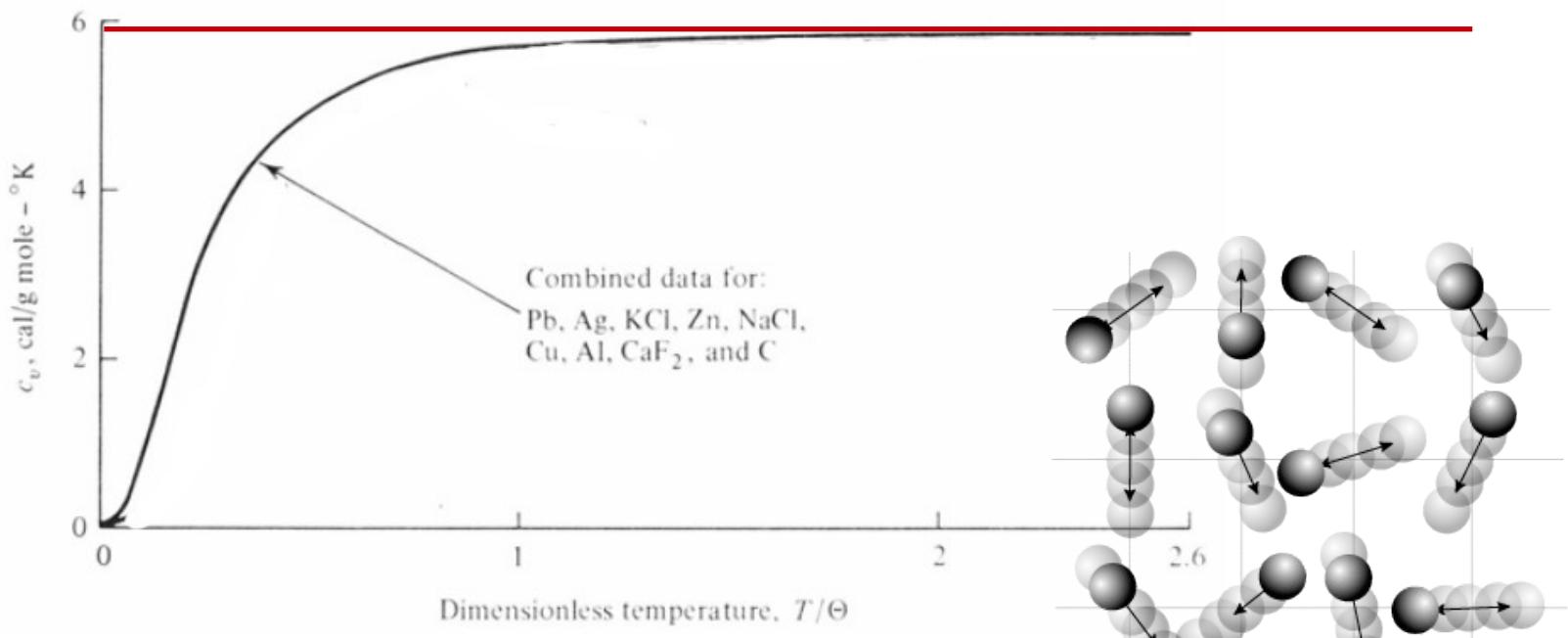
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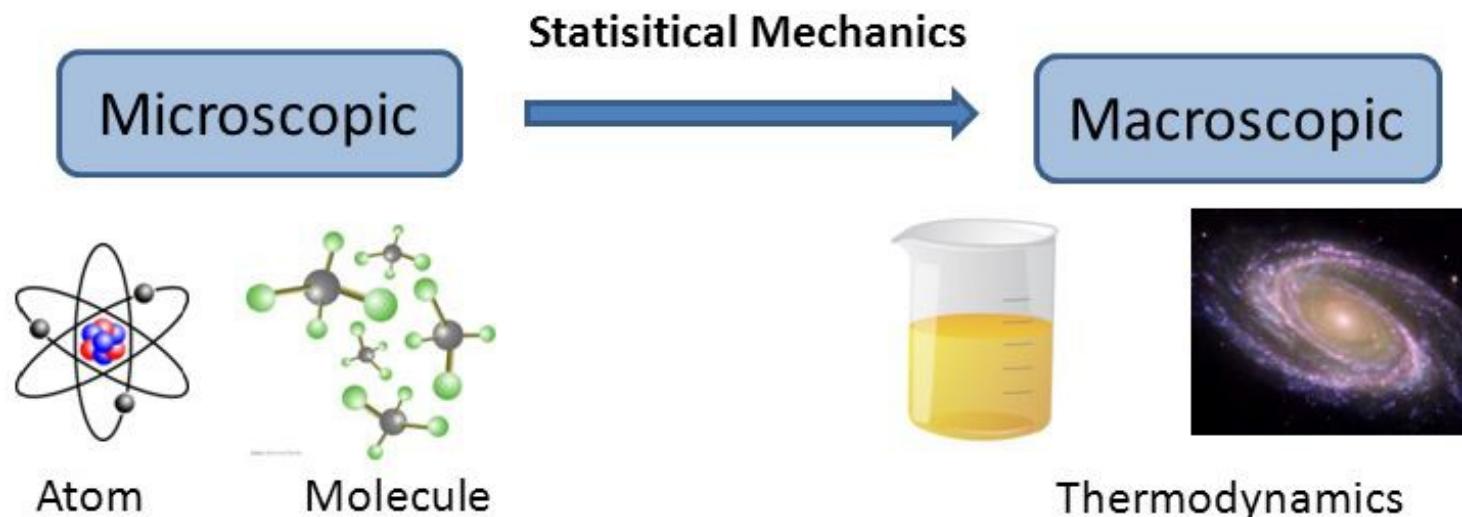


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# Statistical Thermodynamics (1)

**Statistical Thermodynamics** provides a **link** between a **quantum-mechanical description of the microscopic states** accessible to the fundamental constituents of matter and the **thermodynamic properties of the macroscopic system**.



It answers the following question:

*"If particles (atoms, molecules, or electrons and nuclei) obey certain microscopic laws, what are the observable properties of a system containing a very large number of such particles?"*



# Statistical Thermodynamics (2)

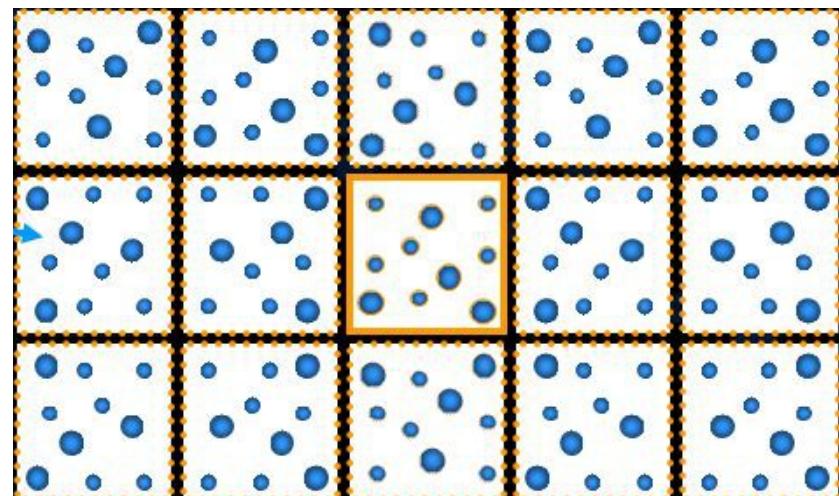
Any macroscopic **thermodynamic measurement** takes a **finite time**, which is much **longer than** the typical **relaxation times of microscopic events** and thus measures a dynamical **time average** over a multitude of accessible microscopic states.

In principle, two possible approaches to model such average macroscopic thermodynamic properties:

**Solve the dynamics of the system**  
(time-dependent)



**Build an “Ensamble” of system replicas**  
(time-independent)



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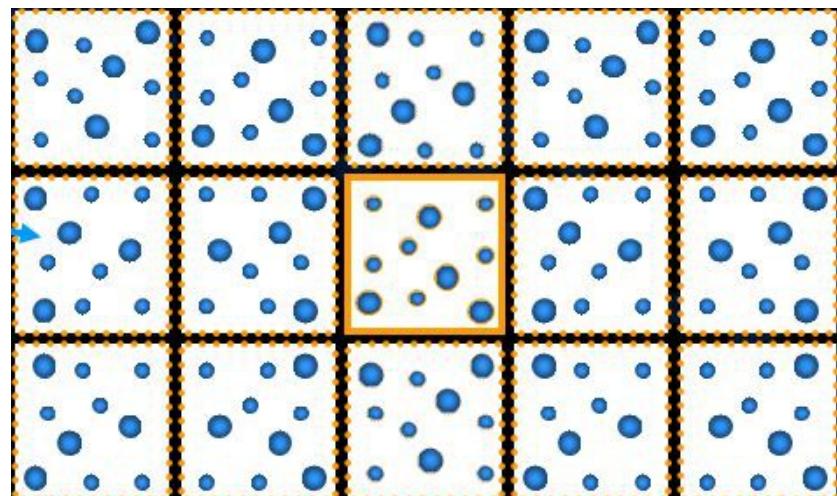
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**OFTEN IMPRACTICAL**

**Build an “Ensemble” of system replicas**  
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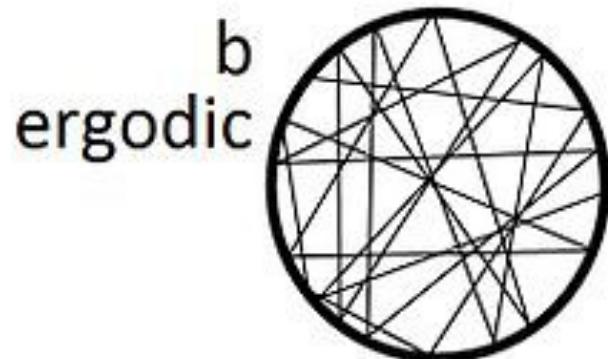
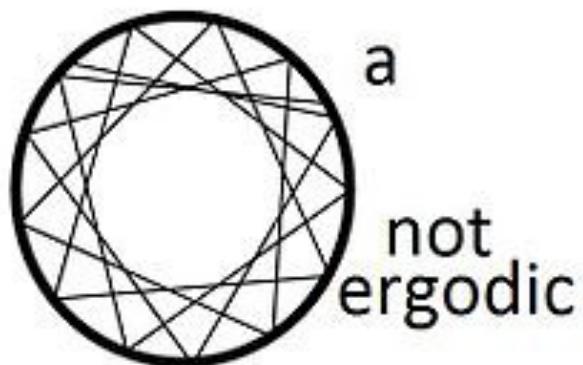


# Statistical Thermodynamics (3)

The “ensamble” approach is valid under the **Ergodic Hypothesis (EH)**, which assumes that this system exhibits the same average properties in space as a single system exhibits in time:

$$\langle X \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau X(t) dt = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M X_i$$

The EH implies that in its dynamical evolution during a very long time, the system “explores” all possible states:



**Example of breaking of the EH:** spontaneous magnetization in ferromagnetic materials below the Curie temperature.



# Statistical Thermodynamics (4)

Different kinds of “ensembles” can be defined based on the “walls” separating the replicas (i.e. depending on the interaction among replicas).

In particular, the **canonical ensemble** describes a system with a fixed number of particles  $N$ , constant volume  $V$ , and held at a constant temperature  $T$  by being in thermal contact with a large heat bath, allowing energy exchange but not particle exchange.

1	2	-
-	-	-
-	-	$\alpha$
-	-	$\alpha$

$T_1 = T_2 = \dots = T_\alpha$   
 $V_1 = V_2 = \dots = V_\alpha$   
 $N_1 = N_2 = \dots = N_\alpha$   
 $U_{\text{total}} = \text{constant}$

In the canonical ensemble, the probability of each microstate  $m$  is given by:

$$\wp_m = \frac{\exp(-\beta E_m)}{\sum_n \exp(-\beta E_n)}$$

where the normalization factor at the denominator is the so-called **canonical partition function**  $Z$  (sometimes  $Q$ ).



# Statistical Thermodynamics (5)

All thermodynamic potentials can be derived directly from the canonical partition function. For instance:

$$\begin{aligned}\langle E \rangle &= \frac{1}{Q} \left( -\frac{dQ}{d\beta} \right) \\ &= -\frac{d \ln Q}{d\beta}\end{aligned}$$

and

$$F(T, V, N) = -k_B T \ln Q(T, V, N)$$

By considering the *electronic*, *rotational*, *translational* and *vibrational* degrees of freedom as **independent**, the canonical partition function can be factorized as:

$$Q_{\text{tot}} = Q_{\text{tra}} \times Q_{\text{rot}} \times Q_{\text{ele}} \times Q_{\text{vib}}$$

For an **ideal solid**, there are no translational nor rotational degrees of freedom, so the partition function reduces to:

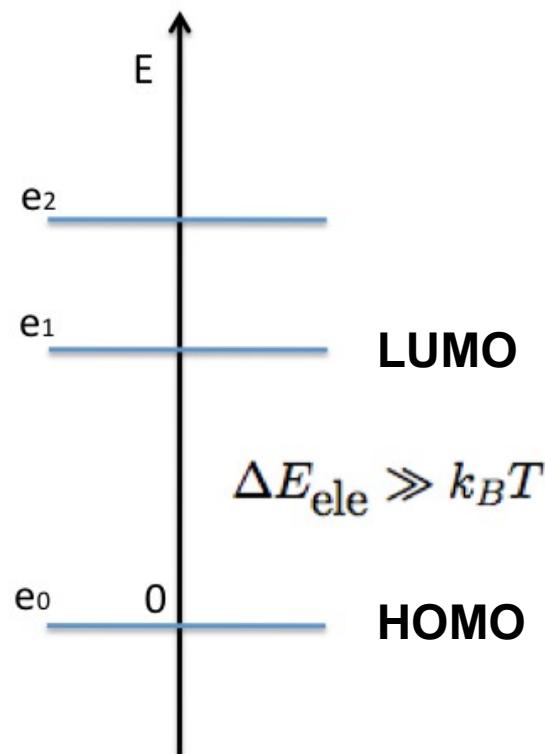
$$Q_{\text{tot}} = Q_{\text{ele}} \times Q_{\text{vib}}$$



# Statistical Thermodynamics (6)

## Electronic Degrees of Freedom - Molecules

Given that the **HOMO-LUMO** energy separation among electronic energy levels is typically much larger than the thermal energy, the electronic contribution to the partition function is negligible:



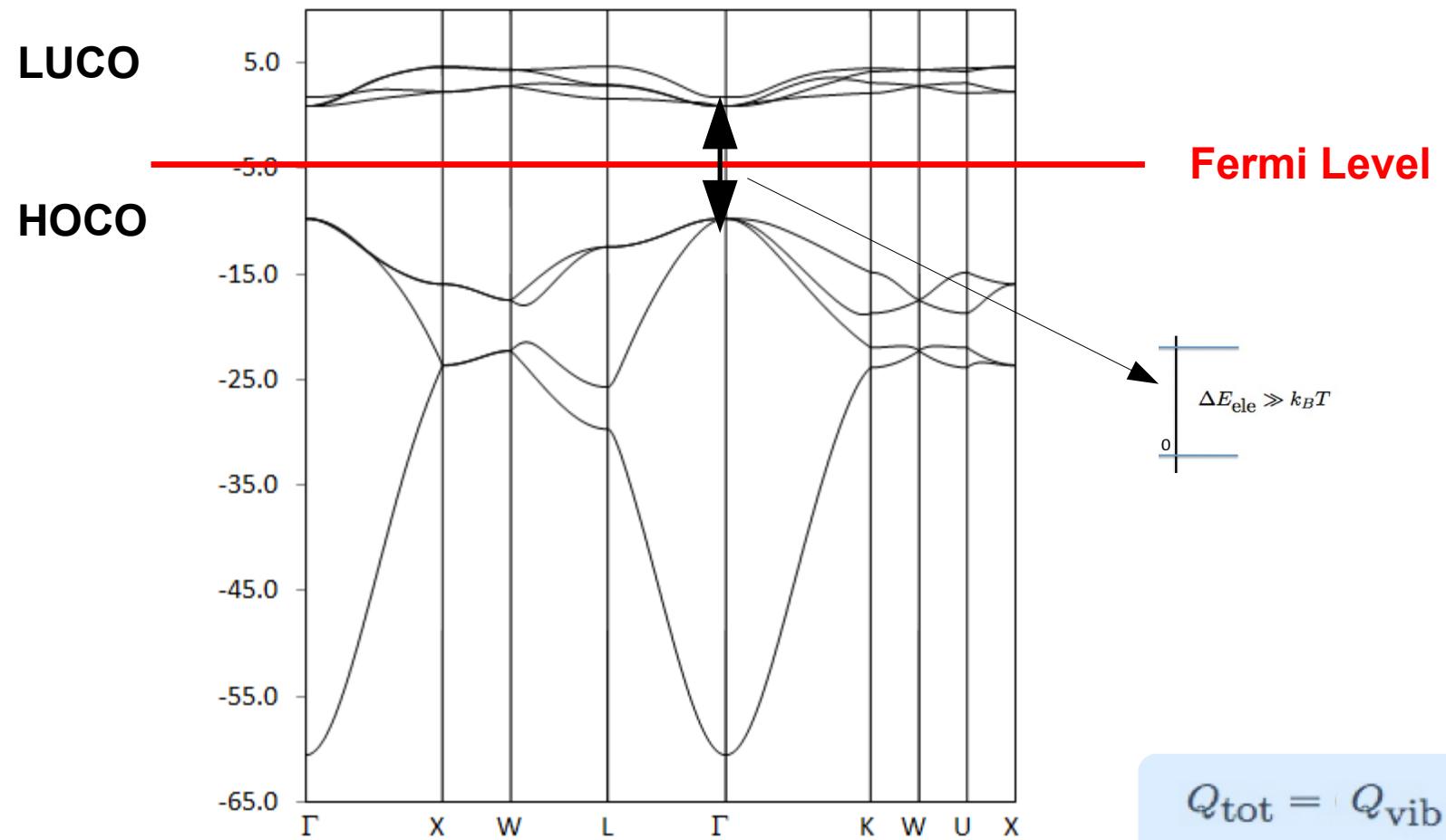
$$\begin{aligned} Q_{\text{ele}} &= \sum_j e^{-\frac{e_j}{k_B T}} \\ &= e^{-\frac{e_0}{k_B T}} + e^{-\frac{e_1}{k_B T}} + \dots \\ &= e^{-\frac{0}{k_B T}} + e^{-\frac{e_1}{k_B T}} + \dots \\ &= 1 + 0 + \dots \\ Q_{\text{ele}} &\approx 1 \end{aligned}$$



# Statistical Thermodynamics (6)

## Electronic Degrees of Freedom - Insulators

For **insulators** it is the same:

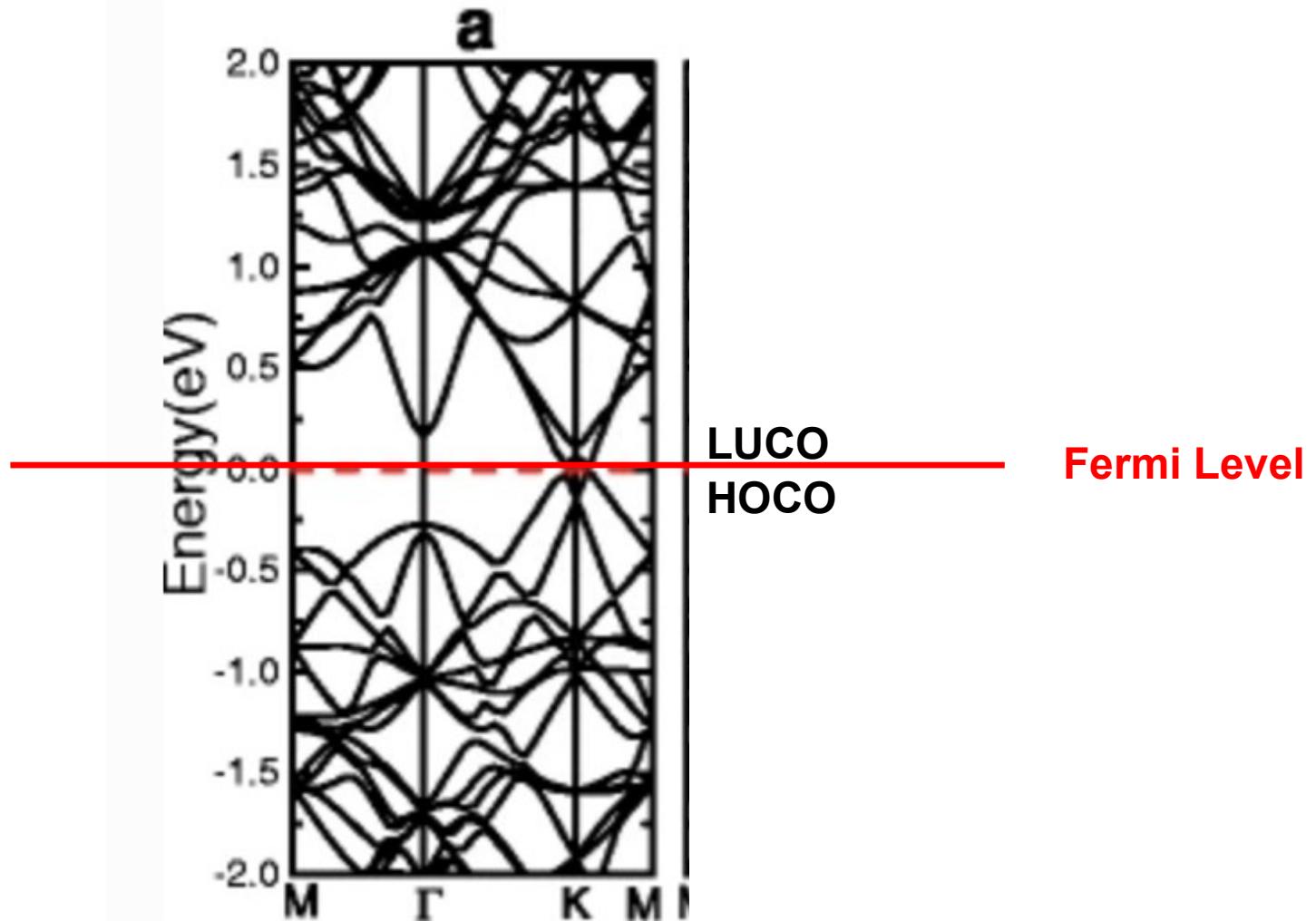




# Statistical Thermodynamics (6)

## Electronic Degrees of Freedom - Metals

For **metals**, a small term from the electronic partition function may arise:

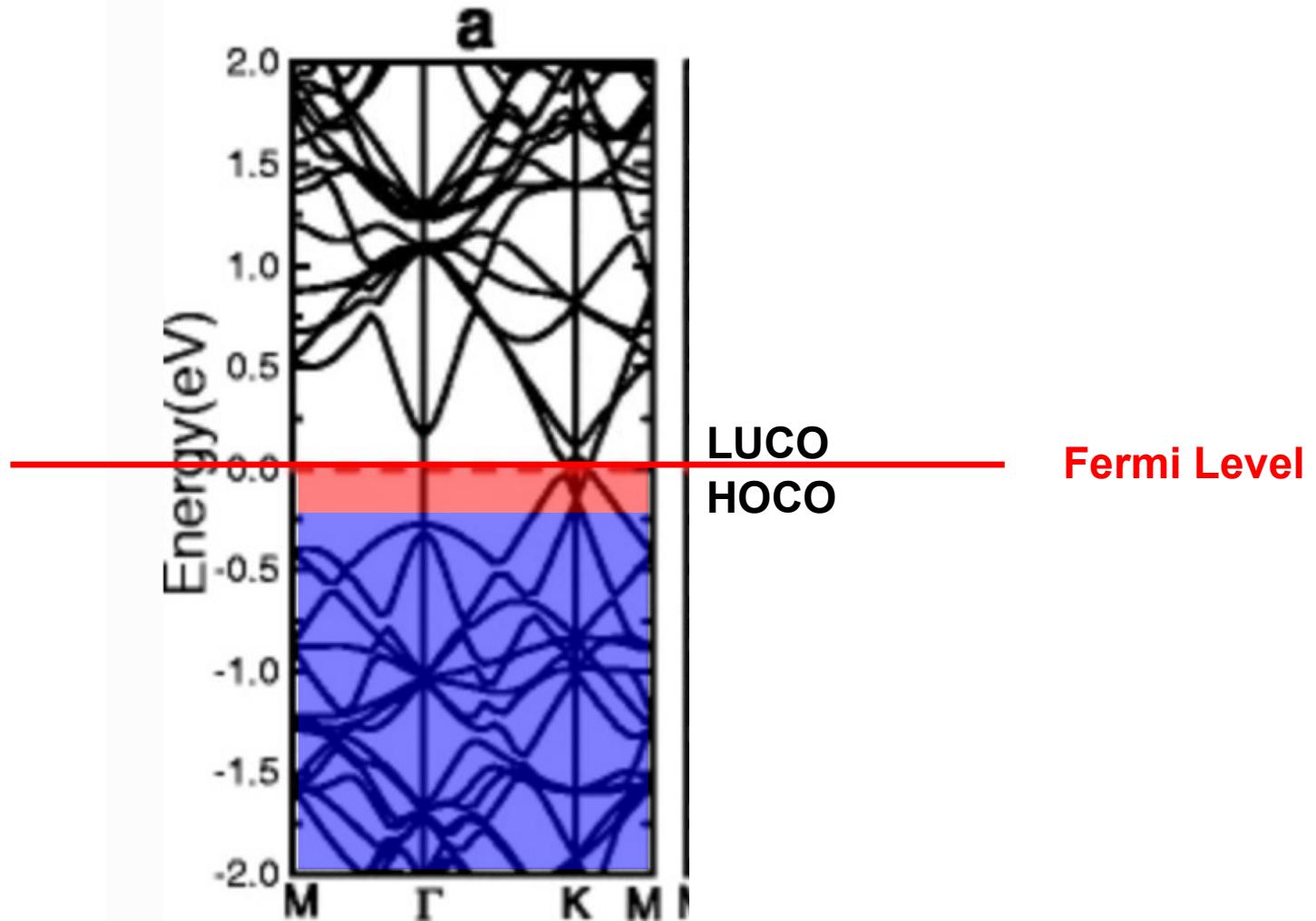




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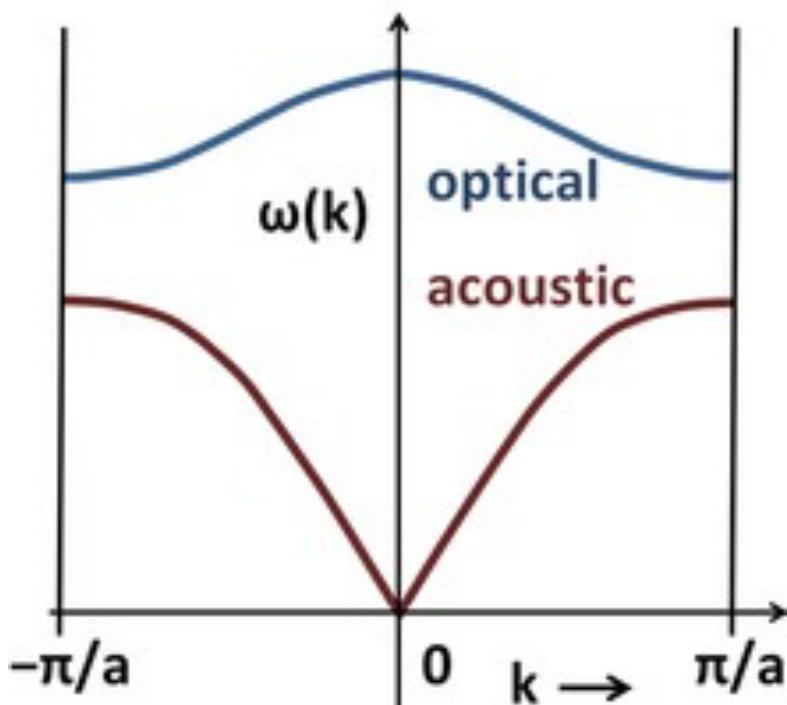
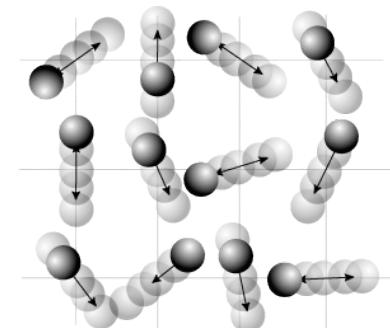


# Einstein's Model for the Specific Heat

In 1907, Einstein showed how the quantization concept that explained Planck's distribution law for blackbody radiation also explained the low-temperature behavior of the heat capacities of the solid elements:

The Einstein model of crystals assumes the following:

- 1) Each direction of each atom gives an independent harmonic oscillator, such that there are  $3N$  oscillators.
- 2) The frequencies of all of the harmonic oscillators are the same, equal to  $\nu$ .



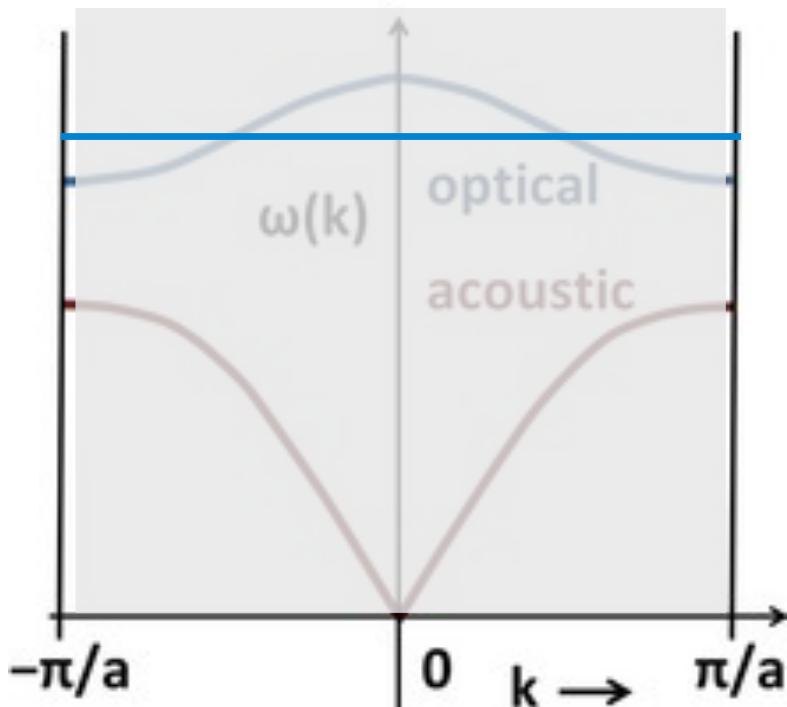
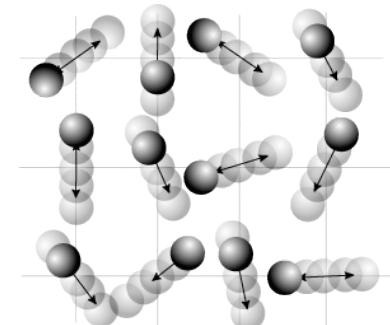


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The **Einstein model of crystals** predicts a vanishing heat capacity as the temperature approaches absolute zero. This is quantum behavior and contrasts classical models, for which the heat capacity of a monatomic crystal is always  $3k_B$ .

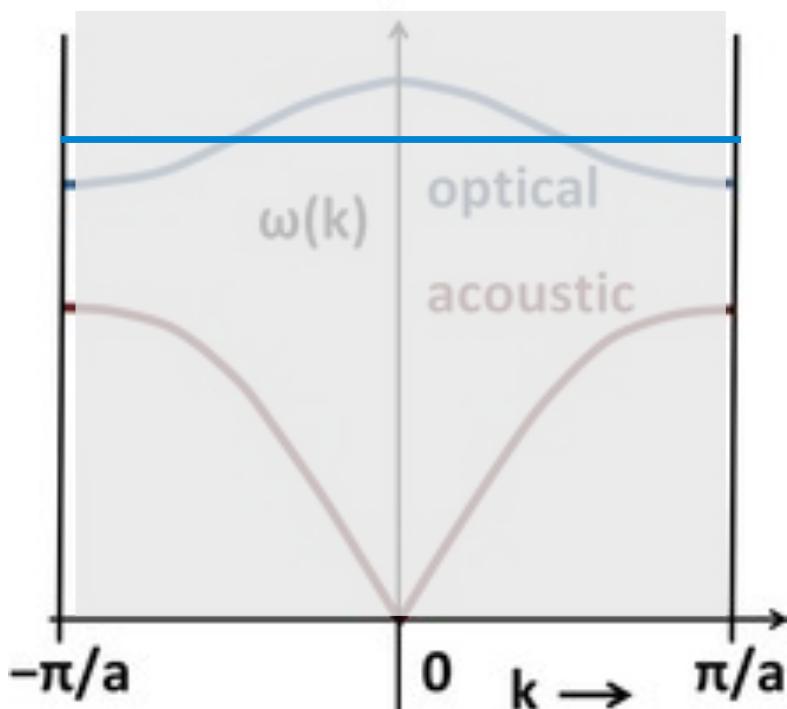
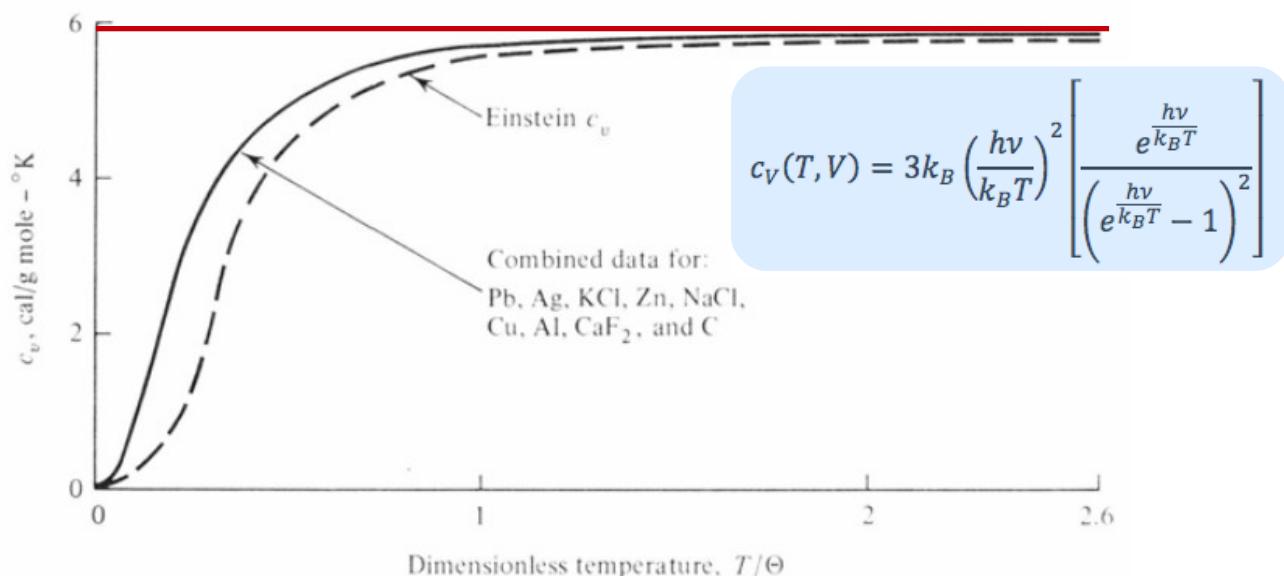


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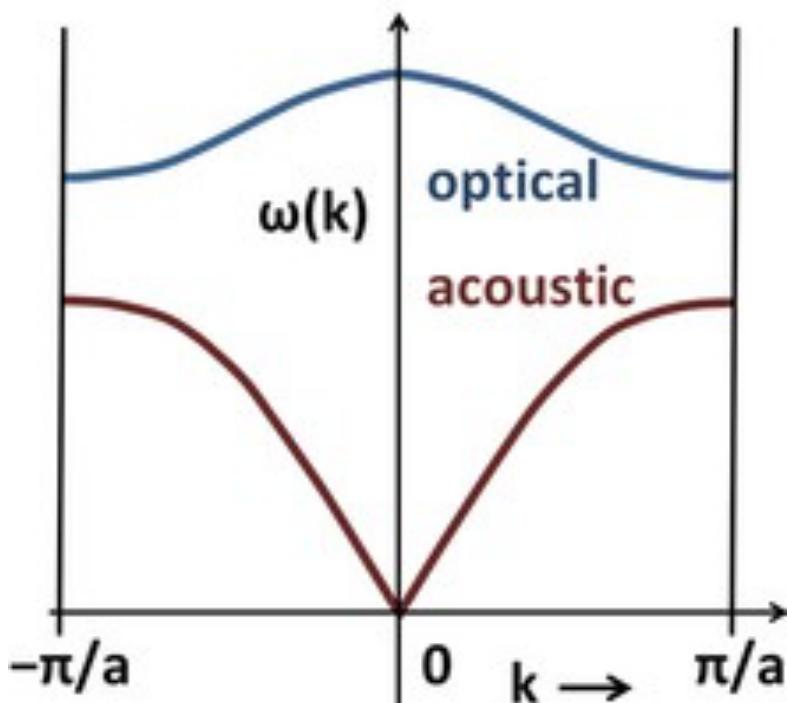
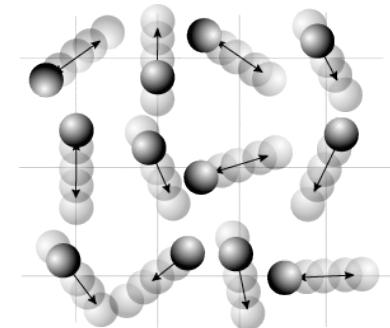




# Debye's Model for the Specific Heat

In 1912, Debye develops his model for estimating the phonon contribution to the specific heat in solids. He basically assumes a linear dependence of phonon frequencies on wave-vector  $\mathbf{k}$ :

The **Debye model of crystals** correctly predicts the experimentally-observed  $T^3$  dependence of the heat capacity in crystals at low temperatures, and demonstrates the origins of this behavior in terms of quantum mechanics.

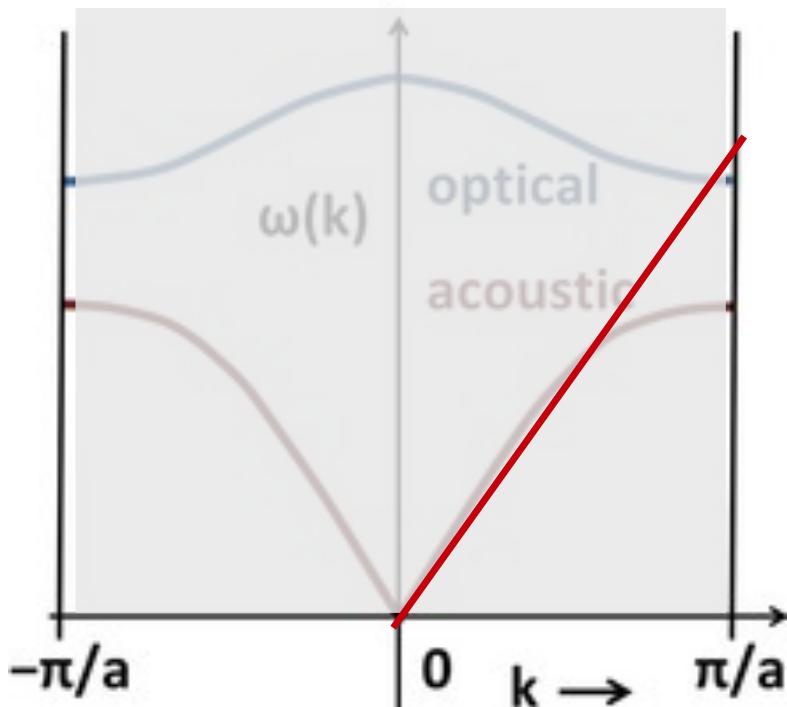
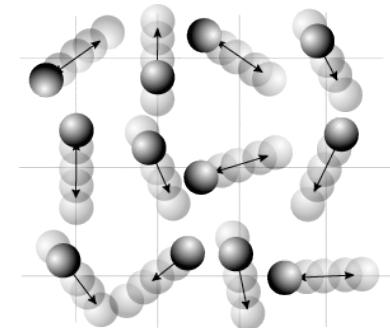




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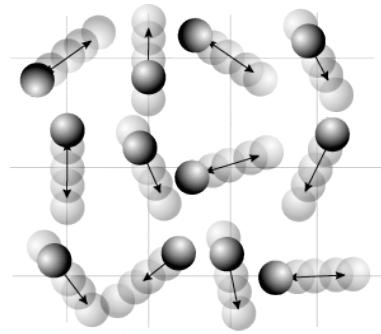
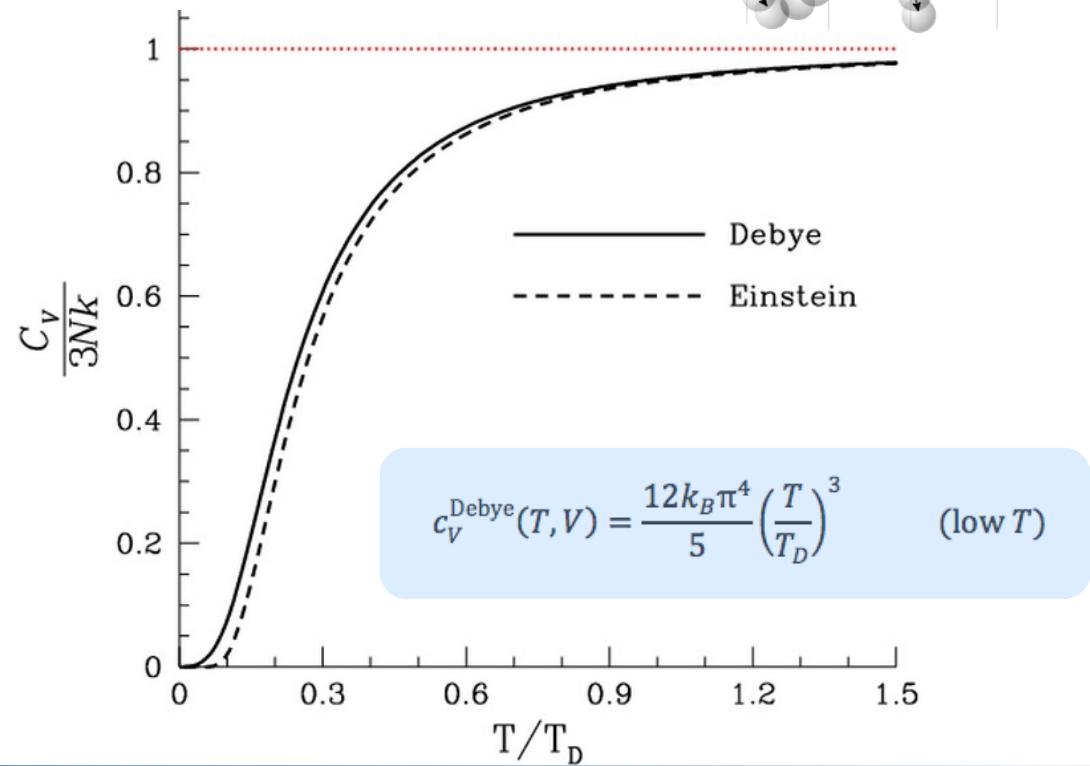
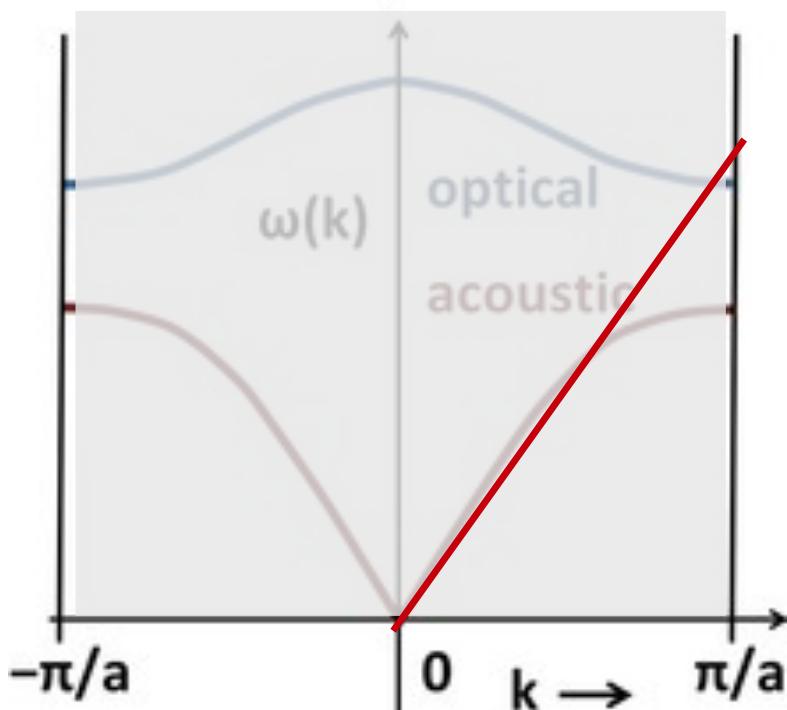




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# Computing Lattice Dynamics

Usually, nuclear motion is described within the **Born-Oppenheimer approximation** (i.e. decoupled from electronic motion). The electronic Schroedinger equation is solved at fixed nuclear configurations:

$$H^{\text{ele}}(\mathbf{r}; \mathbf{R})\Psi(\mathbf{r}; \mathbf{R}) = E(\mathbf{r}; \mathbf{R})\Psi(\mathbf{r}; \mathbf{R})$$

where  $\mathbf{r}$  are electronic coordinates and  $\mathbf{R}$  are nuclear coordinates. Then the nuclear Schroedinger equation is solved:

$$H^{\text{nuc}}(\mathbf{R})\Psi(\mathbf{R}) = \mathcal{E}(\mathbf{R})\Psi(\mathbf{R})$$

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# Computing Lattice Dynamics: Harmonic App.

The nuclear Schroedinger equation is commonly solved by resorting to the **harmonic approximation**, i.e. by expanding the PES in a Taylor's series in the atomic Cartesian displacements  $\mathbf{u}$ , and truncating to second order:

$$E(\mathbf{R}) \simeq \sum_{i,j} \left( \frac{\partial^2 E}{\partial u_i \partial u_j} \right) \mathbf{u}_i \mathbf{u}_j$$

In this way, the nuclear dynamics is described in terms of a set of independent quantum harmonic oscillators, with exact known solutions for energy and wave-functions.

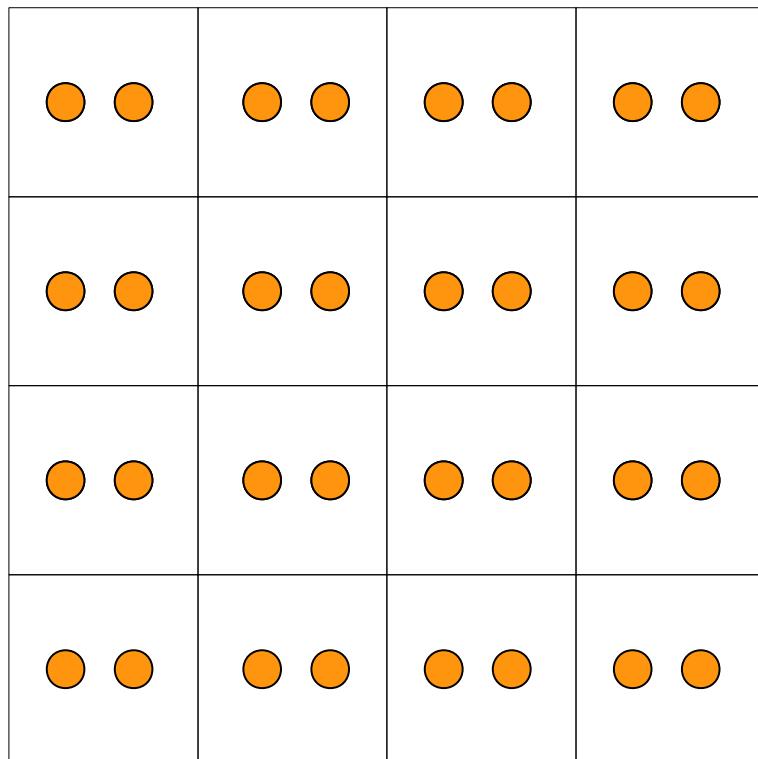
For a finite molecular system, harmonic vibration frequencies  $\omega_i$  and normal modes are obtained from the diagonalization of the mass-weighted Hessian matrix of second energy derivatives with respect to pairs of atomic displacements:

$$H_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j} \quad \mathbf{W} \rightarrow W_{ij} = \frac{H_{ij}}{\sqrt{M_i M_j}} \quad \text{then} \quad \mathbf{WU} = \boldsymbol{\Lambda} \mathbf{U}$$



# Direct Space Approach to Phonon Dispersion

In CRYSTAL, a direct space (**frozen phonon**) approach is implemented where the interatomic force constants are first computed in direct space (in general within a **supercell**) and then Fourier transformed to reciprocal space where the dynamical matrices are built and diagonalized:



$$H_{ij}^{\mathbf{g}} = \frac{\partial^2 E}{\partial u_{i0} \partial u_{jg}}$$

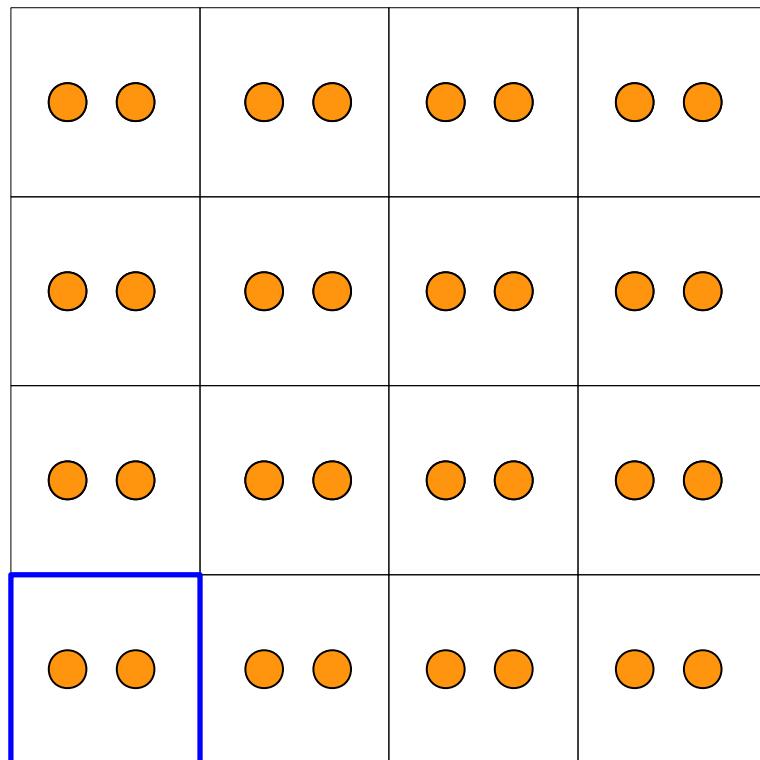
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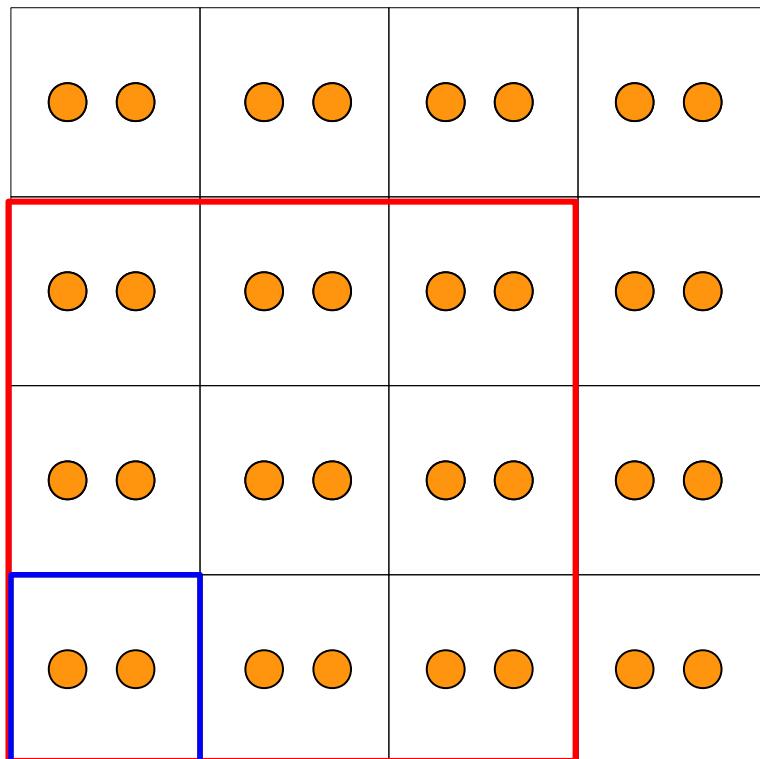
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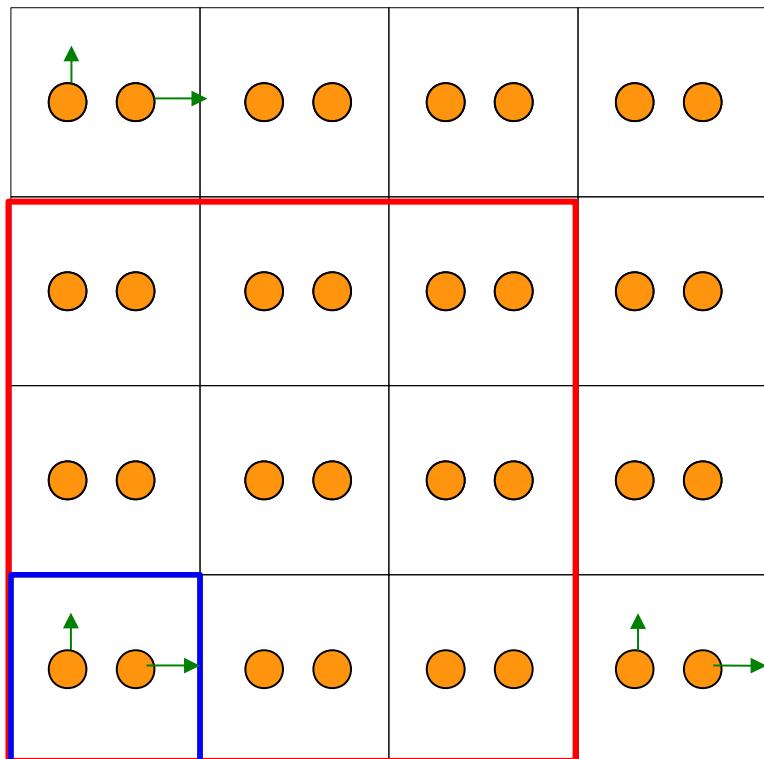
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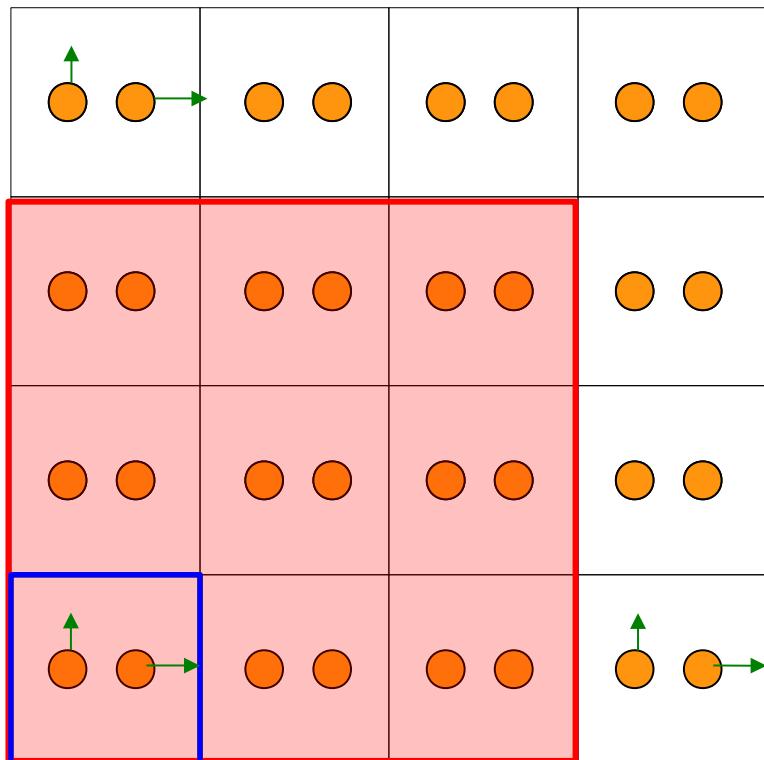
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Atoms are displaced only in the blue cell.



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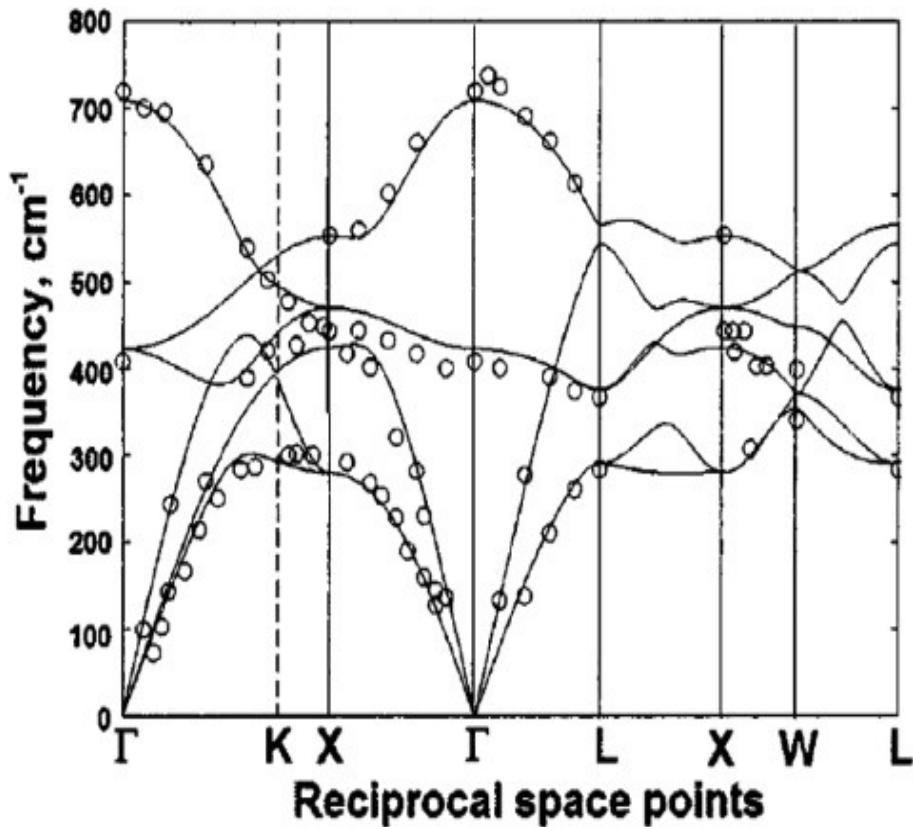
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The forces acting on all the atoms in the red cell are computed.



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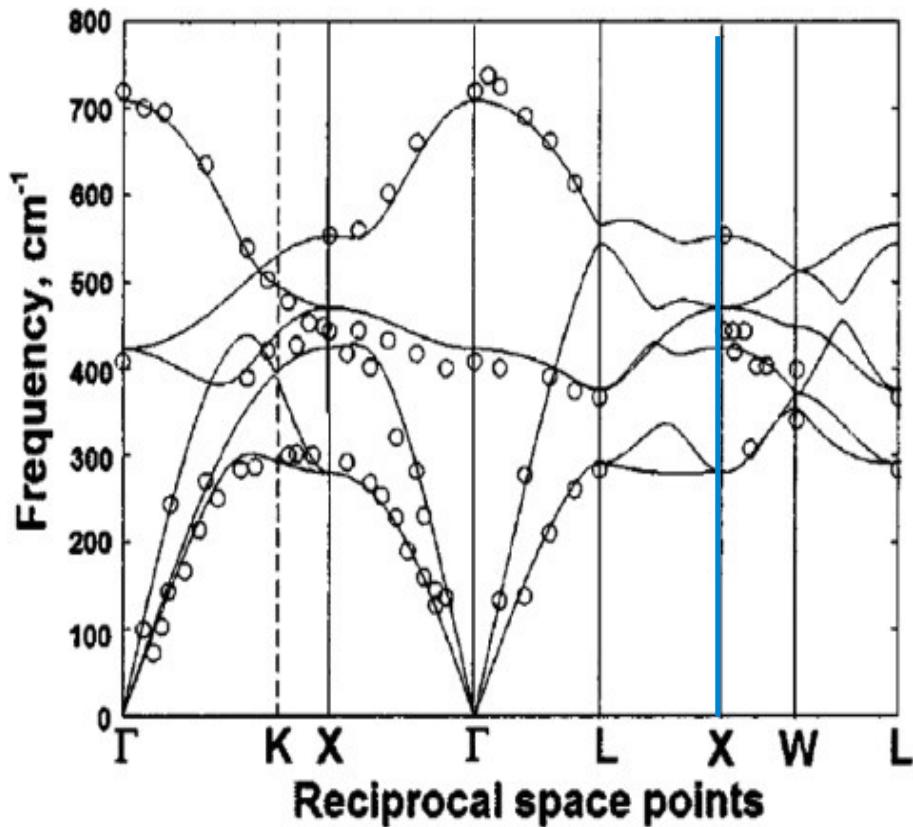
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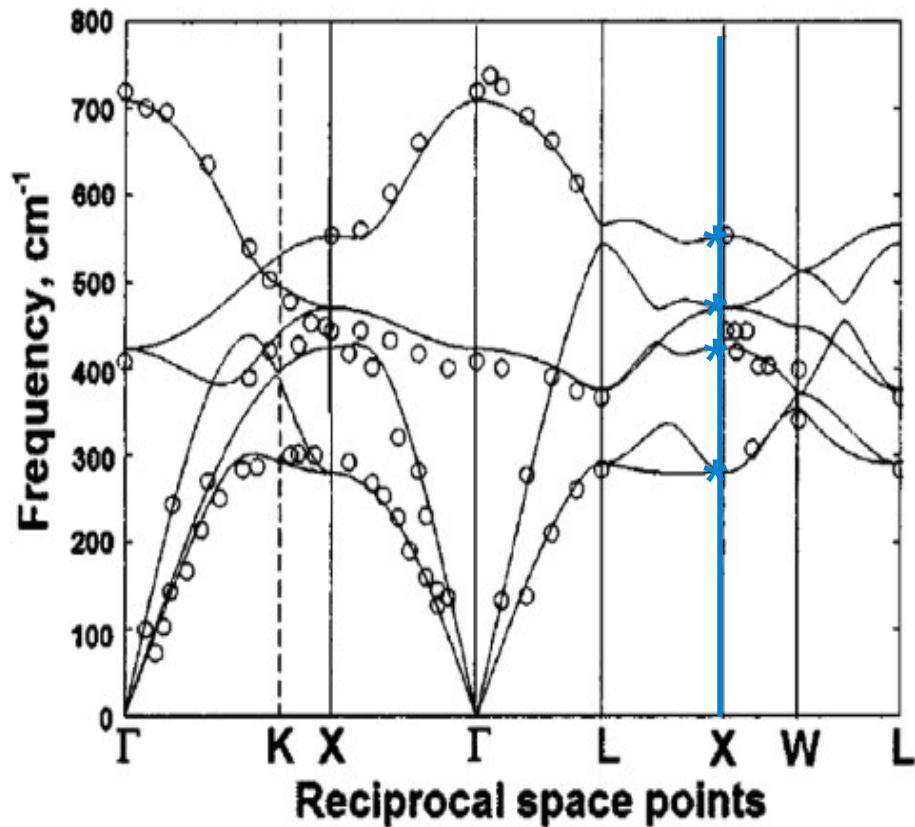
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# From Phonons to Thermodynamics

The **partition function** of the **canonical** ensemble associated to harmonic vibrational degrees of freedom of a solid is defined as follows from phonon frequencies:

$$Z_{\text{vib}}(T) = \prod_{\mathbf{k}} \prod_i \sum_{n=0}^{\infty} e^{-\frac{(\frac{1}{2}+n)\hbar\omega_{\mathbf{k}i}}{k_B T}}$$

All thermodynamic state functions can be derived from it. For instance:

$$U_{\text{vib}}(T) = -\frac{d \ln Z_{\text{vib}}}{d\beta}$$

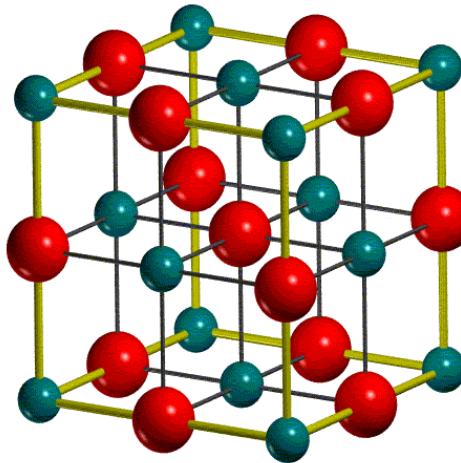
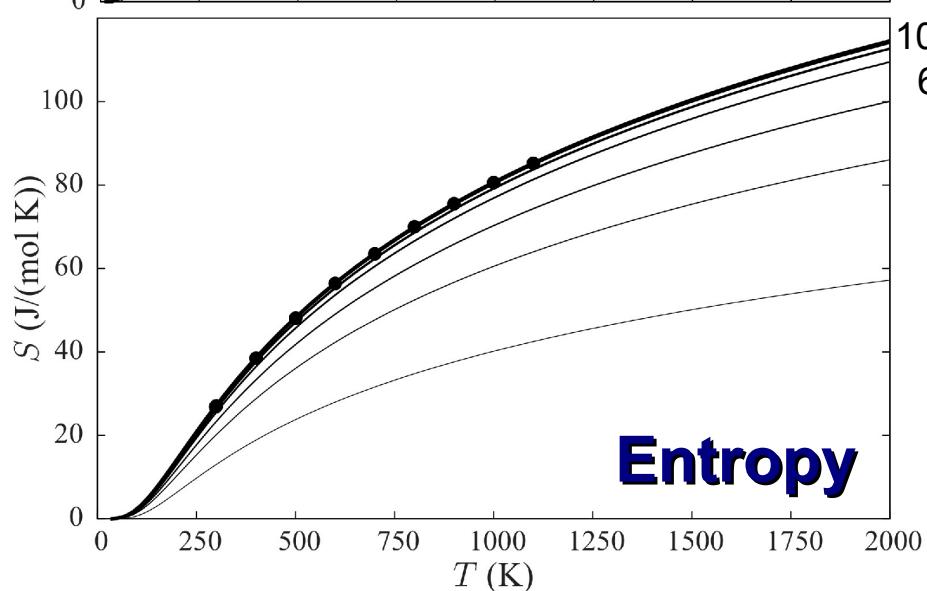
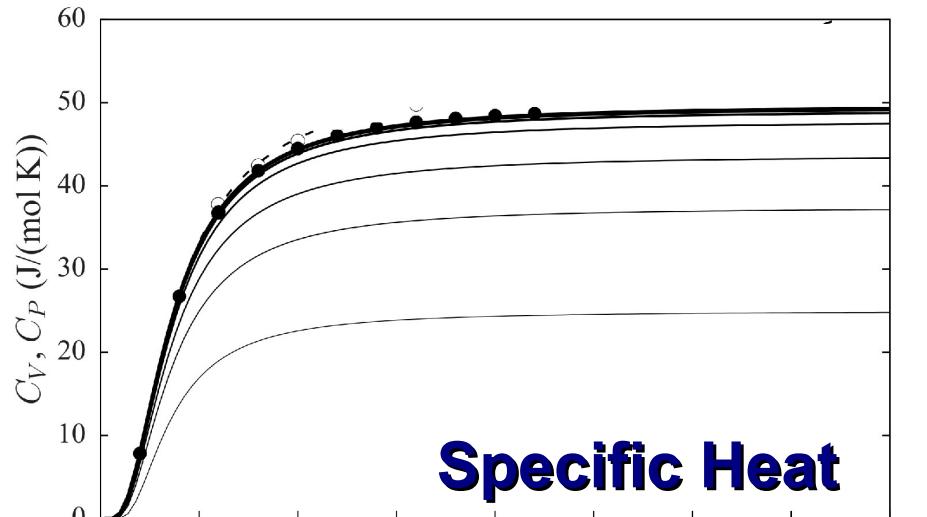
$$S_{\text{vib}}(T) = \frac{U_{\text{vib}}}{T} + k_B \ln Z_{\text{vib}}$$

$$F_{\text{vib}}(T) = -k_B T \ln Z_{\text{vib}}$$



# Harmonic Thermodynamics

How large should the supercell be?

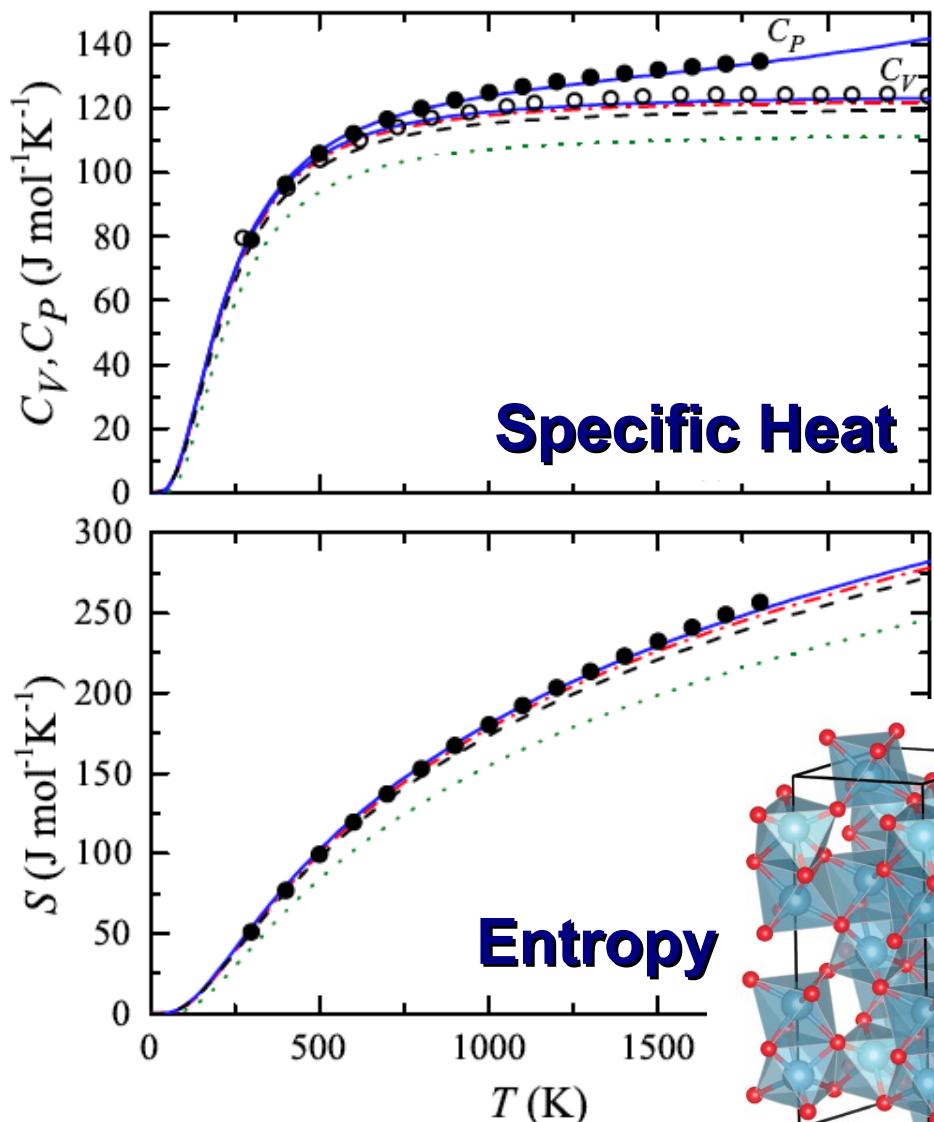


**MgO**

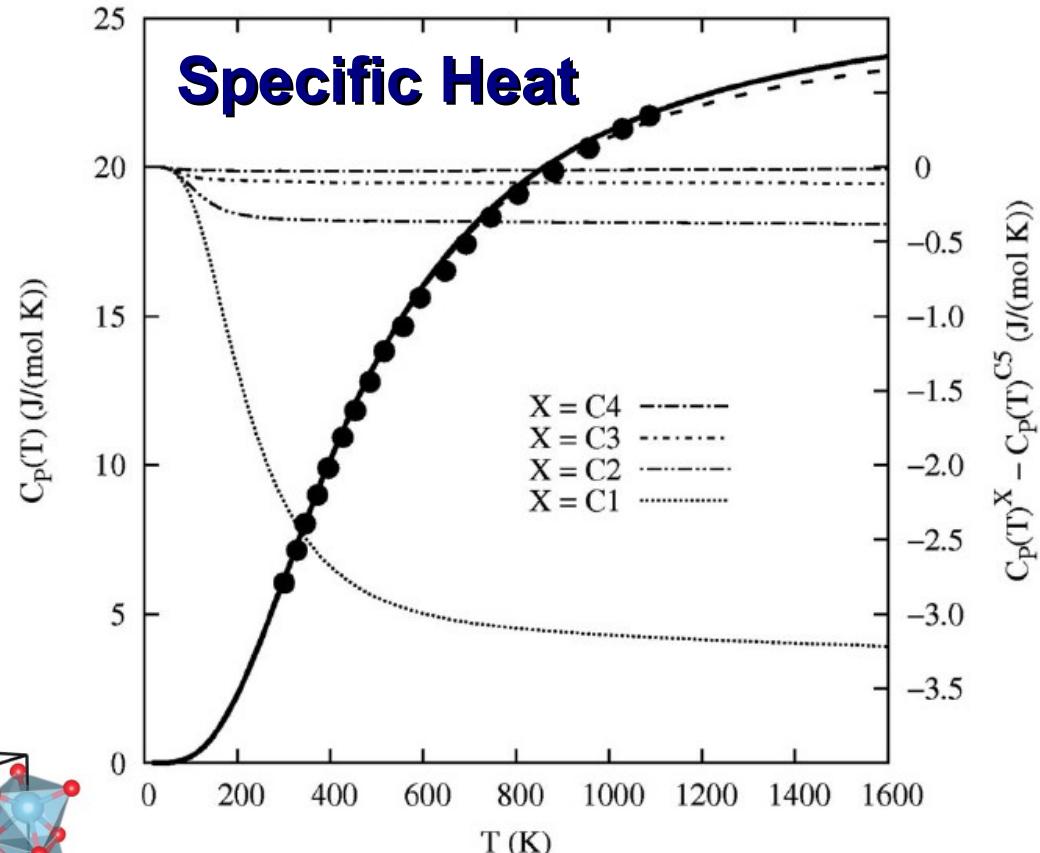
108  $\mathbf{k}$  points / 216 atoms  
64  $\mathbf{k}$  points / 128 atoms  
8  $\mathbf{k}$  points / 16 atoms  
4  $\mathbf{k}$  points / 8 atoms  
1  $\mathbf{k}$  point / 2 atoms

AE, M. Shahrokh, R. Moradian and R. Dovesi,  
*J. Chem. Phys.*, **142**, 044114 (2015)

# Harmonic Thermodynamics

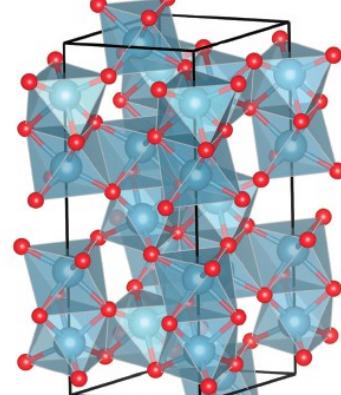


AE, J. Maul, R. Demichelis and R. Dovesi,  
*Phys. Chem. Chem. Phys.*, **17**, 11670-11677 (2015)



AE, *J. Chem. Phys.*, **141**,  
124115 (2014)

Diamond



Corundum



# Limits of the Harmonic Approximation

The harmonic approximation has two main limitations:

**1)** By neglecting higher-than-quadratic terms of the PES, **vibration modes are uncoupled**. As a result:

- Infinite lattice thermal conductivity
- Infinite phonon lifetime
- Zero pyroelectricity
- No mode couplings (i.e. no combination bands, overtones, resonances in spectra)
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**2)** Its description of the lattice dynamics is at **constant volume**. As a result:

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**See next talk by Davide Mitoli**

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**Quasi-Harmonic Approximation**



# Quasi-Harmonic Approximation

The second class of limitations of the HA has mostly to do with **thermal and thermodynamic properties** and can be effectively overcome (at least within a certain temperature range) through the so-called **quasi-harmonic approximation** (QHA):

$$F_{\text{vib}}^{\text{HA}}(T) = U_{\text{zp}} + k_B T \sum_{\mathbf{k}, i} \ln \left[ 1 - e^{-\frac{\hbar \omega_{\mathbf{k}i}}{k_B T}} \right]$$

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The same harmonic expressions for all thermodynamic functions are retained but they gain an additional dependence on volume. The following can be computed:

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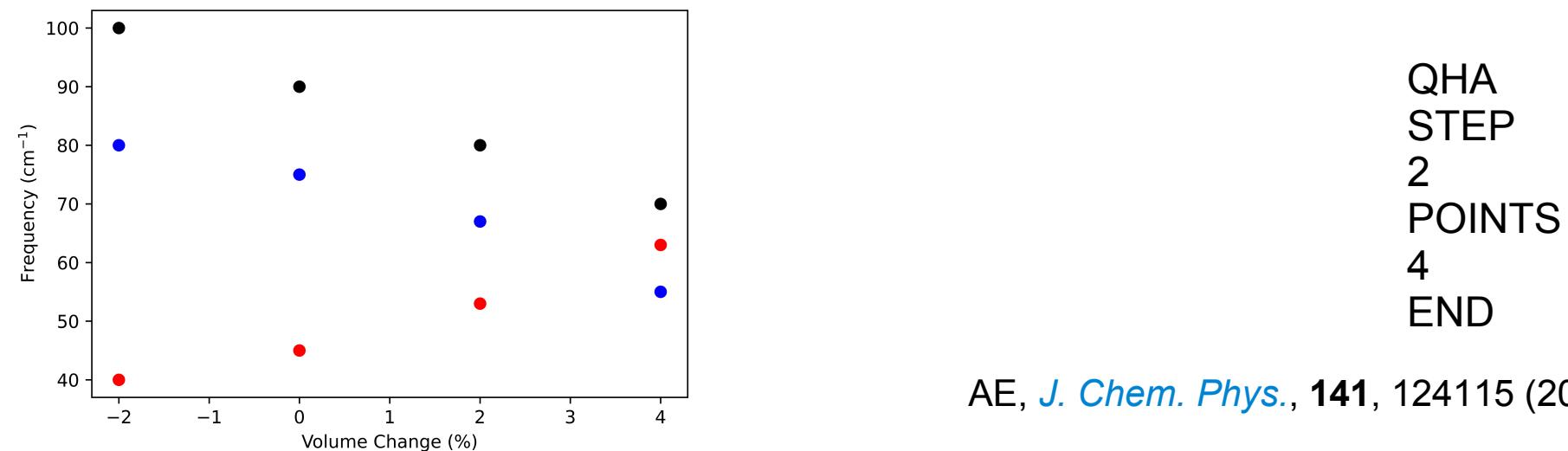
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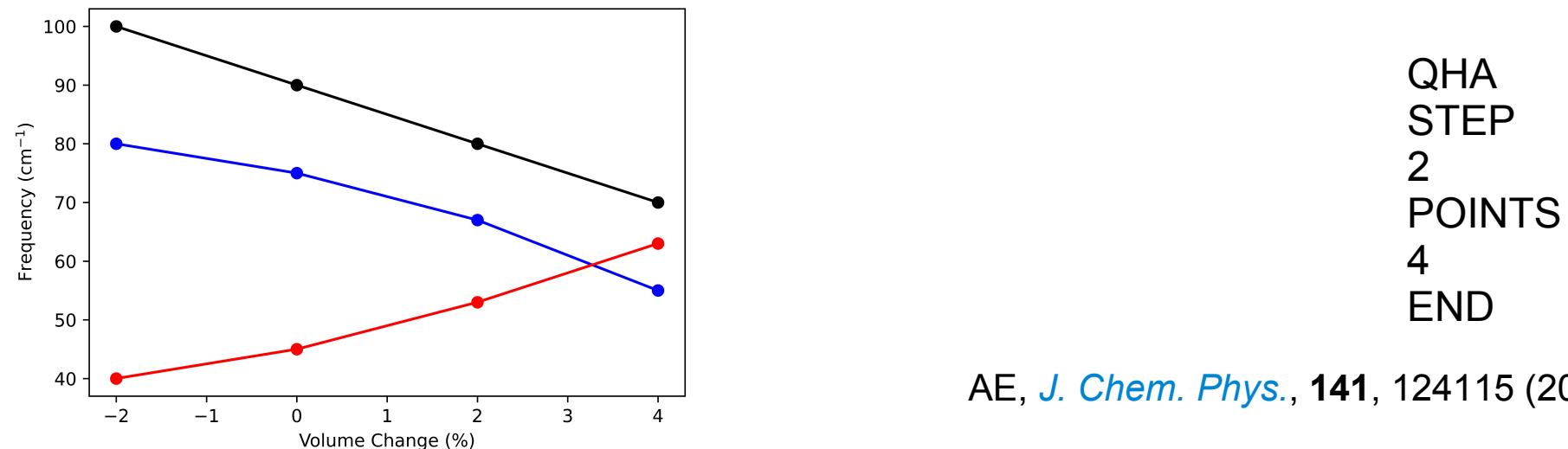


AE, *J. Chem. Phys.*, **141**, 124115 (2014)



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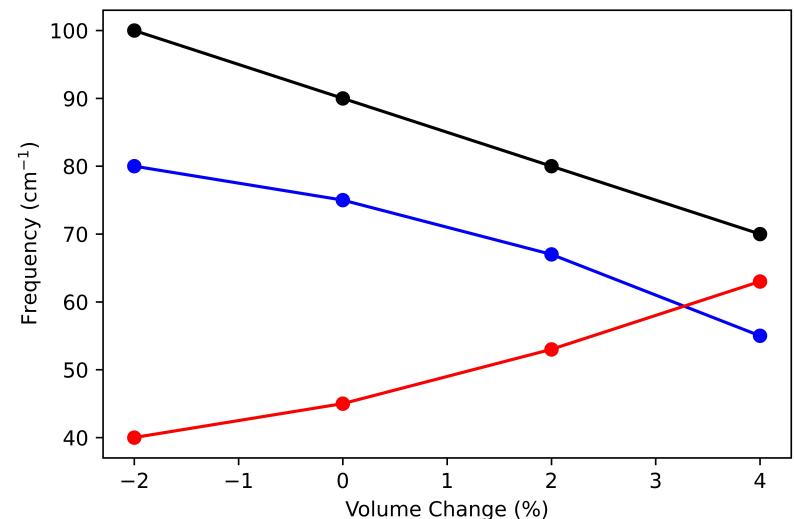
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**Gruneisen parameter > 0**

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**Gruneisen parameter < 0**

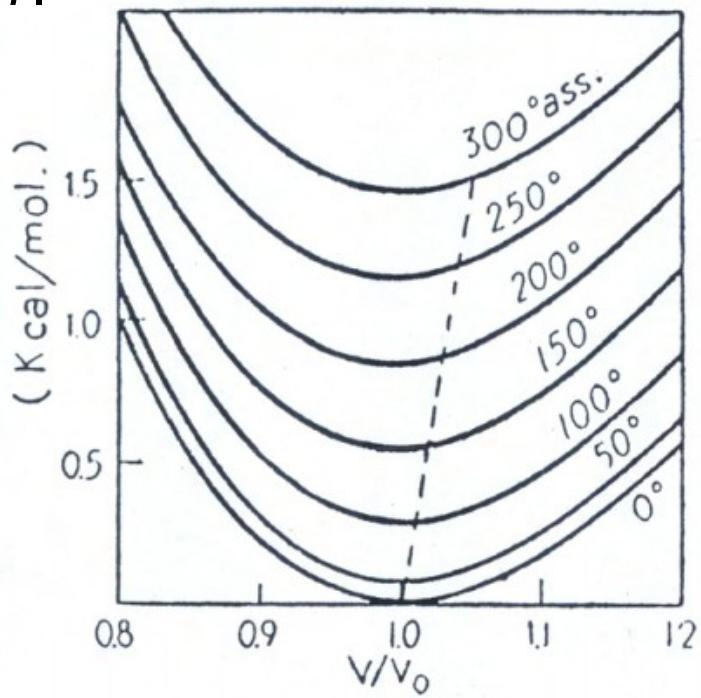
QHA  
STEP  
2  
POINTS  
4  
END

AE, *J. Chem. Phys.*, **141**, 124115 (2014)



# Thermal Expansion

The equilibrium volume  $V(T)$  at a given temperature  $T$  is obtained by minimizing  $F$  with respect to  $V$  at each  $T$ .



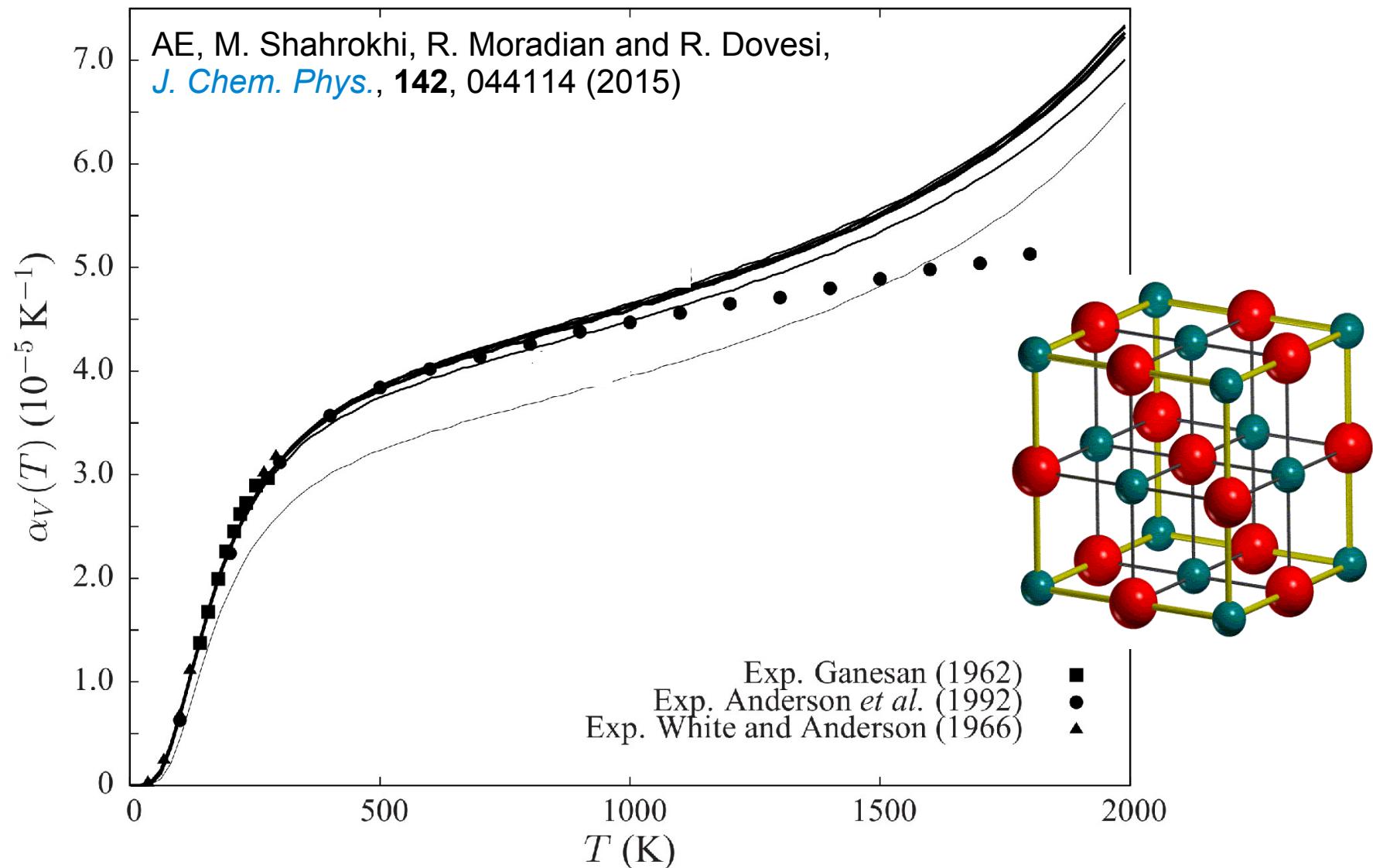
From the  $V(T)$  relation, the **thermal expansion coefficient** is defined as:

$$\alpha_V(T) = \frac{1}{V(T)} \left( \frac{\partial V(T)}{\partial T} \right)_{P=0}$$



# Validity Domain of QHA

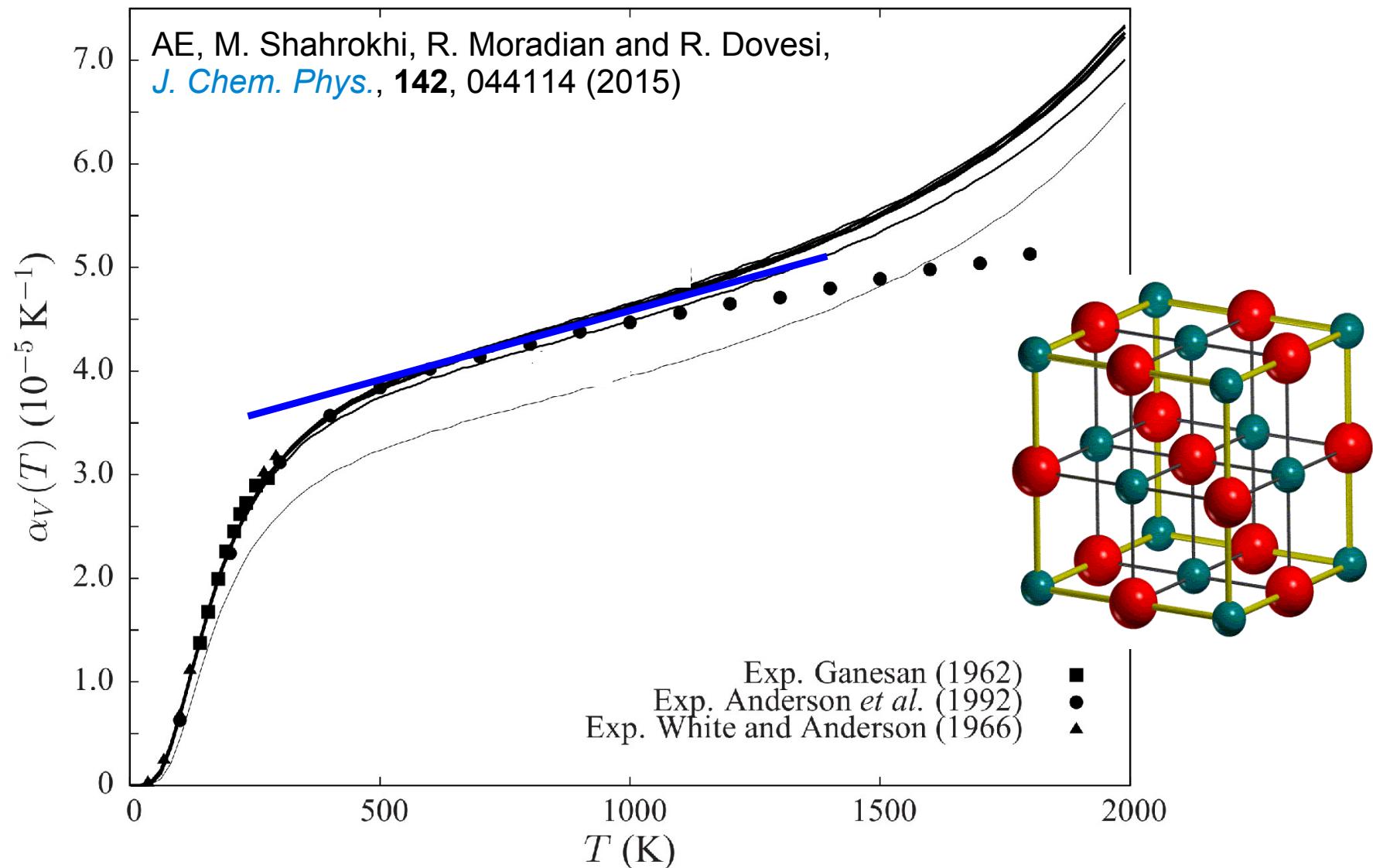
Is the QHA valid at any temperature? Generally not. It depends on the system and on pressure.





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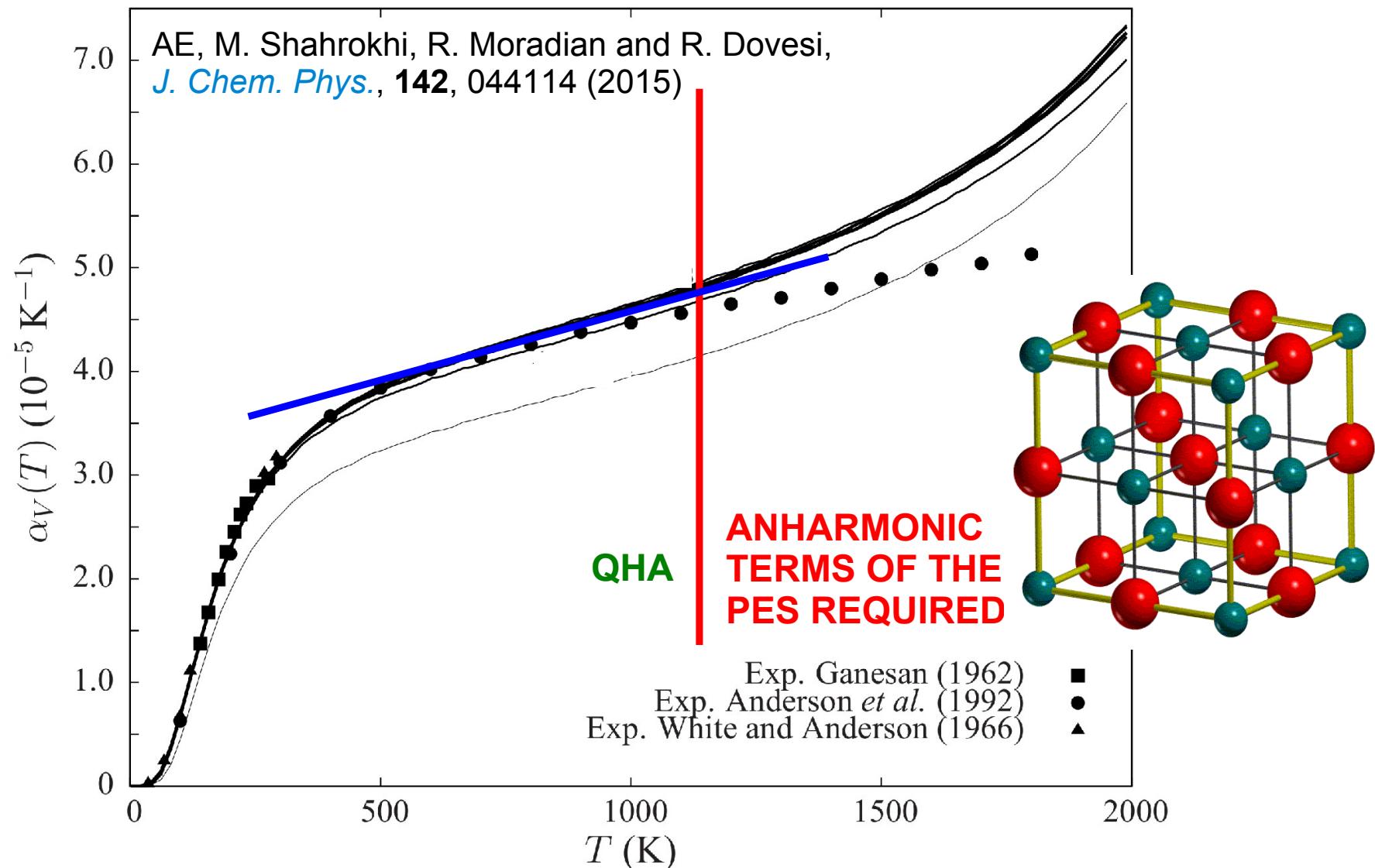
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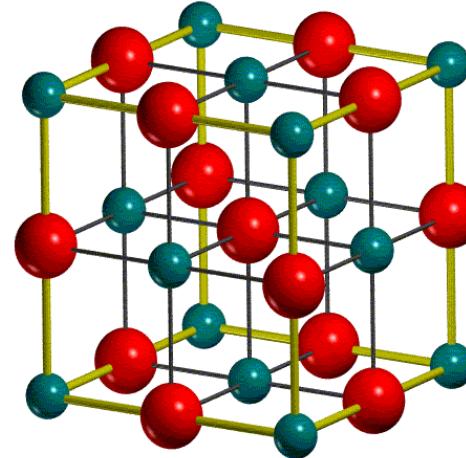
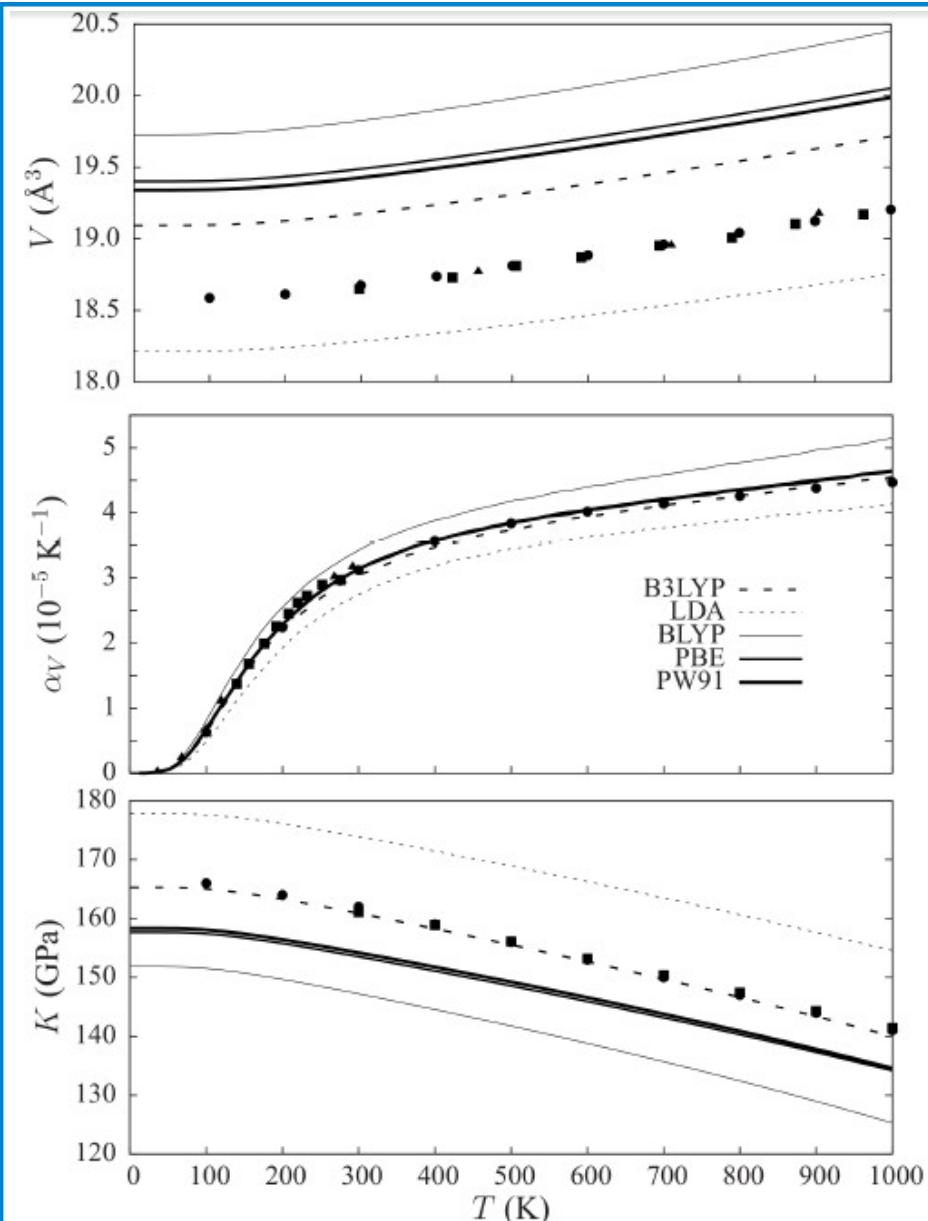
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# Structural and Mechanical Properties



**MgO**

## Bulk Modulus $K(T)$

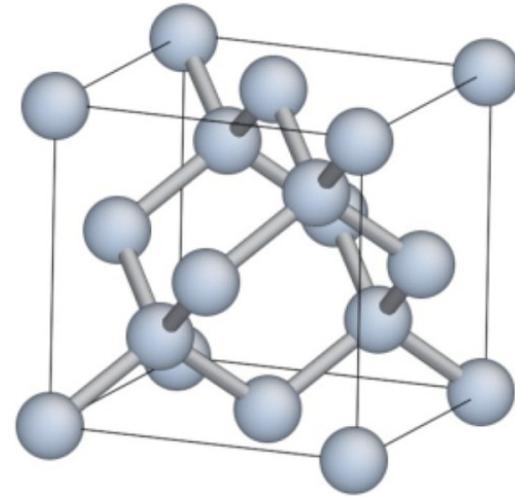
(a measure of the resistance of a substance to bulk compression)

$$K(T) = V(T) \left( \frac{\partial^2 F^{\text{QHA}}(V; T)}{\partial V^2} \right)_T .$$



# Structural and Mechanical Properties

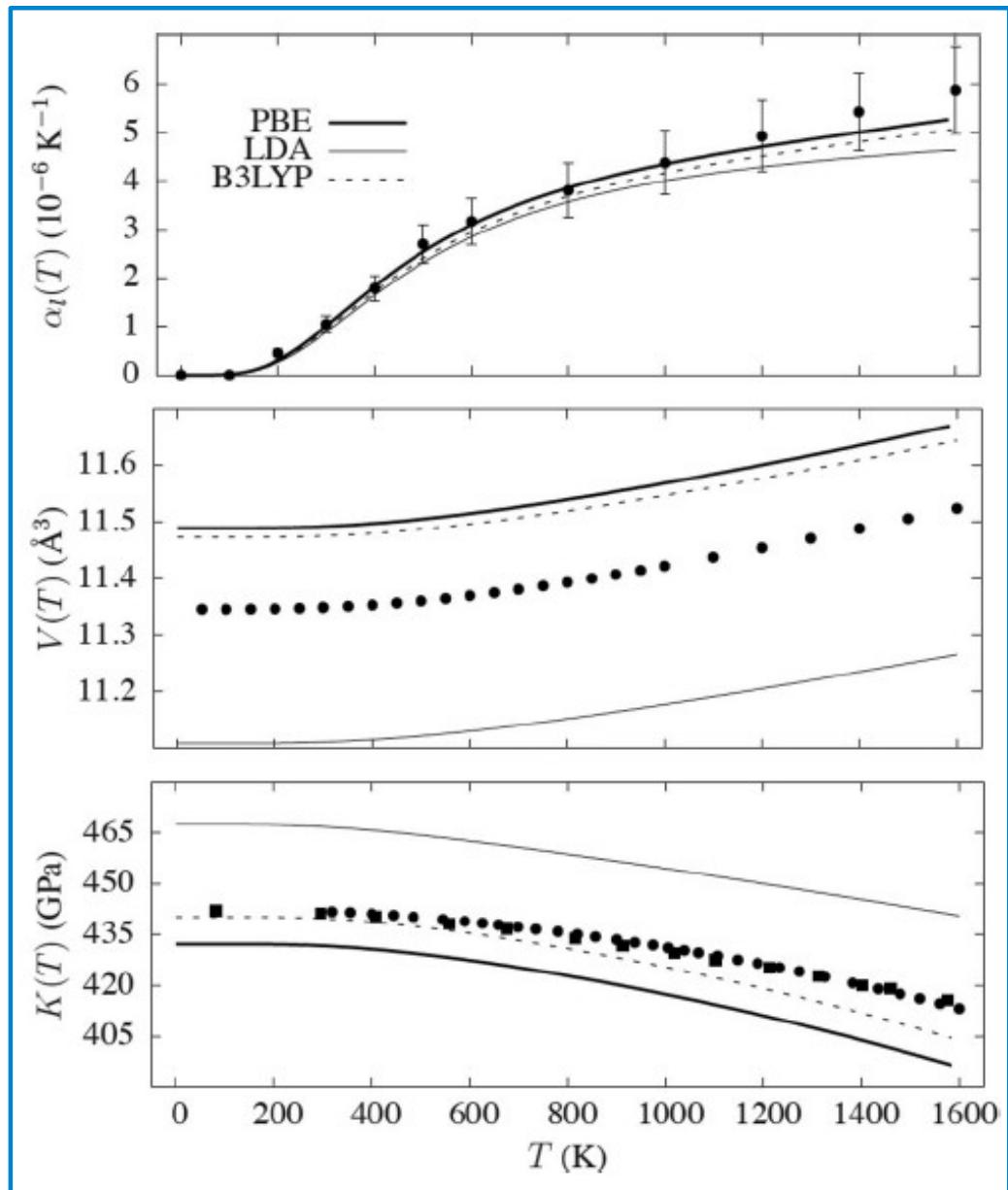
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Diamond

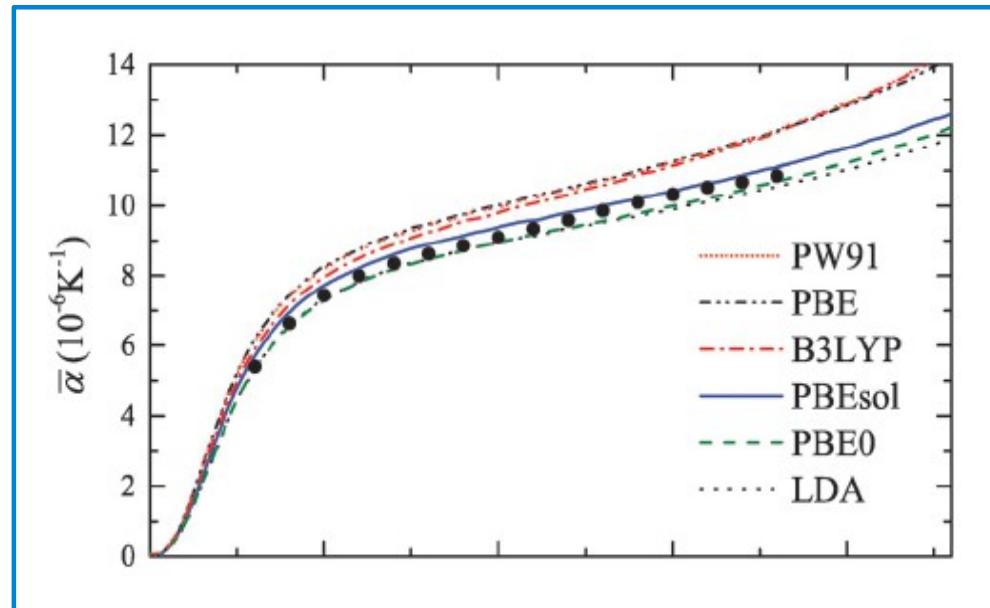
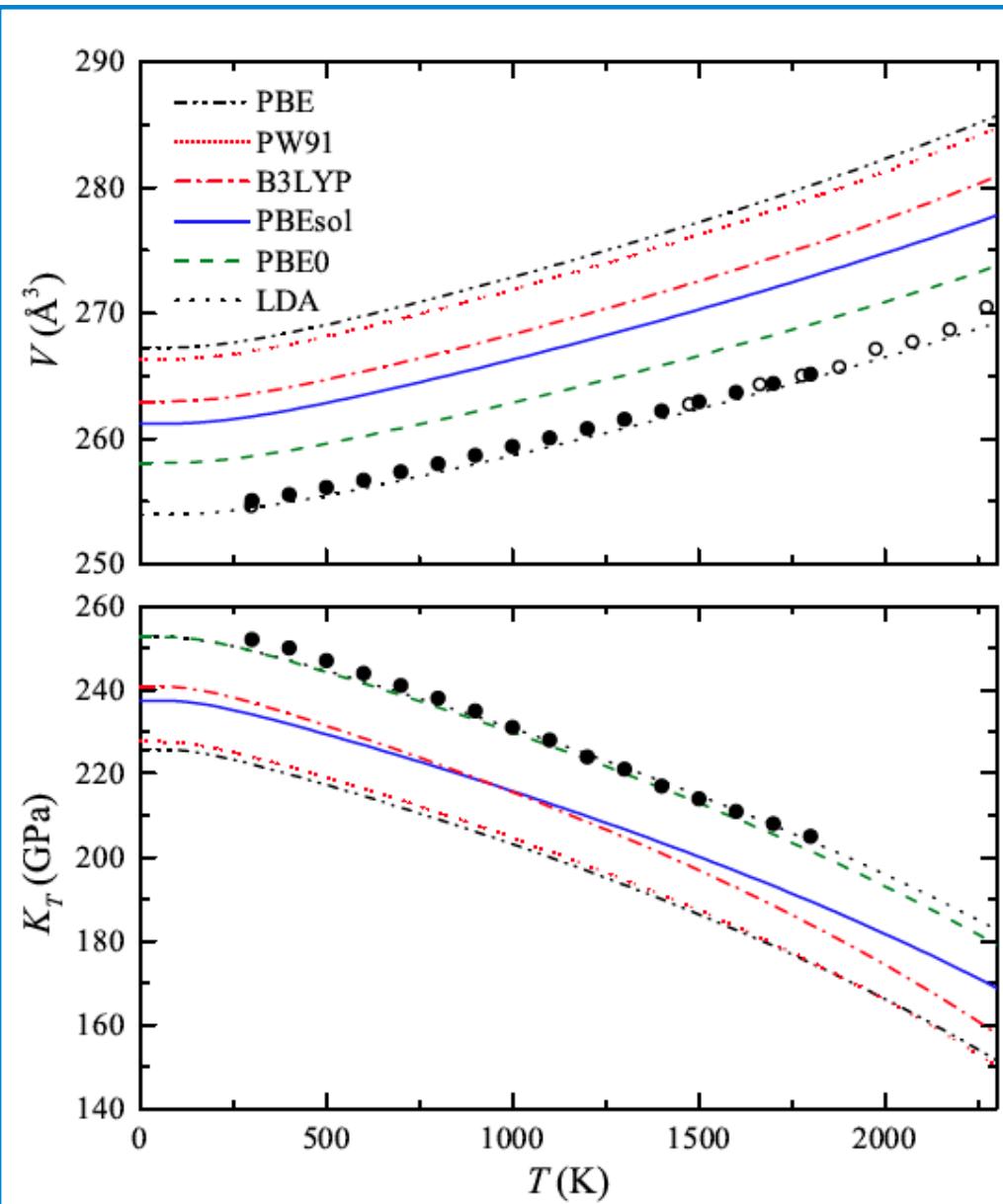
TABLE I. Equilibrium volume of the primitive cell,  $V_0$  (in  $\text{\AA}^3$ ), and bulk modulus,  $K_0$  (in GPa), of diamond at zero pressure and temperature, as computed with different Hamiltonians and compared with experimental values.<sup>50,76</sup> Data in parentheses are obtained by neglecting ZPM effects. The lattice parameter is given by  $a_0 = (4V_0)^{1/3}$ .

	LDA	PBE	B3LYP	Exp.
$V_0$	11.11 (10.99)	11.49 (11.36)	11.48 (11.35)	11.34
$K_0$	467.5 (476.8)	431.2 (441.5)	439.5 (449.2)	442.1

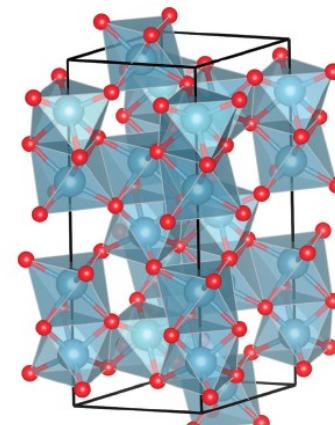




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AE, J. Maul, R. Demichelis and R. Dovesi,  
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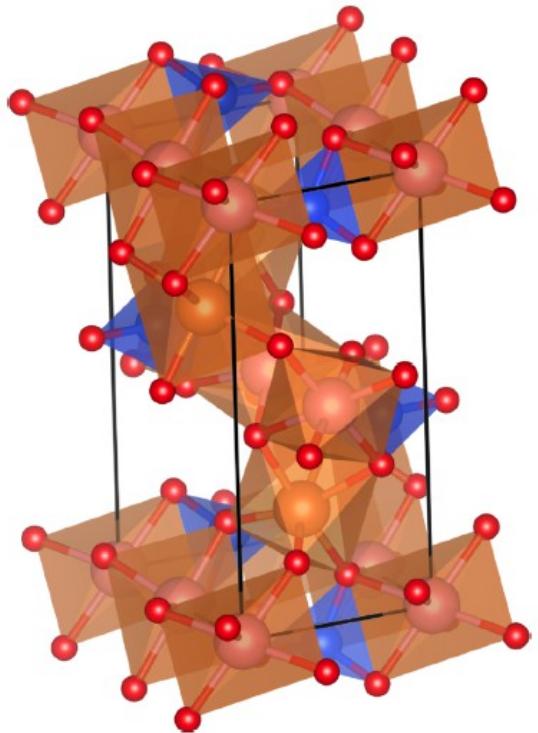


Corundum  $\text{Al}_2\text{O}_3$

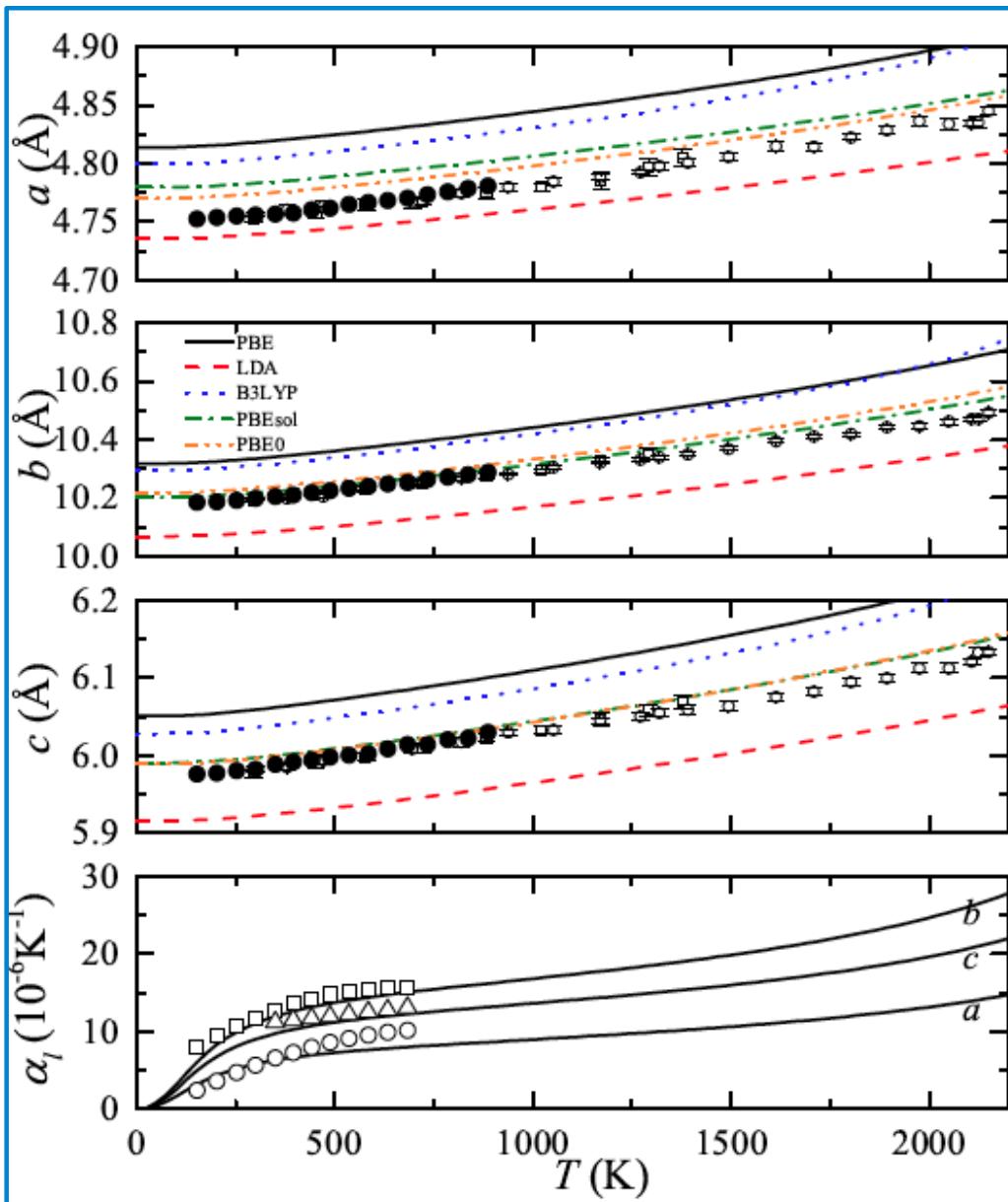


# Anisotropic Thermal Expansion

AE, J. Maul, M. De la Pierre and R. Dovesi,  
*J. Chem. Phys.*, **142**, 204502 (2015)



Forsterite  $\text{Mg}_2\text{SiO}_4$



# Quasi-Harmonic Approximation



## Thermal expansion

**Molecular crystals** still represent a challenge to state-of-the-art quantum-chemical methods:

- 1) A **balanced description** of many **chemical interactions** (including weak ones) is needed. We use Grimme's **DFT-D3**.
- 2) They are typically characterized by **soft phonon modes** (high numerical precision needed).
- 3) **Low symmetry, more atoms** than simple inorganic solids.
- 4) **High anharmonicity** of optical modes (many hydrogens).

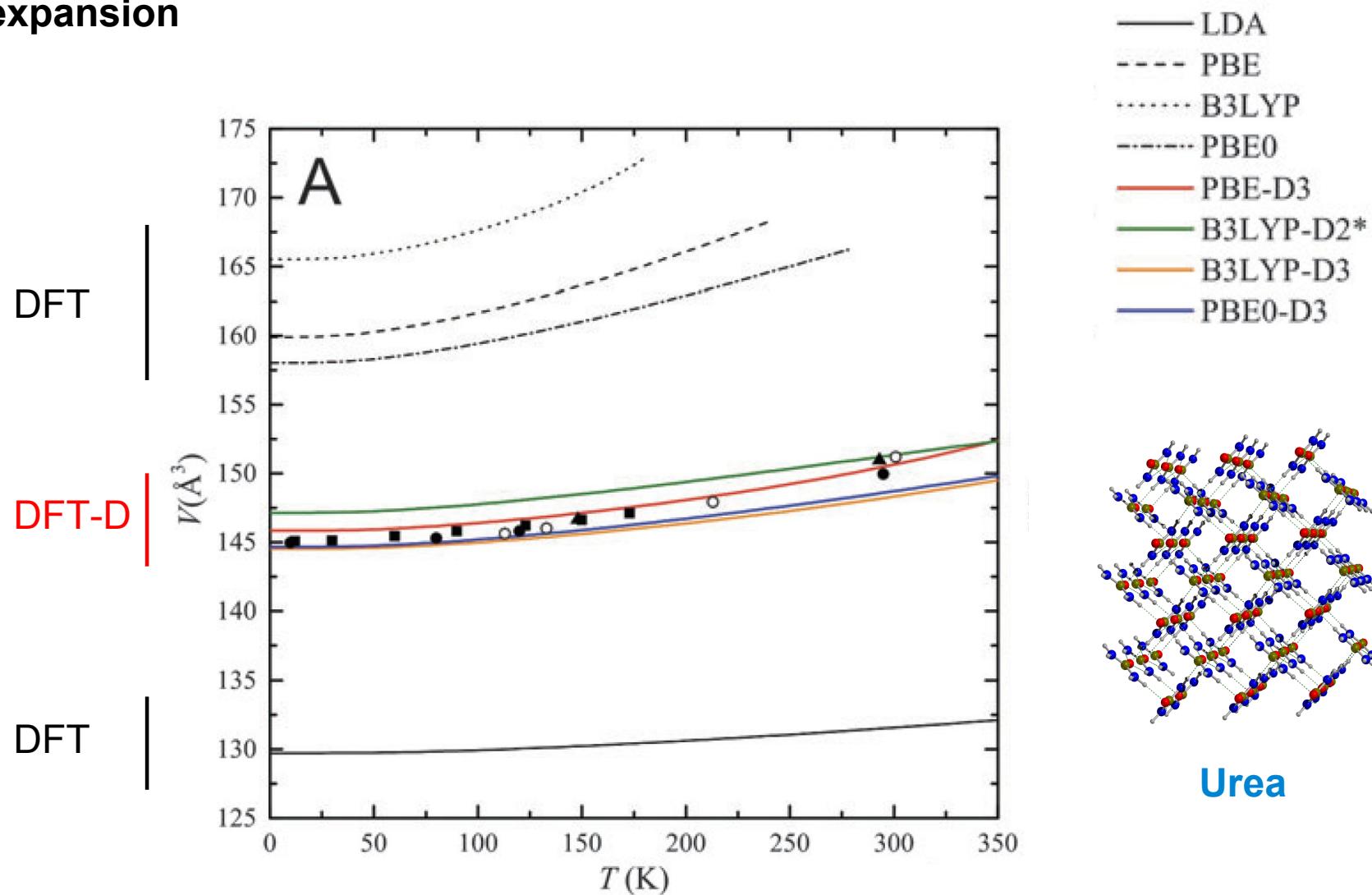
***Can the QHA provide a reliable description of their thermal properties?***

AE, J. Maul and B. Civalleri *Chem. Commun.*, **52**, 1820 (2016)

# Quasi-Harmonic Approximation



## Thermal expansion



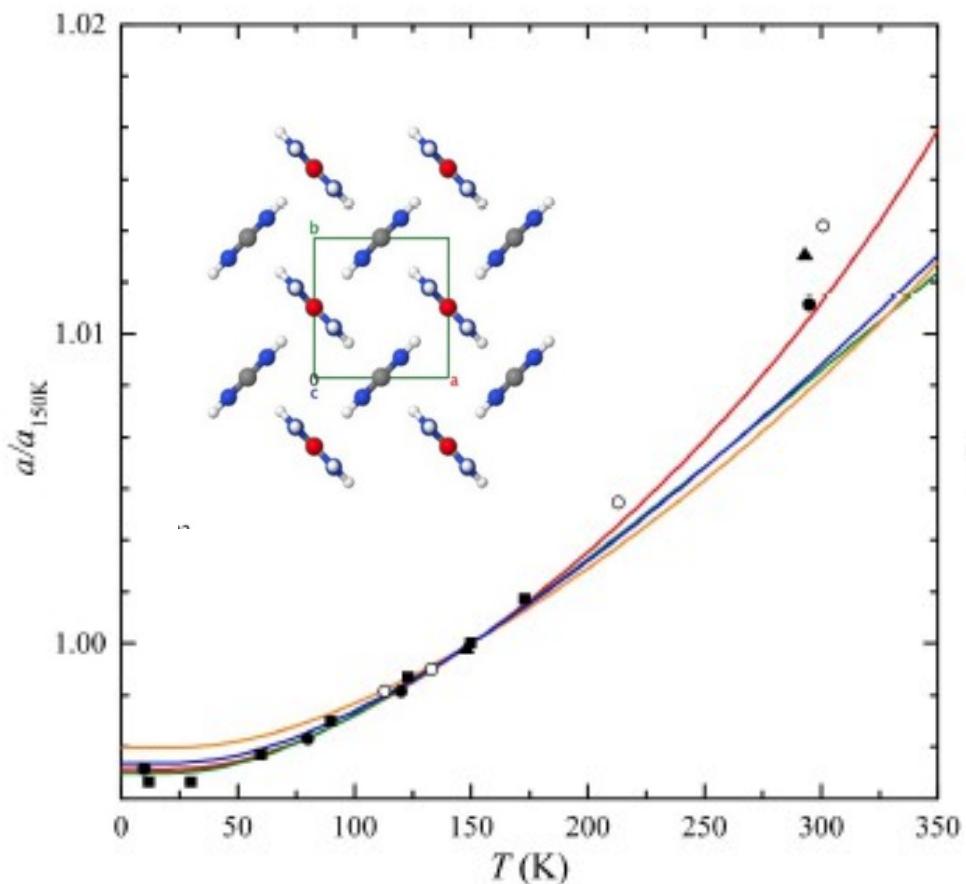
AE, J. Maul and B. Civalleri *Chem. Commun.*, **52**, 1820 (2016)

# Quasi-Harmonic Approximation

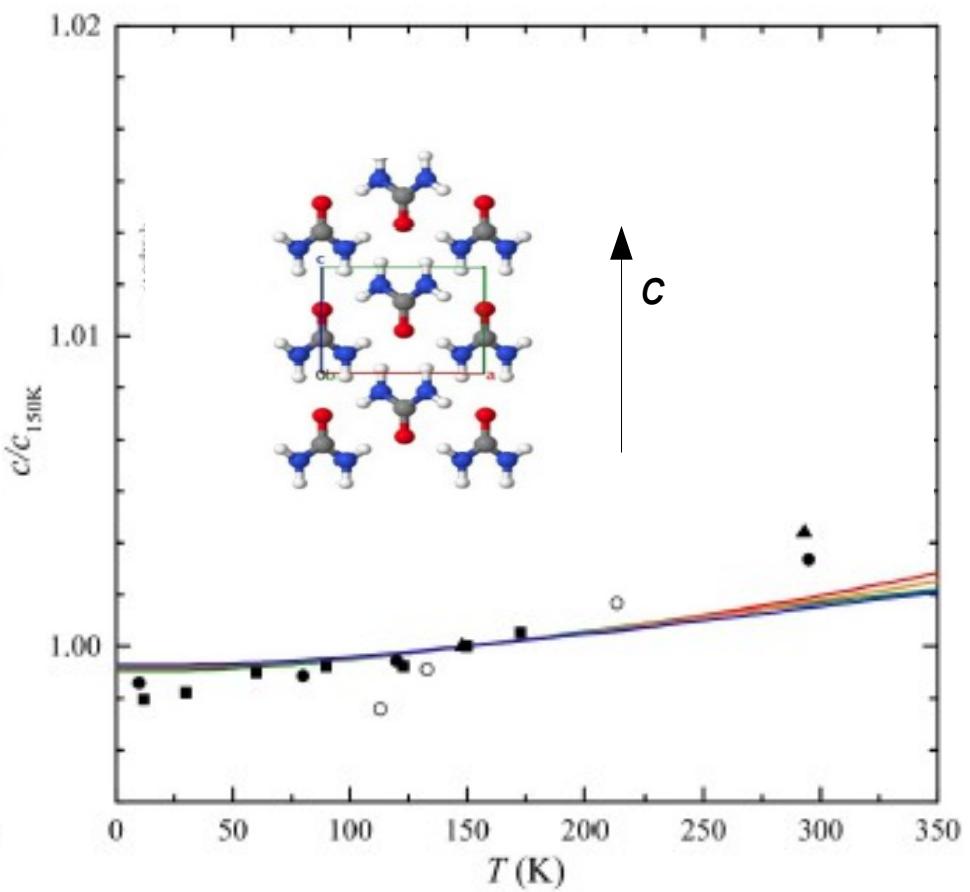


## Thermal expansion (anisotropy)

a-b plane



c axis

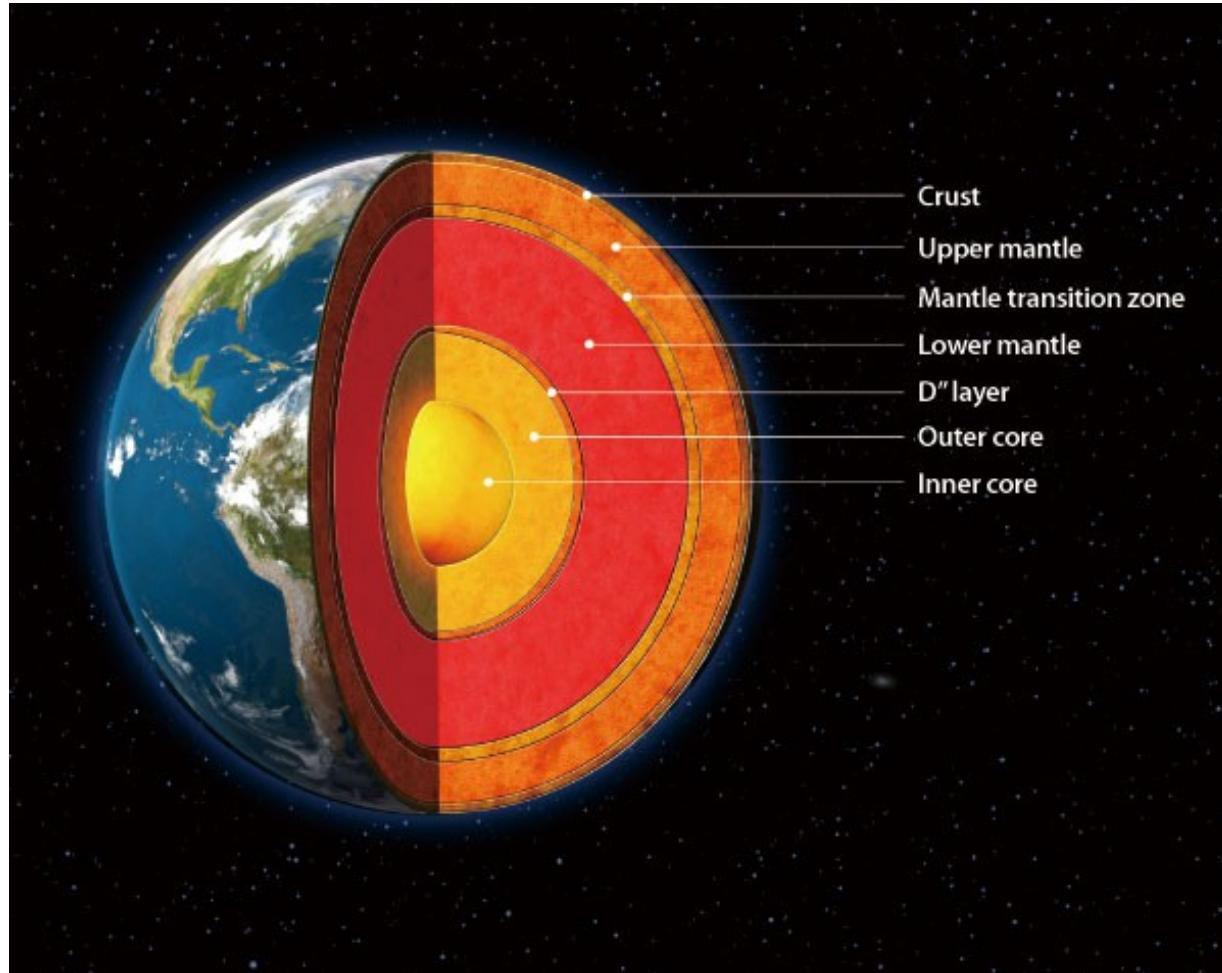


AE, J. Maul and B. Civalleri *Chem. Commun.*, **52**, 1820 (2016)



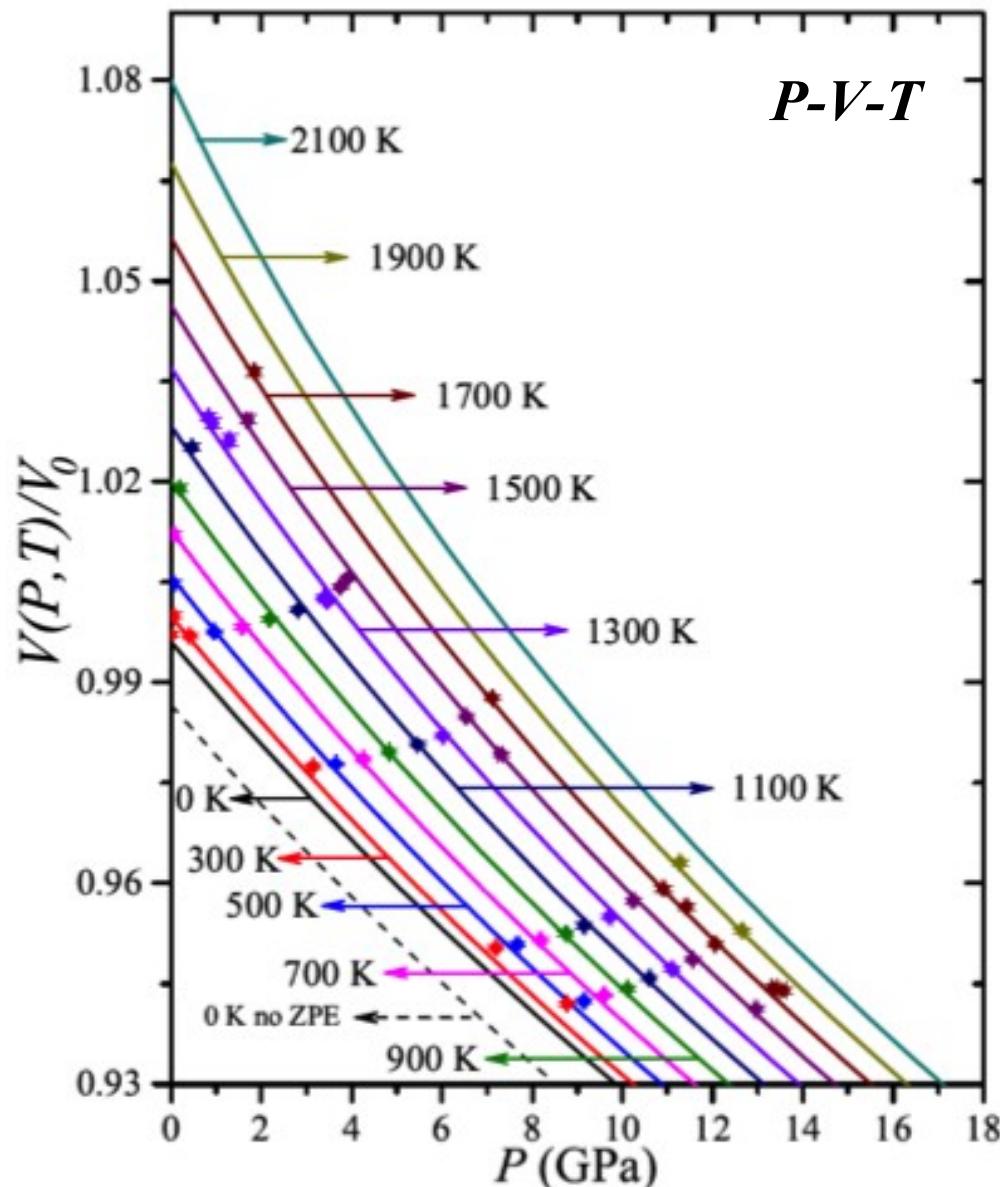
# Combining Temperature and Pressure

$$P(V;T) = -\frac{\partial F^{\text{QHA}}(V;T)}{\partial V} = -\frac{\partial U_0(V)}{\partial V} - \frac{\partial F_{\text{vib}}^{\text{QHA}}(V;T)}{\partial V}$$



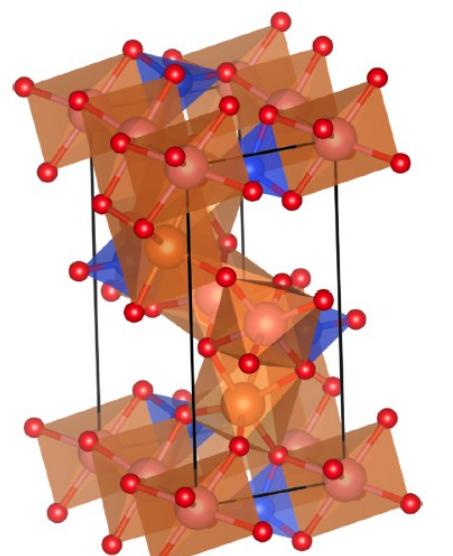


# Combining Temperature and Pressure



*In situ* X-ray diffraction:

T. Katsura, A. Shatskiy, M. G. M. Manthilake, S. Zhai, H. Fukui, D. Yamazaki, T. Matsuzaki, A. Yoneda, E. Ito, A. Kuwata et al., *Phys. Earth Planet. Inter.* **174**, 86 (2009).

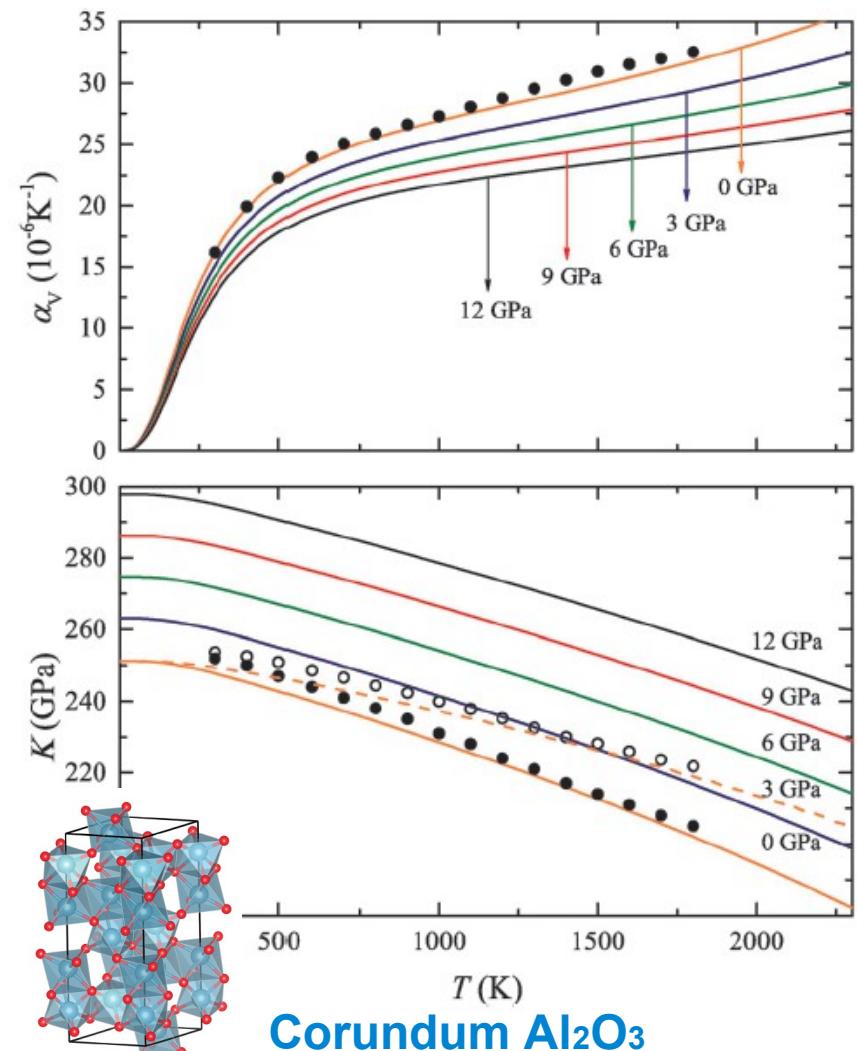


Forsterite  $\text{Mg}_2\text{SiO}_4$

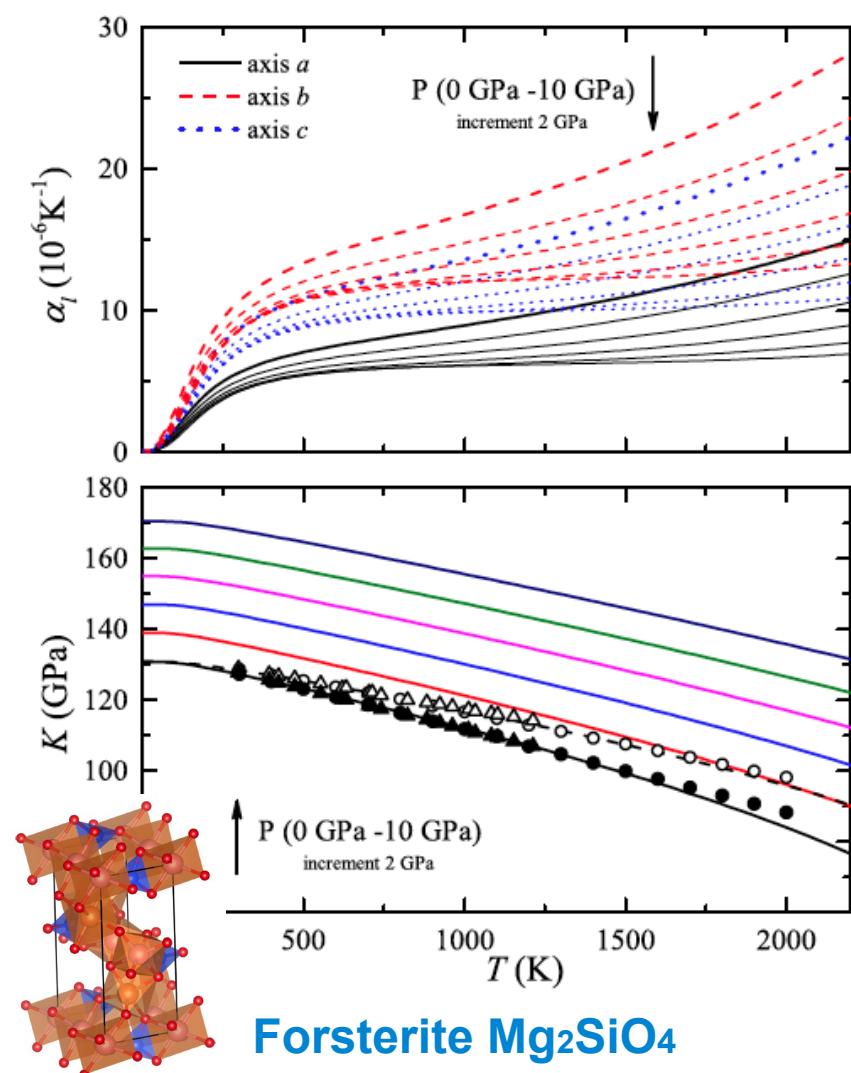
AE, J. Maul, M. De la Pierre and R. Dovesi,  
*J. Chem. Phys.*, **142**, 204502 (2015)



# Combining Temperature and Pressure



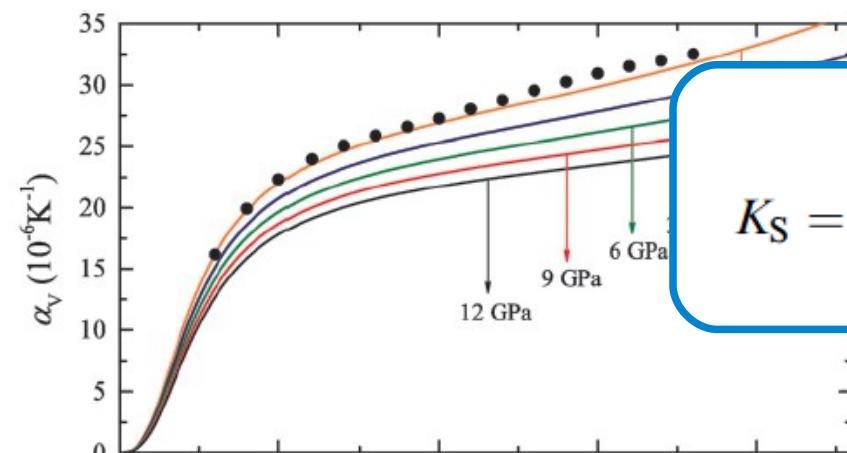
AE, J. Maul, R. Demichelis and R. Dovesi,  
*Phys. Chem. Chem. Phys.*, **17**, 11670-11677 (2015)



AE, J. Maul, M. De la Pierre and  
R. Dovesi, *J. Chem. Phys.*, **142**,  
204502 (2015)

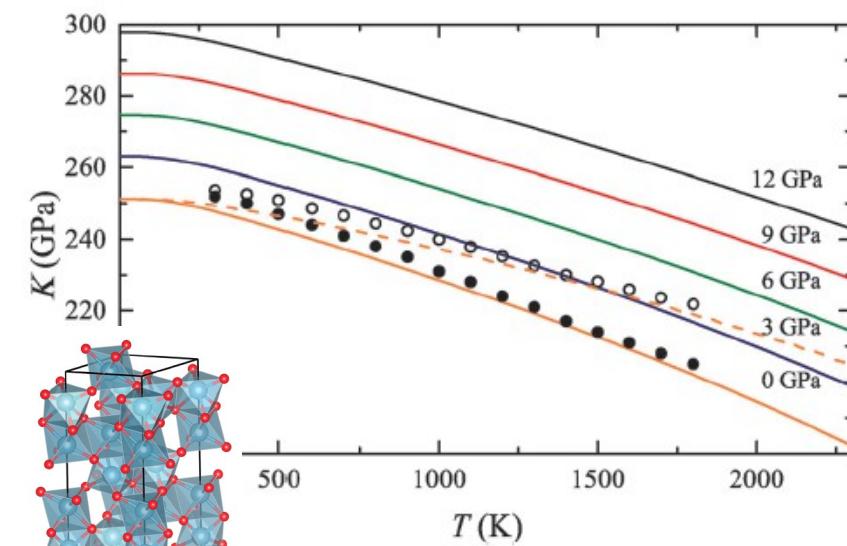


# Combining Temperature and Pressure



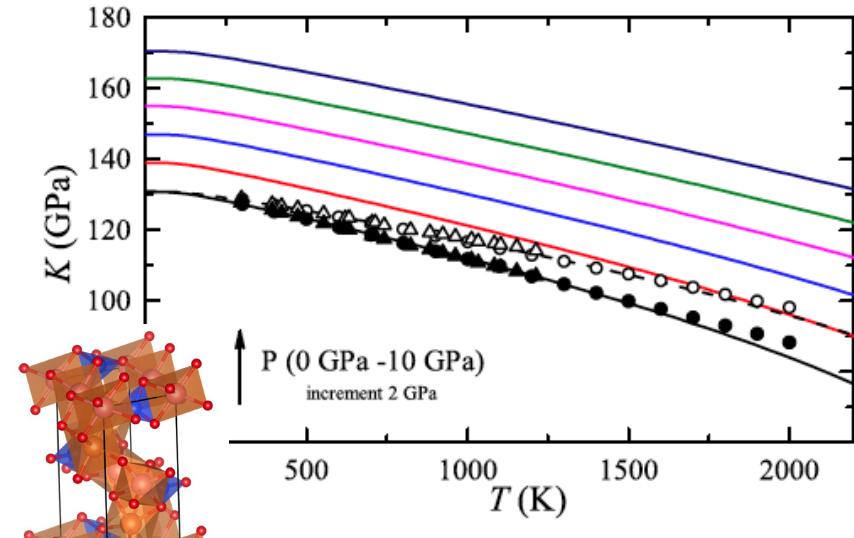
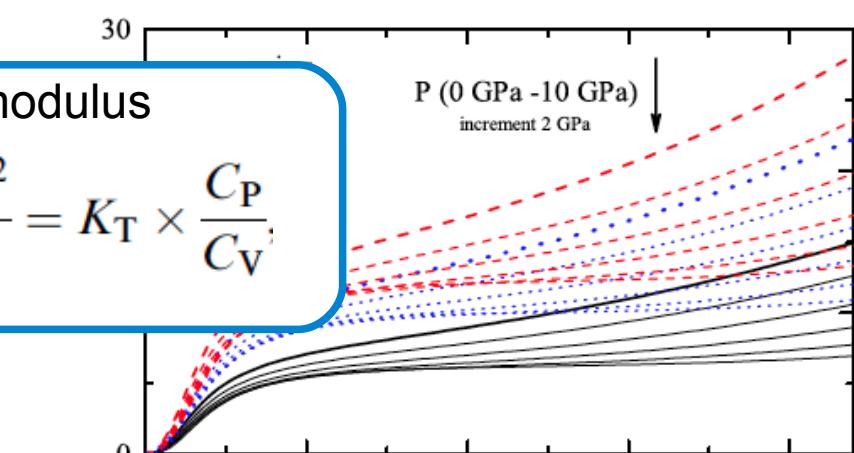
Adiabatic bulk modulus

$$K_S = K_T + \frac{\alpha_V^2 V T K_T^2}{C_V} = K_T \times \frac{C_P}{C_V},$$



Corundum  $\text{Al}_2\text{O}_3$

AE, J. Maul, R. Demichelis and R. Dovesi,  
*Phys. Chem. Chem. Phys.*, **17**, 11670-11677 (2015)

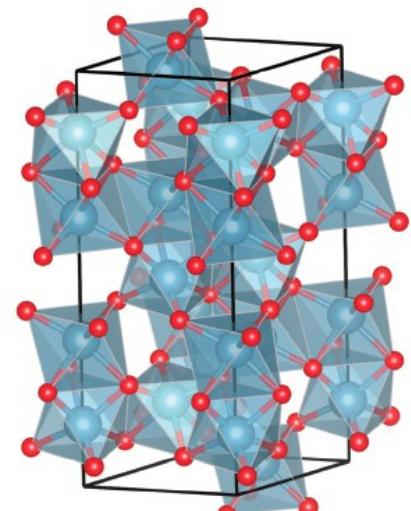
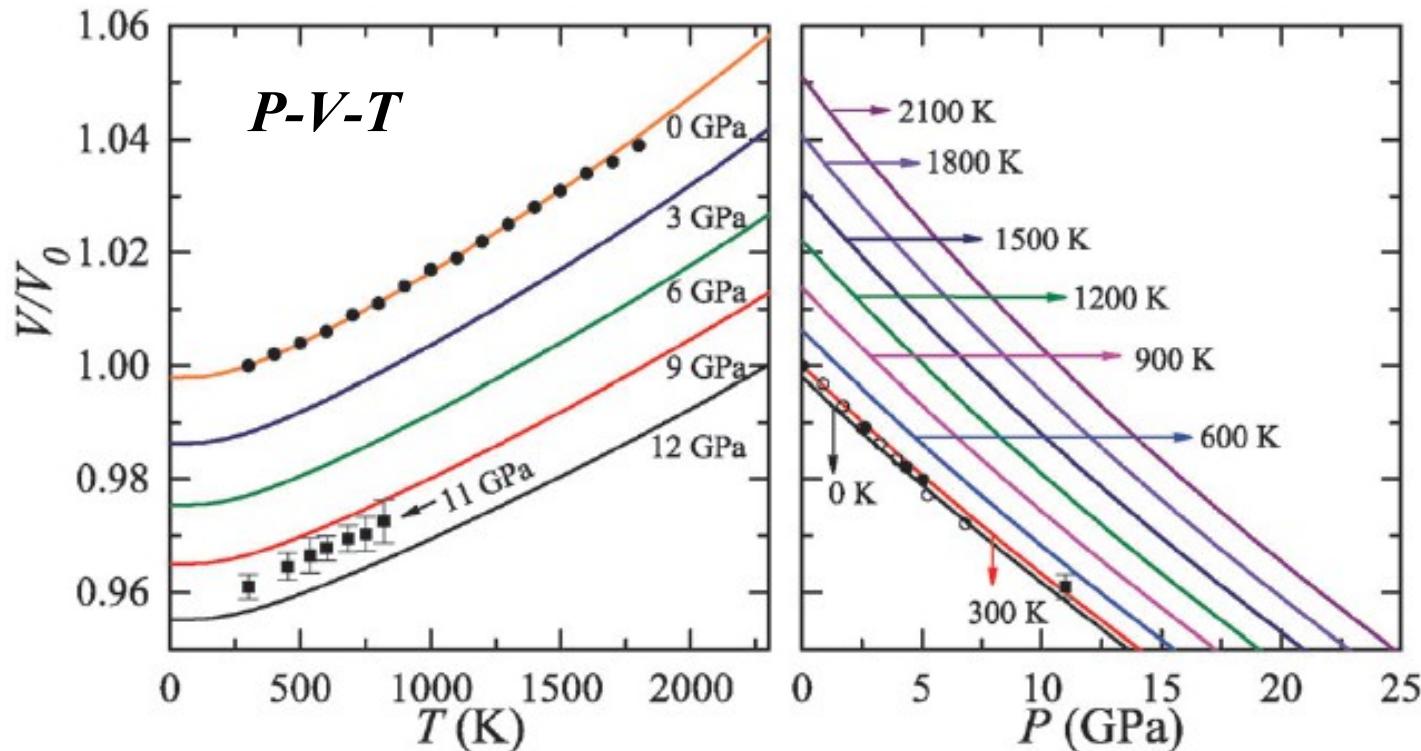


Forsterite  $\text{Mg}_2\text{SiO}_4$

AE, J. Maul, M. De la Pierre and  
R. Dovesi, *J. Chem. Phys.*, **142**,  
204502 (2015)



# Combining Temperature and Pressure



**Corundum  $\text{Al}_2\text{O}_3$**

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*Phys. Chem. Chem. Phys.*, **17**, 11670-11677 (2015)

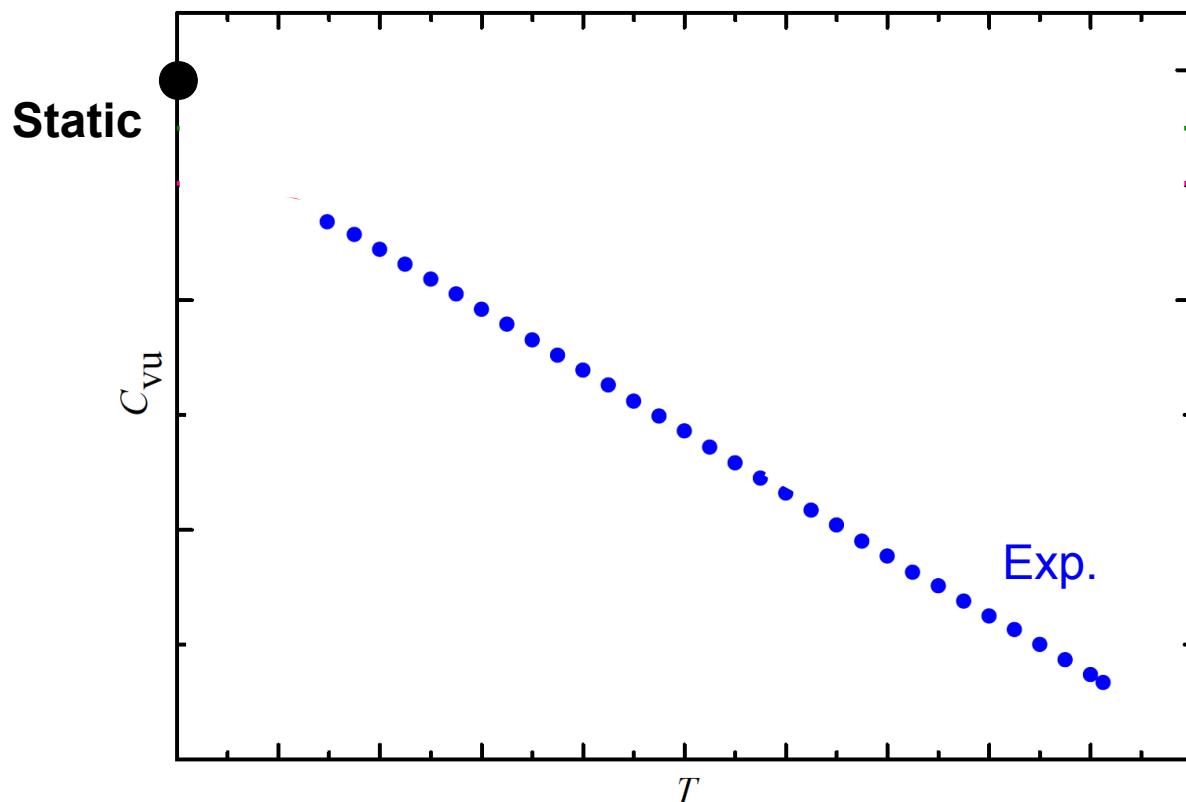


# Thermo-Elasticity

Mechanical properties of materials change with temperature. The elastic tensor defined as:

$$C_{vu} = \frac{1}{V_0} \left. \frac{\partial^2 E}{\partial \eta_v \partial \eta_u} \right|_{\eta=0}$$

allows to compute static, 0 K, values.



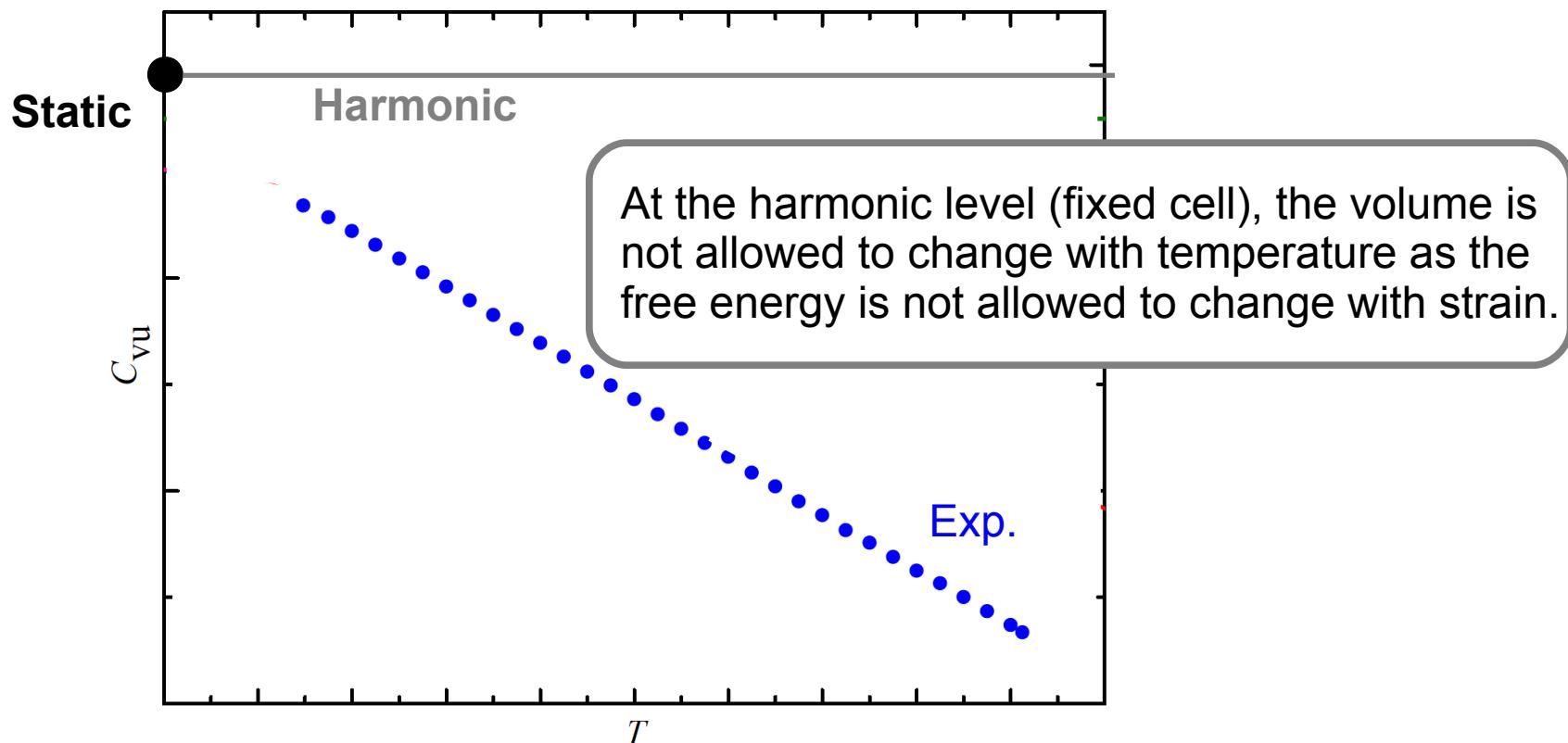


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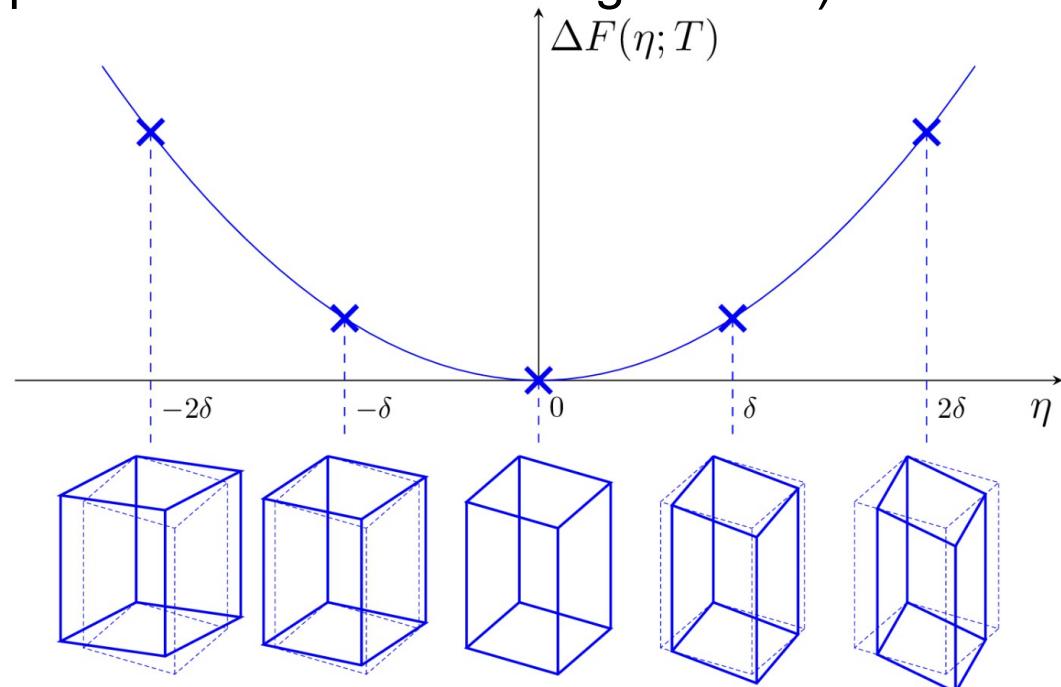


# Thermo-Elasticity

The thermal dependence of the (**isothermal**) elastic stiffness constants (and thus of all mechanical properties) of a material is defined through:

$$C_{vu}^T(T) = \frac{1}{V(T)} \left. \frac{\partial^2 F}{\partial \eta_v \partial \eta_u} \right|_{\eta=0}$$

and can be obtained from a quasi-harmonic approach. As we compute free energy derivatives with respect to strain numerically, this becomes a computationally heavy task (harmonic frequencies at strained configurations).





# Thermo-Elasticity

**Adiabatic elastic constants** can also be computed within a quasi-harmonic approach, that can be more directly compared to those experimentally measured by Brillouin scattering.

$$C_{vu}^S(T) = C_{vu}^T(T) + \frac{T\bar{V}(T)\lambda_v(T)\lambda_u(T)}{\bar{C}_V(T)}$$

with

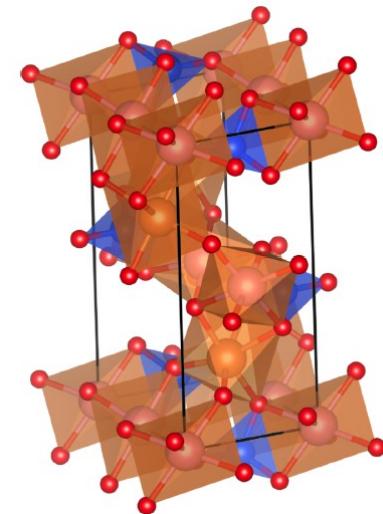
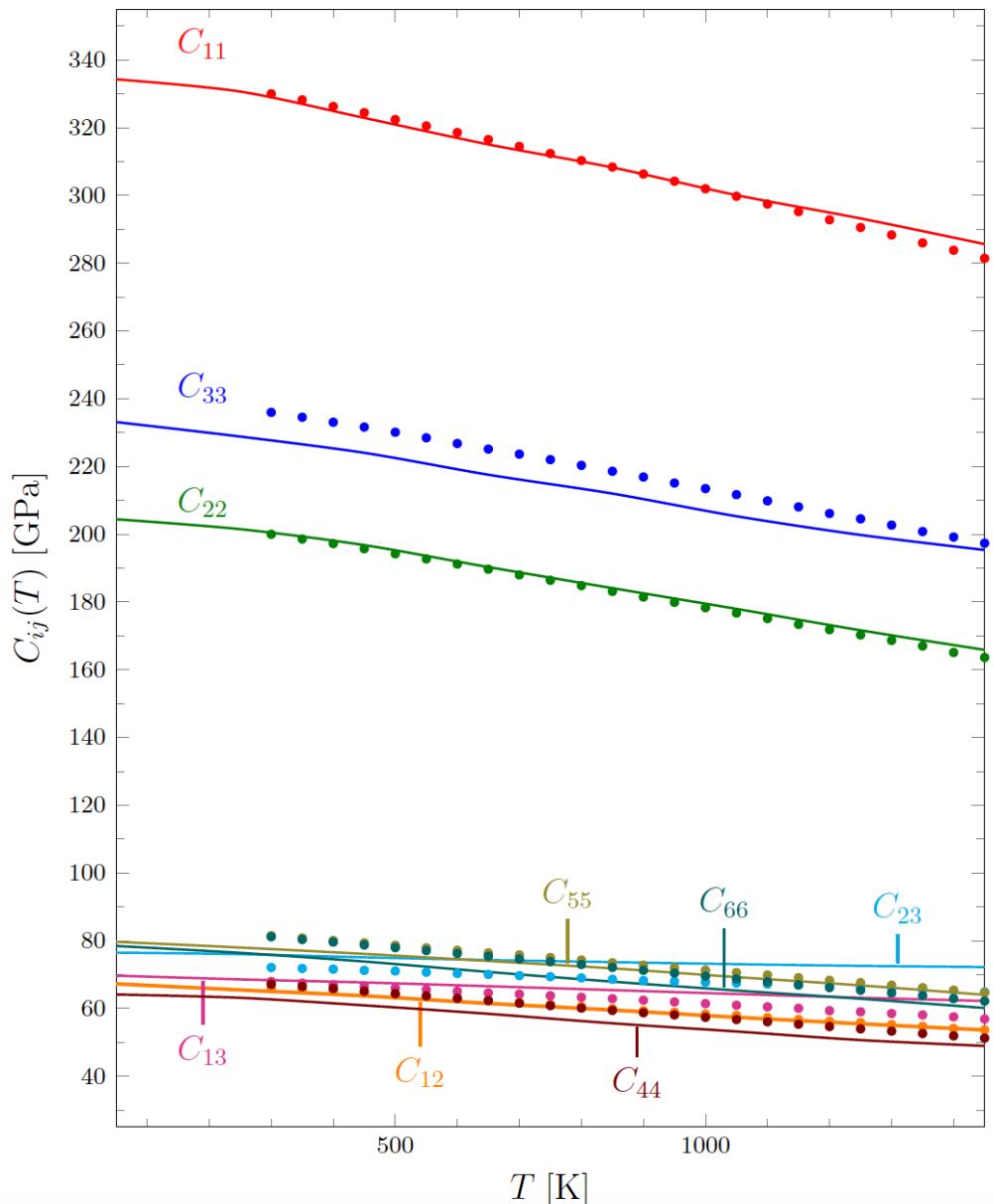
$$\lambda_v(T) = \left. \frac{\partial S}{\partial \eta_v} \right|_T = - \left. \frac{\partial \sigma_v}{\partial T} \right|_\eta = - \sum_u \left. \frac{\partial \eta_u}{\partial T} \right|_\sigma \left. \frac{\partial \sigma_v}{\partial \eta_u} \right|_T = - \sum_u \alpha_u(T) C_{vu}^T(T)$$

An algorithm has been implemented in **CRYSTAL23** for the quasi-harmonic evaluation of isothermal and adiabatic elastic constants.

M. Destefanis, C. Ravoux, A. Cossard, AE  
*Minerals*, **9**, 16 (2019)



# Thermo-Elasticity



Forsterite  $\text{Mg}_2\text{SiO}_4$

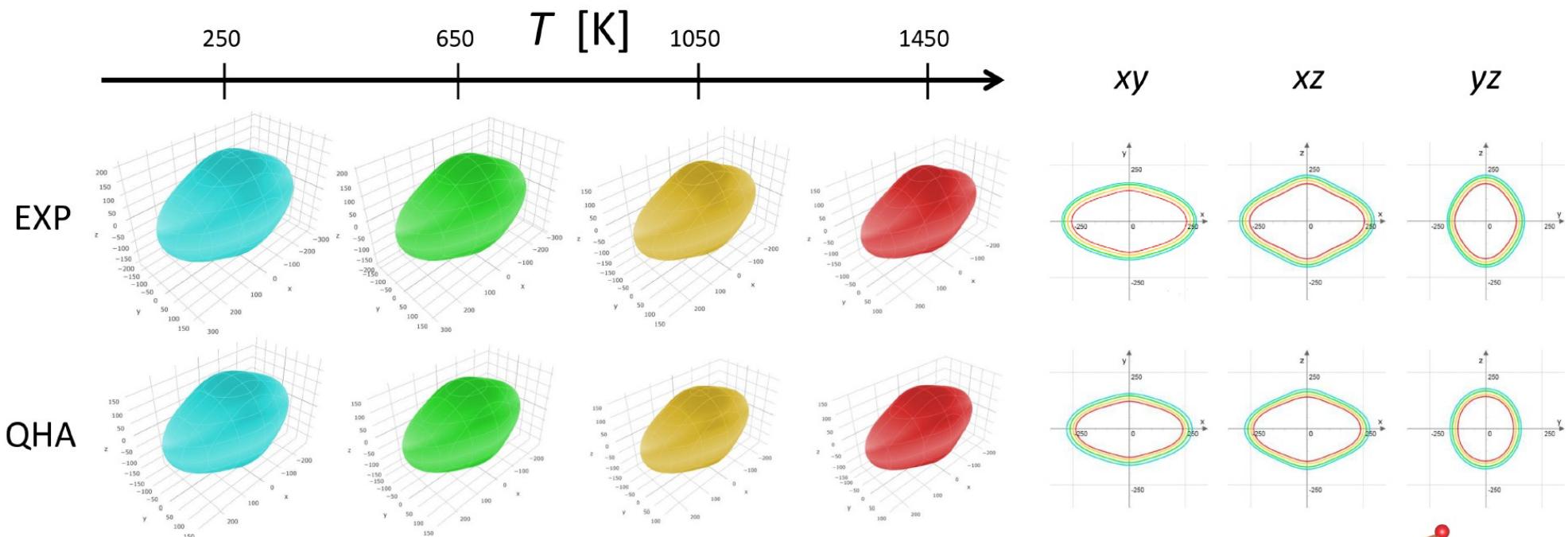
Adiabatic elastic constants of Forsterite as a function of temperature as computed with the quasi-harmonic approximation and compared to experimental values.

B3LYP functional.

M. Destefanis, C. Ravoux, A. Cossard, AE  
*Minerals*, **9**, 16 (2019)

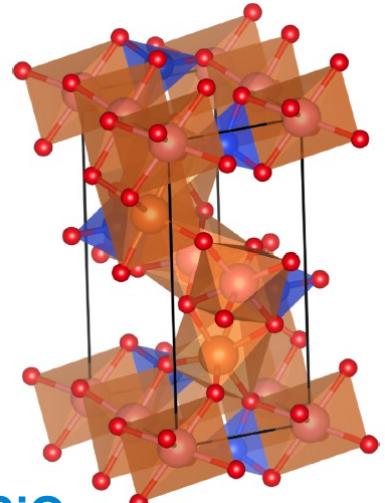


# Thermo-Elasticity



3D and 2D view of the effect of temperature on the Young modulus of forsterite.

M. Destefanis, C. Ravoux, A. Cossard, AE  
*Minerals.*, 9, 16 (2019)



Forsterite  $\text{Mg}_2\text{SiO}_4$



# Thermo-Elasticity

A computationally (**much!**) **cheaper** approximation can be introduced. Instead of computing the isothermal elastic constants from a **full quasi-harmonic approach** as:

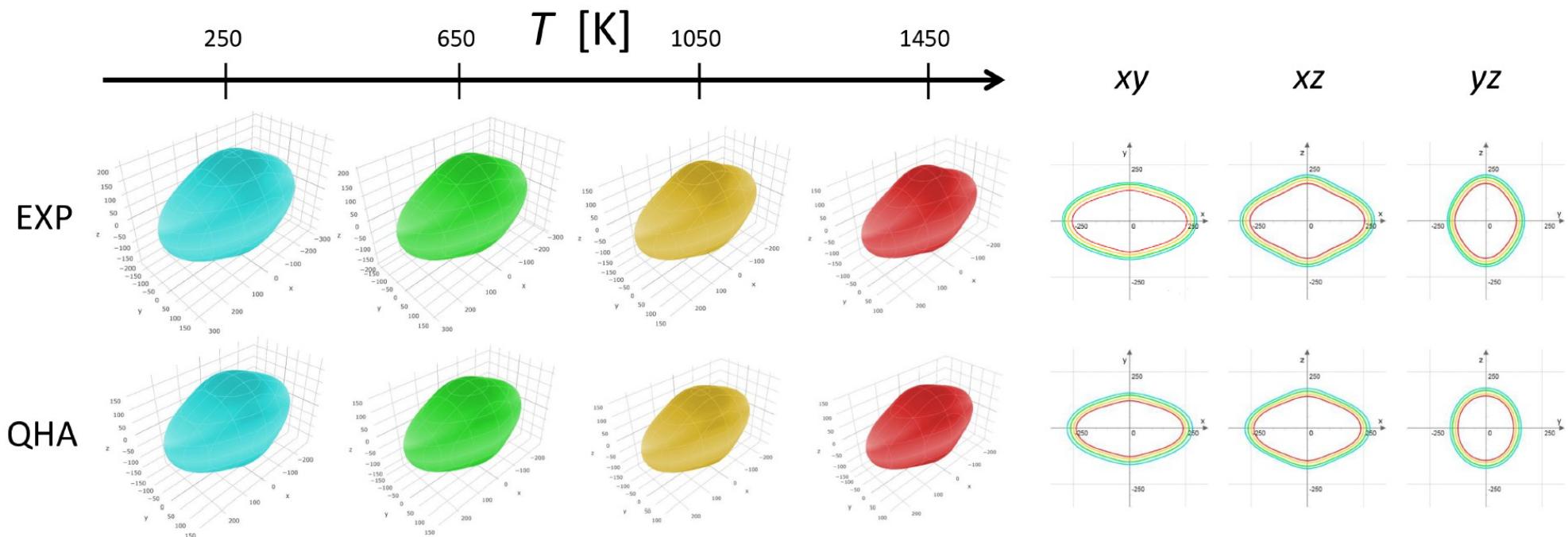
$$C_{vu}^T(T) = \frac{1}{V(T)} \left. \frac{\partial^2 F}{\partial \eta_v \partial \eta_u} \right|_{\eta=0}$$

We can use a **quasi-static approximation** where thermal expansion is accounted for while neglecting thermal contributions to the free energy derivatives with strain:

$$C_{vu}^T(T) = \frac{1}{V(T)} \left. \frac{\partial^2 E}{\partial \eta_v \partial \eta_u} \right|_{\eta=0}$$

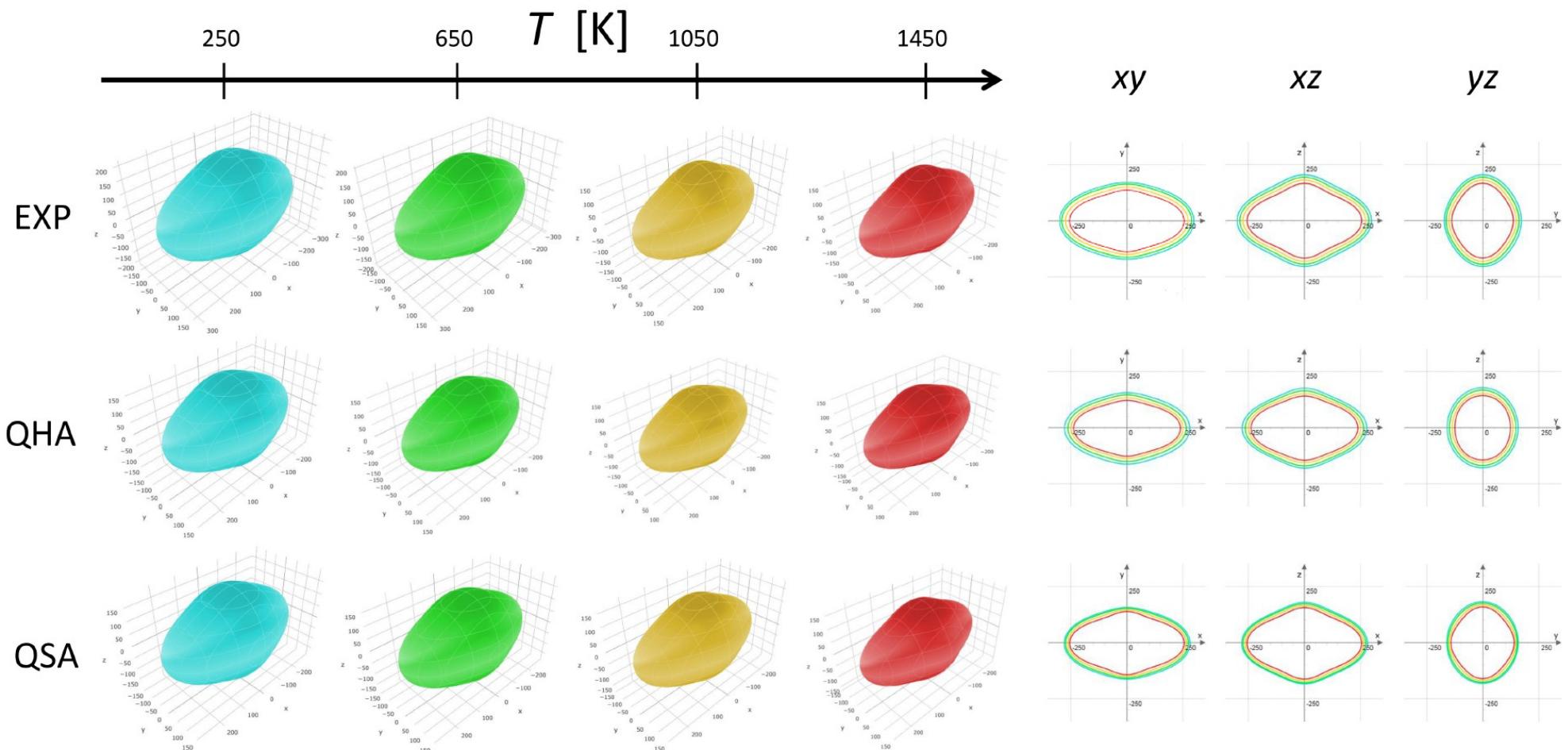


# Thermo-Elasticity





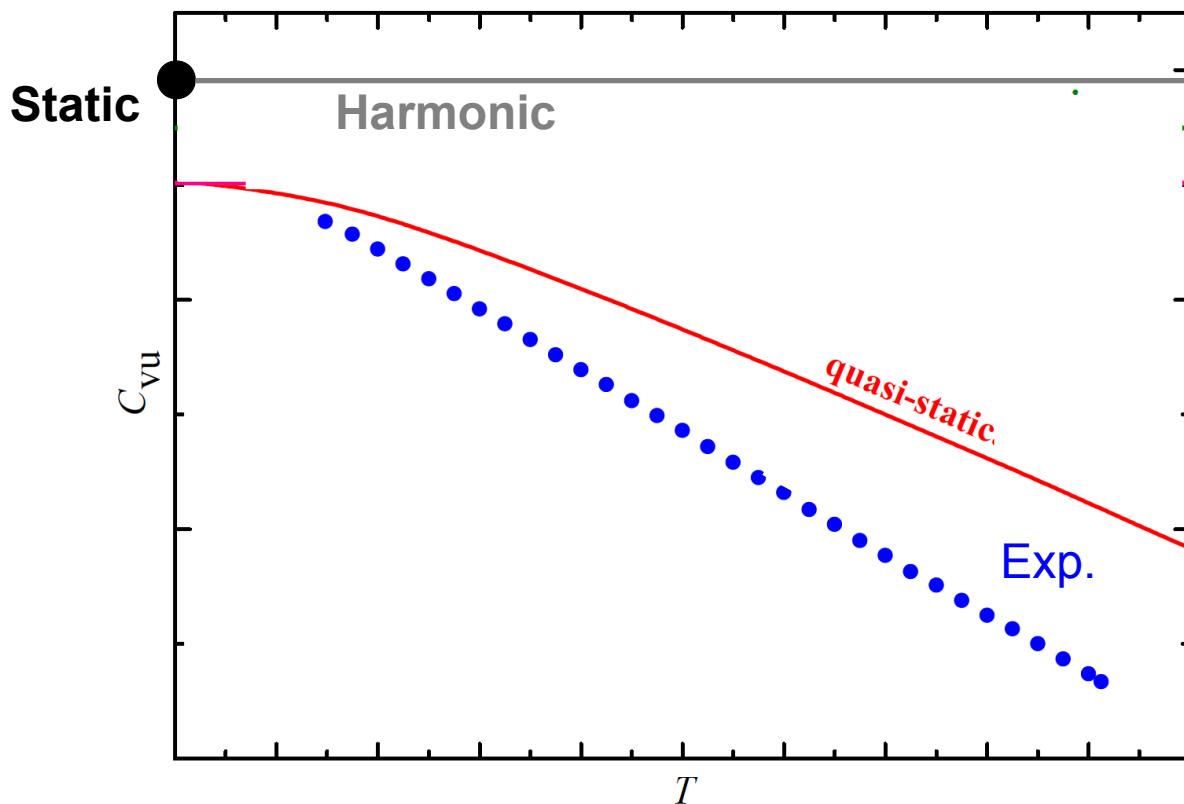
# Thermo-Elasticity





# Thermo-Elasticity

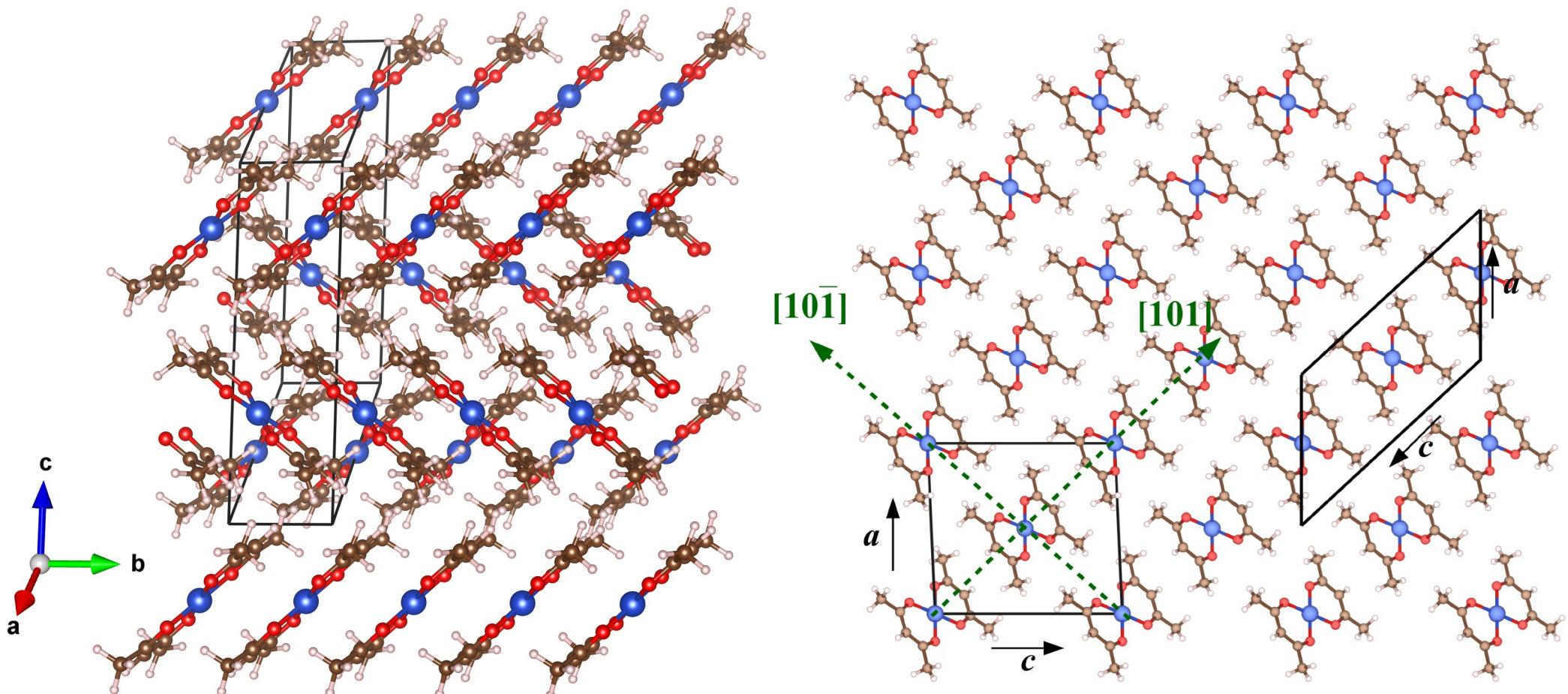
The QSA is able to describe a large fraction of thermal effects.





# Thermo-Elasticity

## Copper Acetylacetonate Crystals

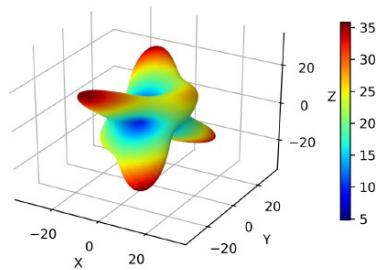




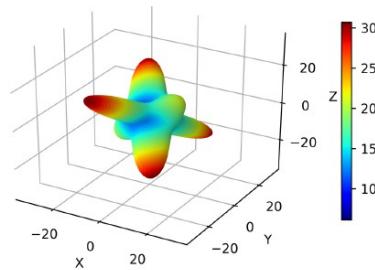
# Thermo-Elasticity

## Copper Acetylacetonate Crystals

0 K no ZPE

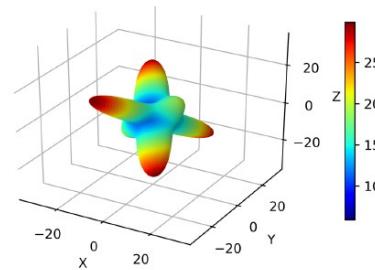


0 K

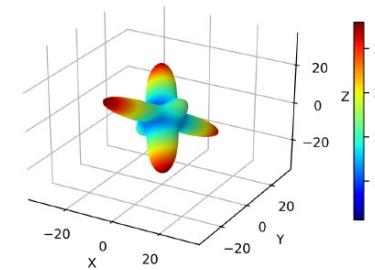


## Young Modulus

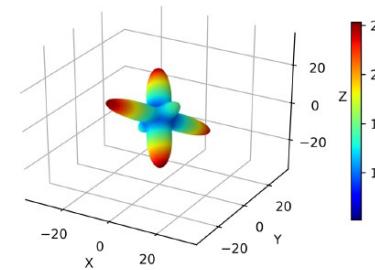
100 K



200 K



300 K



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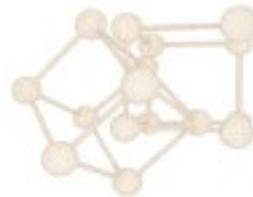
$T$  (in K)     $E_{[10\bar{1}]}^{} \text{ (in GPa)}$      $E_{[101]}^{} \text{ (in GPa)}$

0 static	25.3	5.3
0 with ZPE	18.6	7.1
100	16.7	6.8
200	13.8	6.6
300	11.3	6.2

---

300 (Exp.)    11.3 - 13.8    4.8 - 6.9

J. Maul, D. Ongari, S. M. Moosavi, B. Smit, AE  
*J. Phys. Chem. Lett.*, 11, 8543--8548 (2020)



Advanced School on  
**QUANTUM MODELLING**  
of Materials with CRYSTAL

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