EXAFS and thermal disorder

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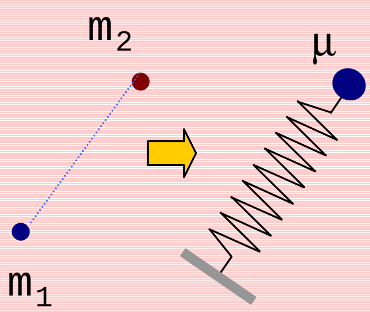
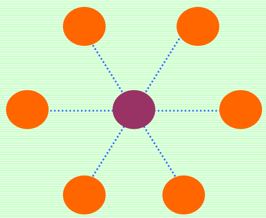
EXAFS and thermal disorder

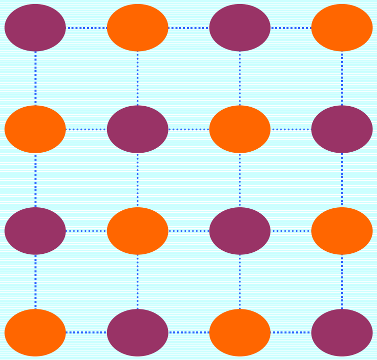
Two-atomic molecules



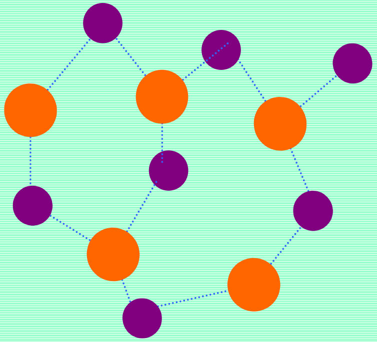
Large molecules, clusters



Crystalline solids



Non-crystalline solids



1-dimens. config. space

Single Scattering

3n-dimensional configuration space

Single Scattering + Multiple Scattering

Different approaches ⇒

	Harm.	Anharm.
Classical		
Quantum		

Harmonic oscillator - Energy

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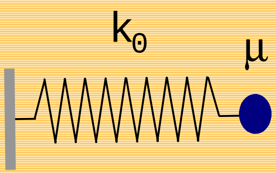
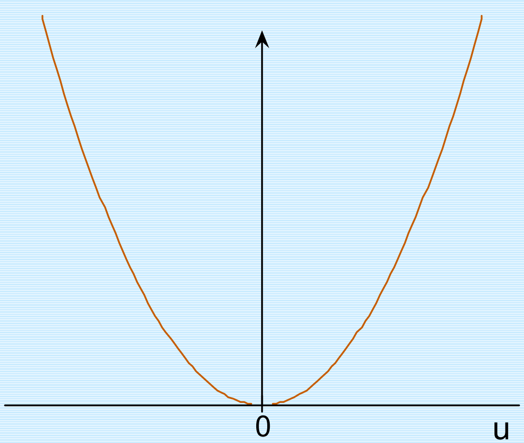


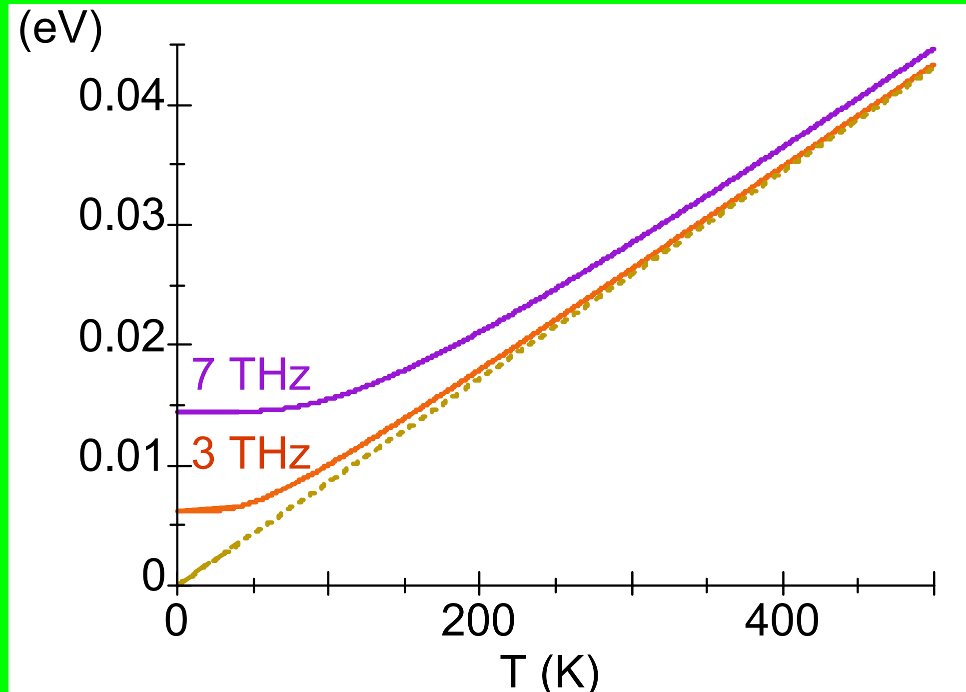
$$\omega = \sqrt{k_0 / \mu}$$

$T = 1/K_B\beta$

$$V(u) = \frac{1}{2} k_0 u^2$$



$$\langle E \rangle = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]$$



Harmonic oscillator - Cumulants

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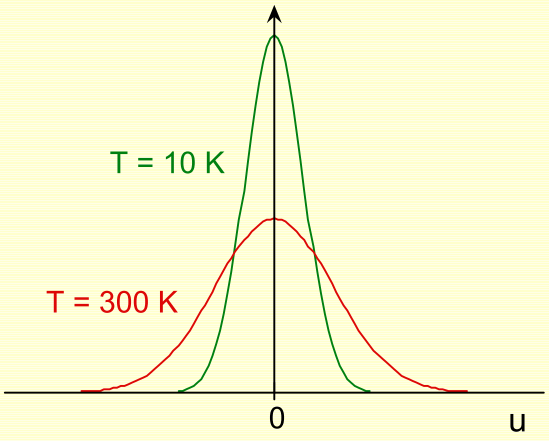
$$\rho(u) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{u^2}{2\sigma^2}\right]$$



Gaussian distribution

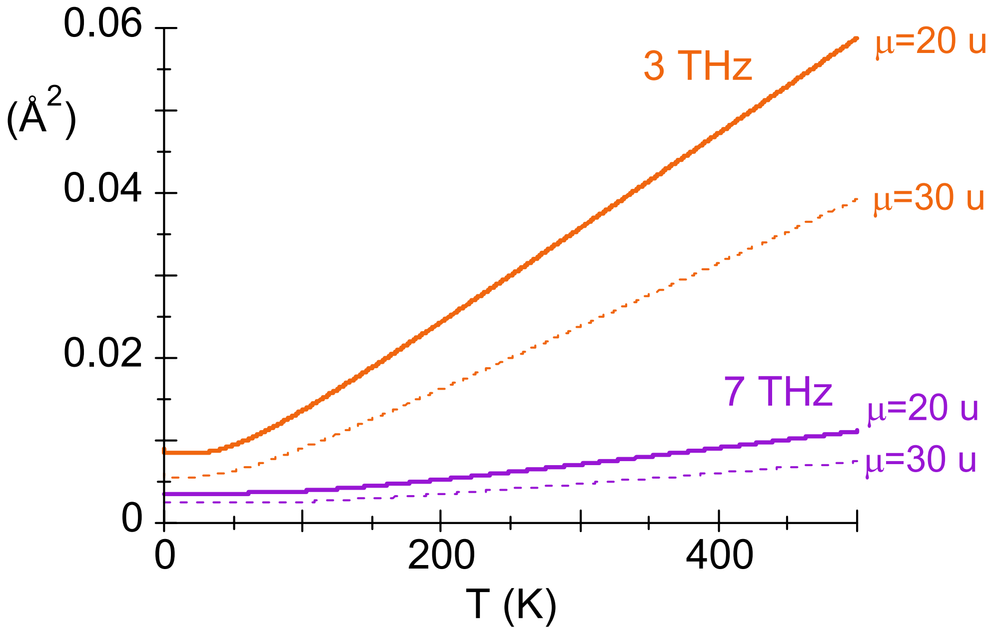
$$C_1^* = R_0 + \langle u \rangle = R_0$$

$$C_2^* = \sigma^2 = \frac{\hbar}{\mu\omega}\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$

$$C_3^* = 0$$

....

Variance



Zero-point effects

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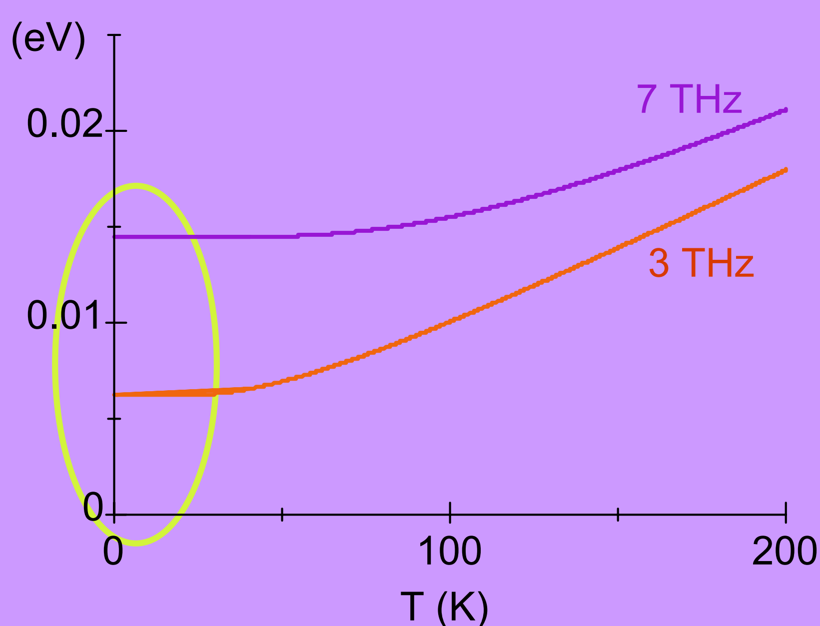
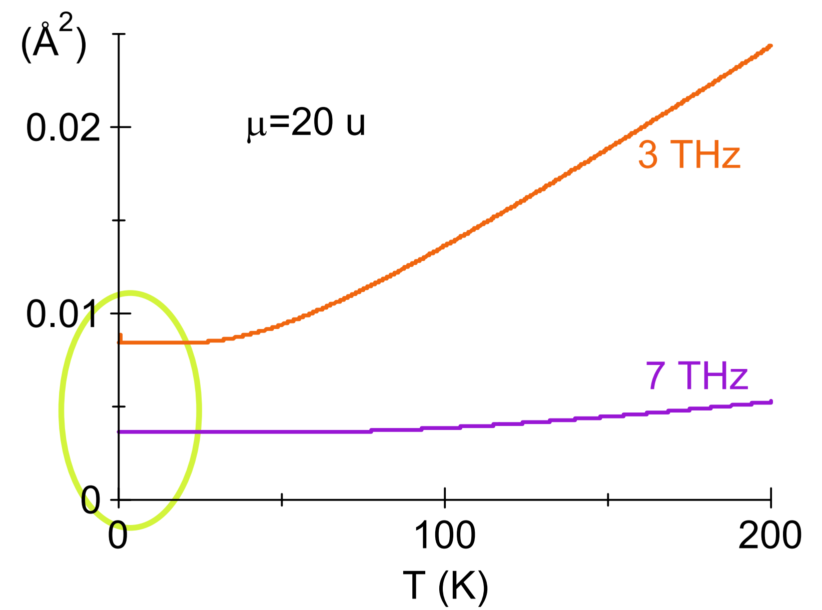
Energy

$$\langle E \rangle = h\omega \left[\frac{1}{2} + \frac{1}{e^{\beta h\omega} - 1} \right]$$



MSRD

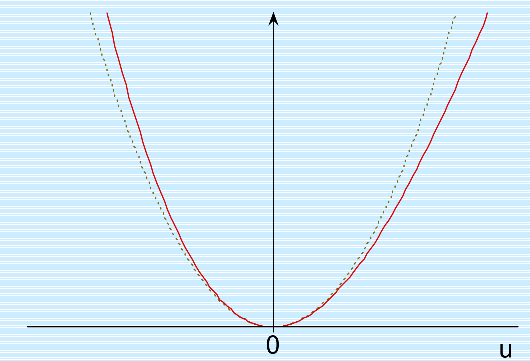
$$C_2^* = \sigma^2 = \frac{h}{\mu\omega} \left[\frac{1}{2} + \frac{1}{e^{\beta h\omega} - 1} \right]$$



Anharmonic oscillator (a)

classical approximation

$$V(u)=\frac{1}{2}k_0 u^2 + k_3 u^3 + k_4 u^4 + \ldots.$$



$$\delta C_1^*(T) = -\frac{3k_3}{k_0^2}k_B T - \frac{3k_3}{k_0^4}\left(\frac{45k_3^2}{k_0} - 32k_4\right)(k_B T)^2 + K$$

$$C_2^*(T) = \frac{k_B T}{k_0} + \frac{3}{k_0^3}\left(\frac{12k_3^2}{k_0} - 4k_4\right)(k_B T)^2 + K$$

$$C_3^*(T) = -\frac{6k_3}{k_0^3}(k_B T)^2 - \frac{36k_3}{k_0^5}\left(\frac{24k_3^2}{k_0} - 14k_4\right)(k_B T)^3 + K$$

$$C_4^*(T) = \frac{12}{k_0^4}\left(\frac{9k_3^2}{k_0} - 2k_4\right)(k_B T)^3 + K$$

$$\delta C_1^* = \frac{C_3^*}{2C_2^*}$$

[Tranquada & Ingalls, PRB 28 (1983)]

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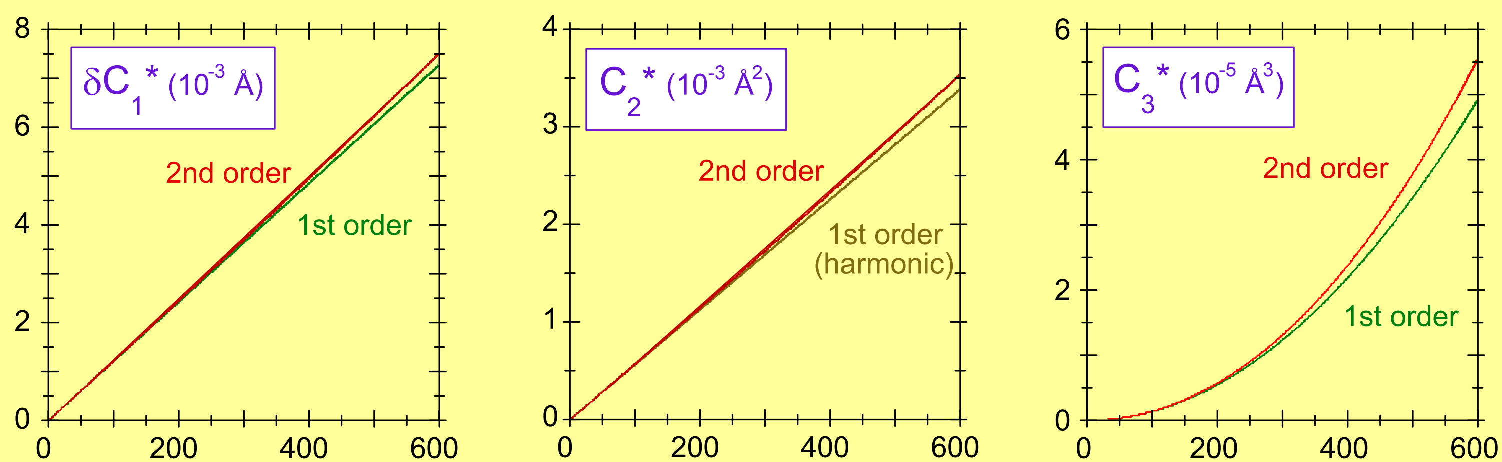
Br_2



Anharmonic oscillator (b)

perturbative quantum approach

$$V(u) = \boxed{\frac{1}{2}k_0 x^2} + k_3 x^3 + k_4 x^4 + \ldots.$$

$$\omega = \sqrt{k_0/\mu}$$

$$\sigma_0^2 = \hbar/2\mu\omega$$

$$z = \exp\left[-\hbar\omega/k_B T\right]$$

$$\delta C_1^*(T) = -\frac{3k_3\sigma_0^2}{k_0}\,\frac{1+z}{1-z} + \ldots$$

$$C_2^*(T) = \boxed{\sigma_0^2\,\frac{1+z}{1-z}} - \frac{12k_4\sigma_0^6}{\hbar\omega}\,\frac{(1+z)^2}{(1-z)^2} - \frac{24k_4\sigma_0^6}{k_B T}\,\frac{z(1+z)}{(1-z)^3} + \ldots$$

$$C_3^*(T) = -\frac{2k_3\sigma_0^4}{k_0}\,\frac{z^2+10z+1}{(1-z)^2} + \ldots$$

$$C_4^*(T) = -\frac{12k_4\sigma_0^8}{(\hbar\omega)^2}\,\frac{z^3+9z^2+9z+1}{(1-z)^3} - \frac{144k_4\sigma_0^8}{k_B T}\,\frac{z^2}{(1-z)^4} + \ldots$$

[Yokoyama, JSR 6 (1999)]

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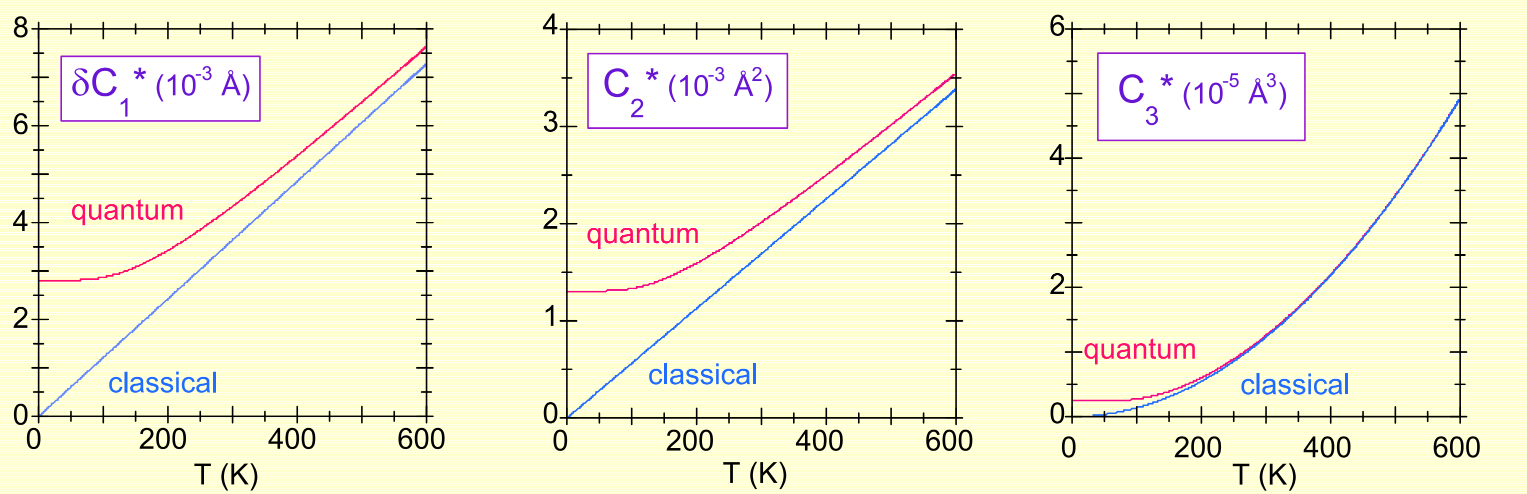
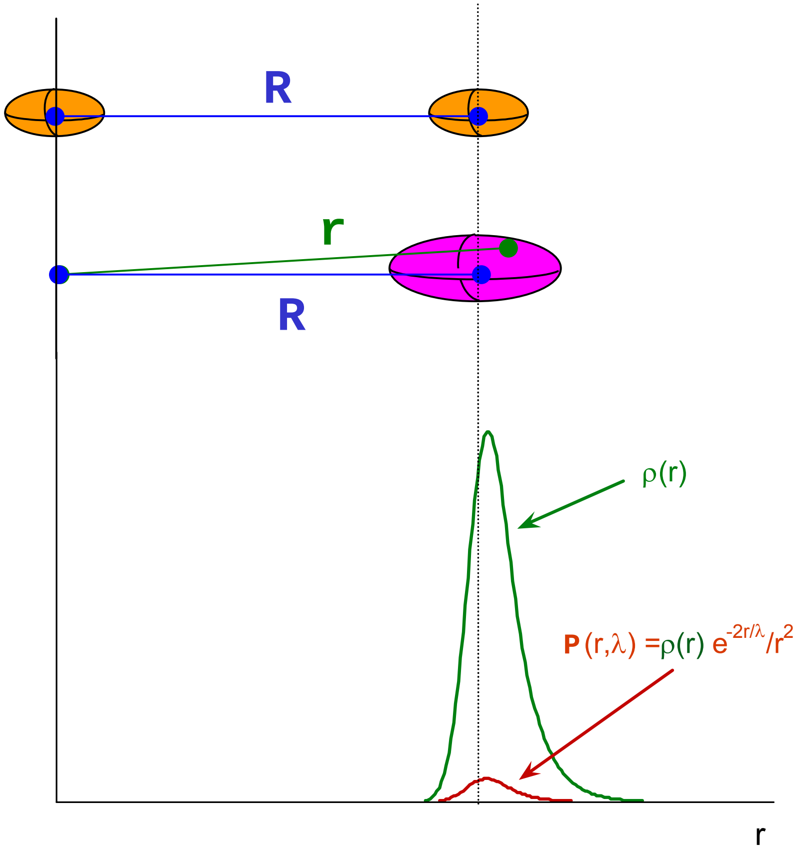
Br_2



EXAFS
and local dynamics



- **Absolute → relative motion**
- **3-dim. → 1-dim.**

	P (r,λ)		ρ (r)		
$\frac{2C_2}{C_1}\left(1+\frac{C_1}{\lambda}\right)+$	C_1	$\approx$	C_1^*	$=\langle r\rangle$	Mean
	C_2	$\approx$	C_2^*	$=\left\langle (r-\langle r\rangle)^2\right\rangle$	Variance
	C_3	$\approx$	C_3^*	$=\left\langle (r-\langle r\rangle)^3\right\rangle$	Asymmetry

Relative thermal motion

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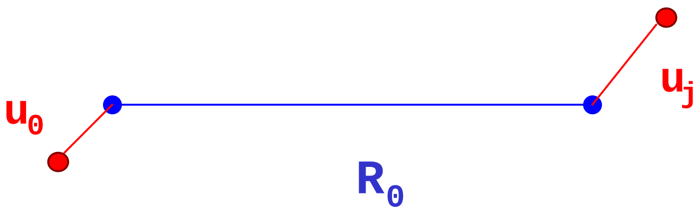
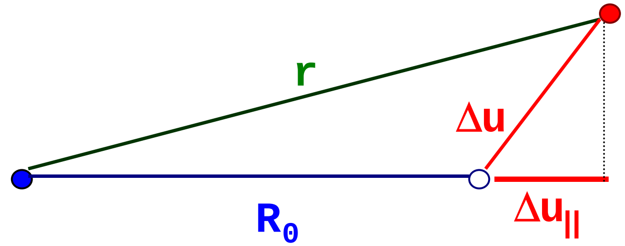
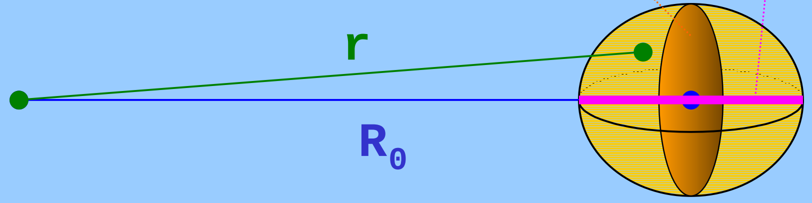




$$\Delta u^2 = \left(\vec{u}_j - \vec{u}_0\right)^2 = \Delta u_\perp^2 + \Delta u_\parallel^2$$

Perpendicular **Parallel**



Instantaneous distance

$$r \approx R_0 + \Delta u_\parallel + \frac{\Delta u_\perp^2}{2R_0}$$

Mean Square Relative Displacements

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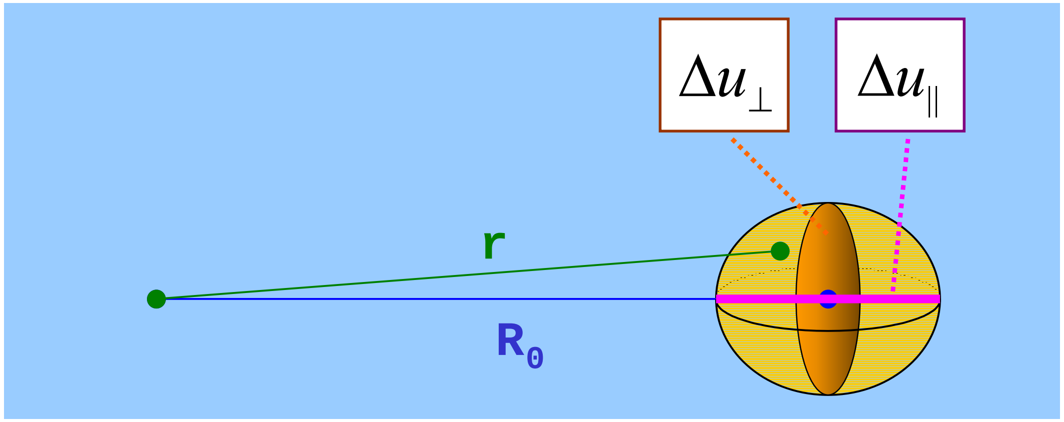

Mean values (harmonic approximation)

$$\langle \Delta u_{\parallel} \rangle = 0$$

$$C_1^* = \langle r \rangle \approx R_0 + \frac{\langle \Delta u_{\perp}^2 \rangle}{2 R_0}$$

$MSRD_{\perp}$

$$C_2^* = \langle \Delta u_{\parallel}^2 \rangle$$

$MSRD_{\parallel}$

MSRD$_{||}$ and correlation

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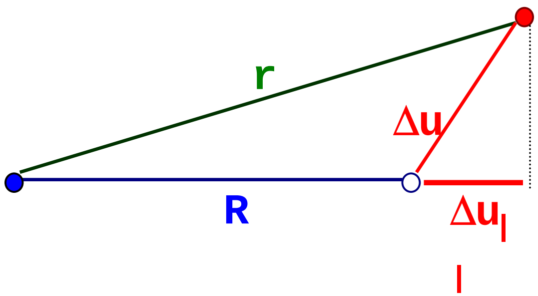
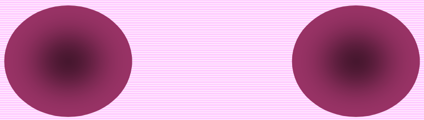
$$C_2 = MSRD \approx \langle \Delta u_{\parallel}^2 \rangle = \left\langle \left[\hat{R}\cdot\left(\vec{u}_j - \vec{u}_0\right)\right]^2 \right\rangle$$

$$= \left\langle \left(\hat{R}\cdot\vec{u}_j\right)^2 \right\rangle + \left\langle \left(\hat{R}\cdot\vec{u}_0\right)^2 \right\rangle - 2\left\langle \left(\hat{R}\cdot\vec{u}_j\right)\left(\hat{R}\cdot\vec{u}_0\right) \right\rangle$$

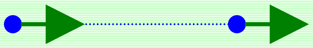


MSD
Mean Square Displacements

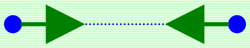
DCF
Displacement Correlation Function



Uncorrelated motion
(from Bragg diffraction)



DCF > 0



DCF < 0

MSRD$_{||}$ and lattice dynamics

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Harmonic approximation

eigenvectors   inter-cell phase-shift

$$\left\langle \Delta u_{\parallel}^2 \right\rangle = \frac{1}{\mathbf{N}\mu}\sum_{\mathbf{q},\lambda} \left\langle |Q(\vec{\mathbf{q}},\lambda,t|^2 \right\rangle \left| \left[\frac{\vec{\mathbf{w}}_j(\vec{\mathbf{q}},\lambda)\, e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{R}}}}{\sqrt{m_j/\mu}} - \frac{\vec{\mathbf{w}}_0(\vec{\mathbf{q}},\lambda)}{\sqrt{m_0/\mu}} \right] \cdot \hat{\mathbf{R}} \right|^2$$

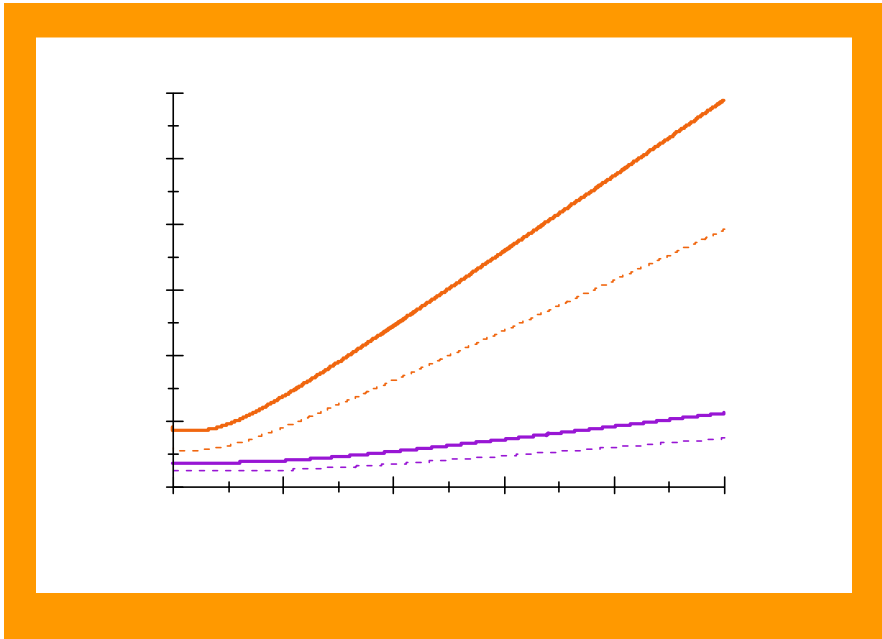
projection

normal coordinate

$$\left\langle |Q(\vec{\mathbf{q}},\lambda,t|^2 \right\rangle = \frac{\left\langle E(\vec{\mathbf{q}},\lambda)\right\rangle}{\omega^2(\vec{\mathbf{q}},\lambda)} = \frac{\hbar}{2\omega(\vec{\mathbf{q}},\lambda)} \coth\frac{\hbar\omega(\vec{\mathbf{q}},\lambda)}{2k_BT}$$

$$= \frac{\hbar}{\omega(\vec{\mathbf{q}},\lambda)}\left\{\frac{1}{\exp\left[\hbar\omega(\vec{\mathbf{q}},\lambda)/kT\right]} + \frac{1}{2}\right\}$$

T dependence →



MSRD$_{||}$ - Debye correlated model

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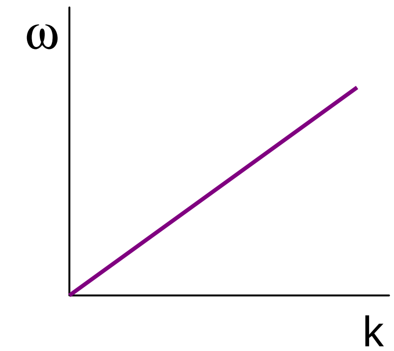
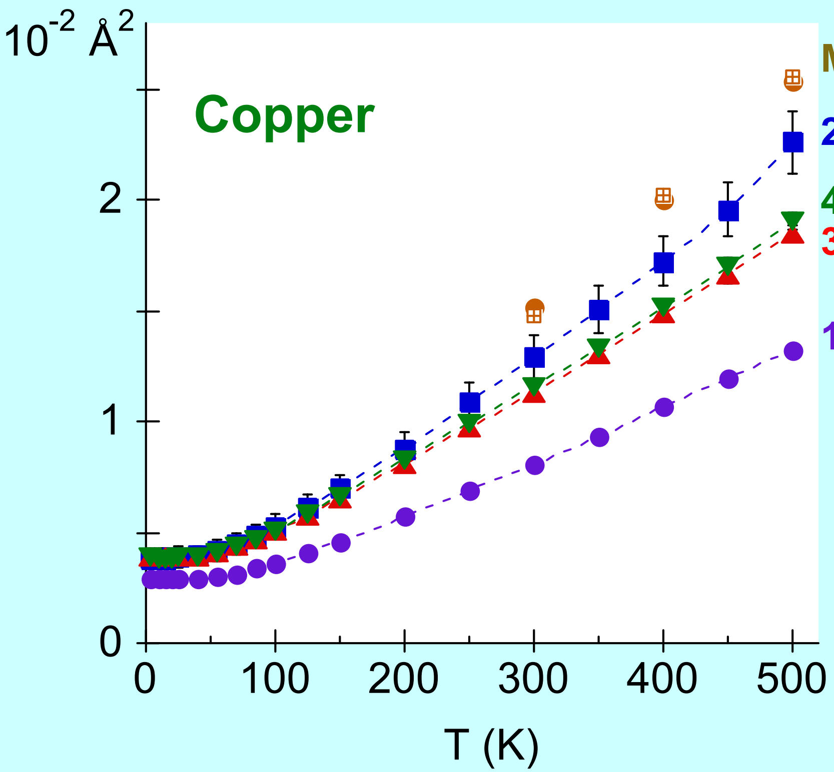
$$\left\langle \Delta u_{\parallel}^{2} \right\rangle = \frac{3\hbar}{2\omega_D^3 \mu} \int_0^{\omega_D} \omega \coth \frac{\hbar\omega}{2k_B T} \left[1 - \frac{\sin(\omega q_D R)}{\omega q_D R} \right] d\omega$$

MSD DCF

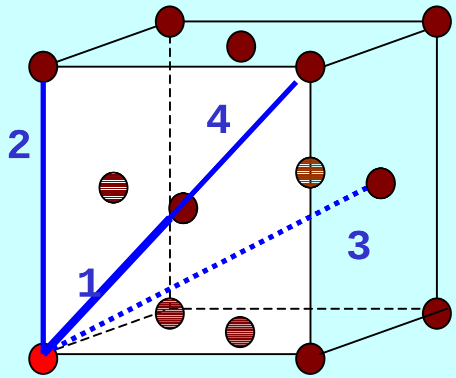




Best-fitting Debye temperatures

θ_D = 315 K
θ_M = 313 K

θ_4 = 321 K
θ_3 = 322 K
θ_2 = 283 K
θ_1 = 328 K



$MSRD_{||}$ - Einstein correlated model

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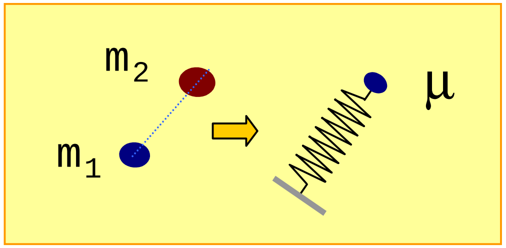
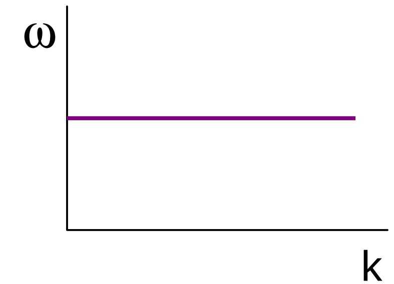
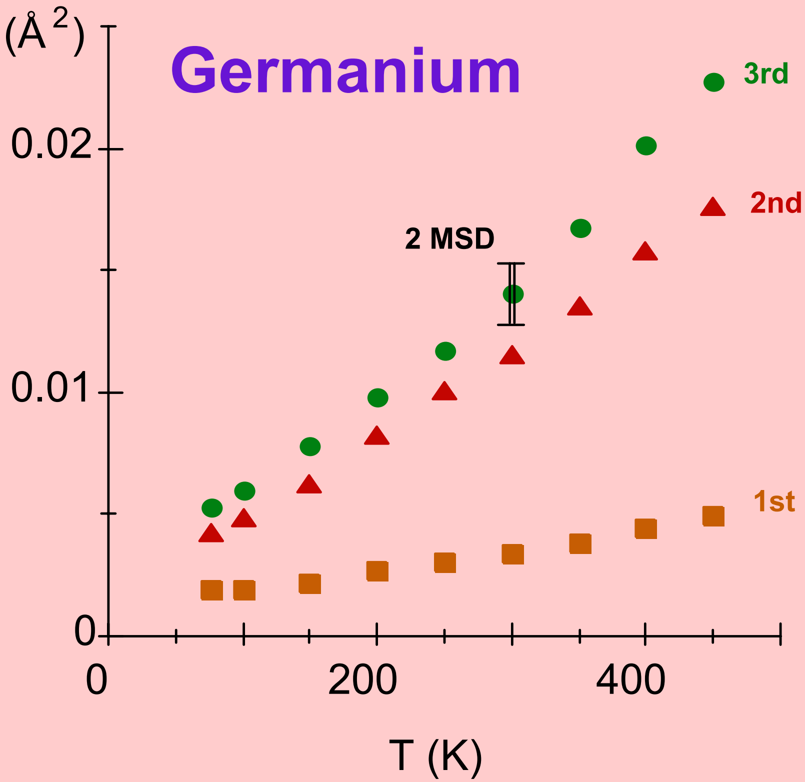


$$\left\langle \Delta u_{||}^2 \right\rangle = \frac{h}{2\mu\omega_E} \coth\left(\frac{h\omega_E}{2kT}\right)$$





Non-Bravais crystals

Debye

θ_D = 354 K
θ_M = 290 K

θ_3 = 290 K
θ_2 = 299 K
θ_1 = 460 K

Einstein

$\nu = \omega / 2\pi$
(THz)

ν_3 = 3.95
ν_2 = 4.21
ν_1 = 7.55

$k = \mu\omega^2$
(eV/Å2)

k_3 = 3.95
k_2 = 4.21
k_1 = 7.55

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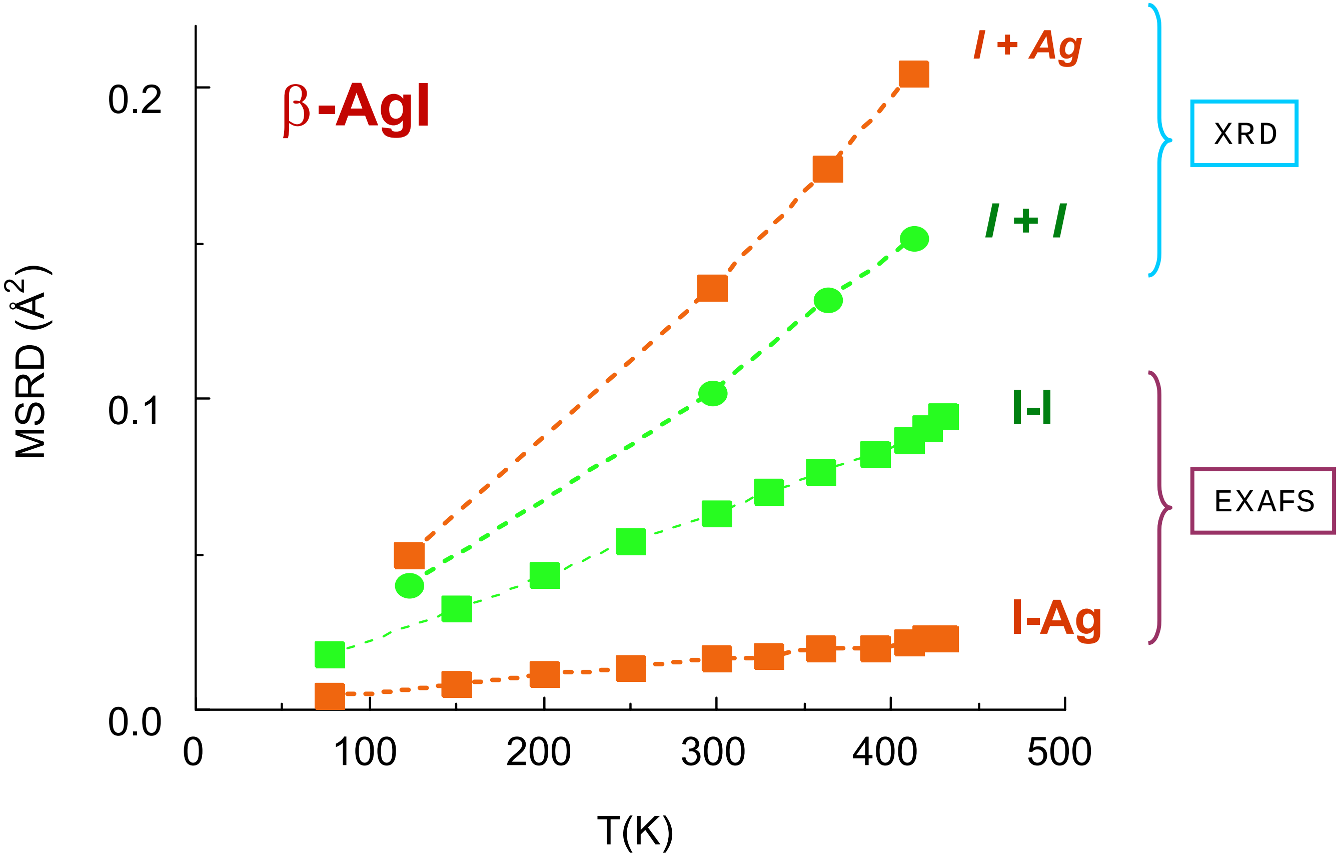
$MSRD_{||}$ - Correlation effects in AgI



G. Dalba et al., PRB **41**, 9668 (1990)

AgI: displacement patterns

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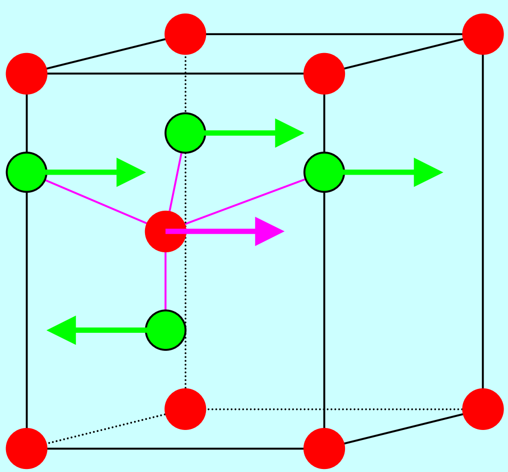
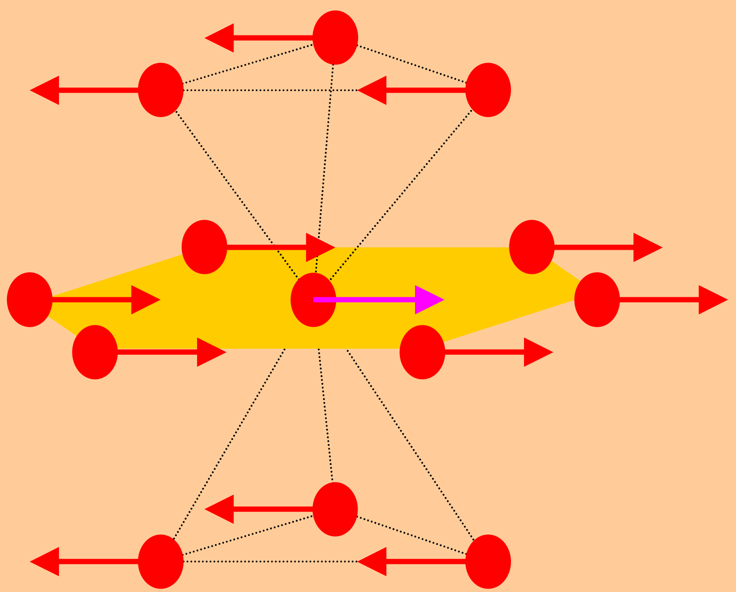
$$\left\langle \Delta u_{\parallel}^{2} \right\rangle = \frac{1}{\mathbf{N}\mu} \sum_{\mathbf{q},\lambda} \frac{\left\langle E(\vec{\mathbf{q}},\lambda) \right\rangle}{\omega^{2}(\vec{\mathbf{q}},\lambda)} \left| \left[\frac{\vec{\mathbf{w}}_{j}(\vec{\mathbf{q}},\lambda) e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{R}}}}{\sqrt{m_{j}/\mu}} - \frac{\vec{\mathbf{w}}_{0}(\vec{\mathbf{q}},\lambda)}{\sqrt{m_{0}/\mu}} \right] \cdot \hat{\mathbf{R}} \right|^{2}$$

0.5 THz optical modes
(@ BZ center)

I - Ag



I - I



Anharmonicity

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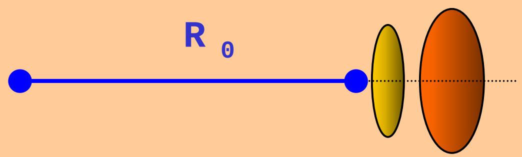
$$\langle \Delta u_{\parallel} \rangle = \langle \Delta u_{\parallel} \rangle_{\text{an}} + \langle \Delta u_{\parallel} \rangle_{\text{harm}}$$

Relative translation



$$\langle \Delta u_{\parallel} \rangle_{\text{harm}} = 0$$

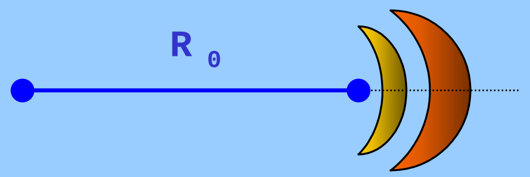
$$C_1^* \approx R_0 + \langle \Delta u_{\parallel} \rangle_{\text{an}} + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_0}$$

$$R_c = R_0 + \langle \Delta u_{\parallel} \rangle_{\text{an}}$$

EXAFS

Diffraction

Relative libration



$$\langle \Delta u_{\parallel} \rangle_{\text{harm}} \approx -\frac{\langle \Delta u_{\perp}^2 \rangle}{2R_0}$$

$$C_1^* \approx R_0 + \langle \Delta u_{\parallel} \rangle_{\text{an}}$$

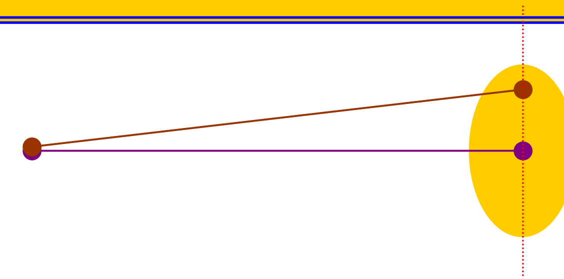
$$R_c \approx R_0 + \langle \Delta u_{\parallel} \rangle_{\text{an}} - \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_0}$$

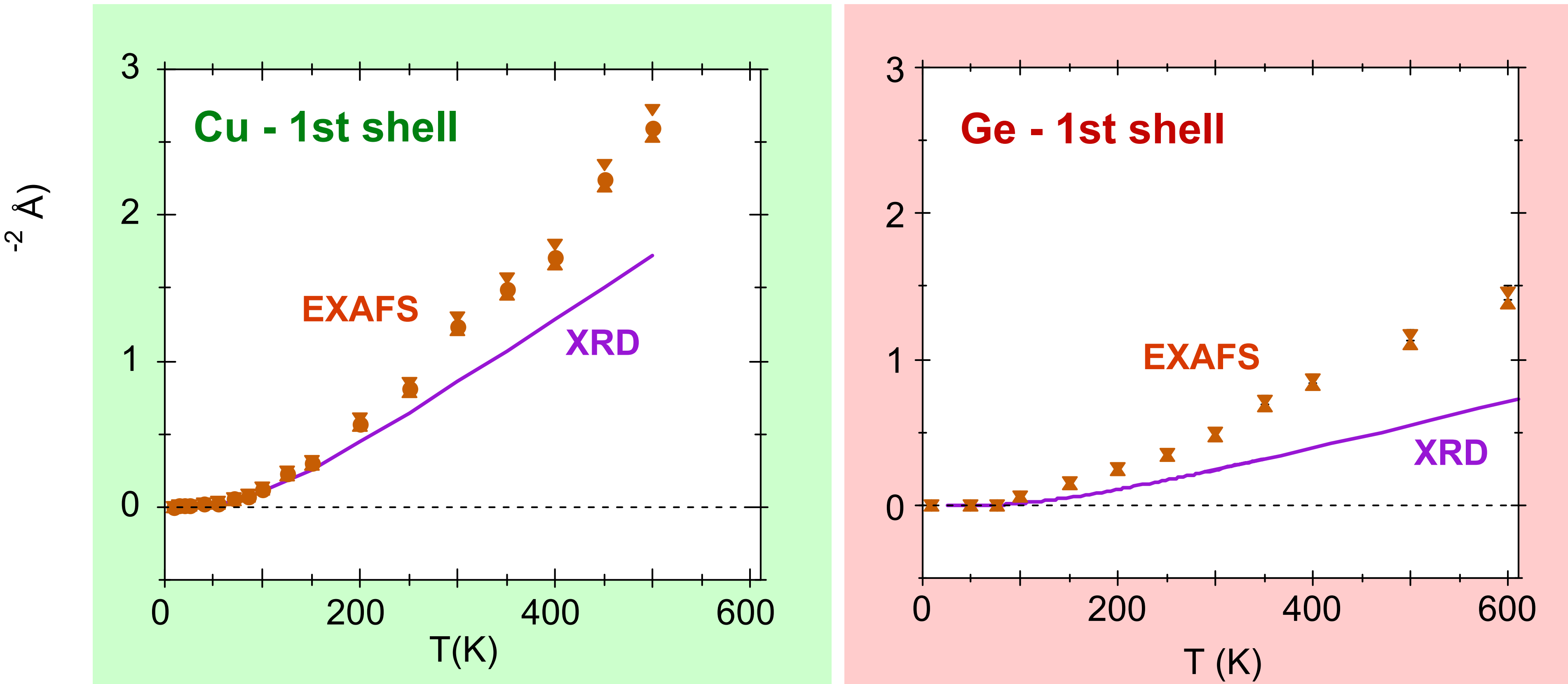
$$C_1^* \approx R_c + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_0}$$

Thermal expansion

$$C_1^* \approx R_c + \frac{\langle \Delta u_\perp^2 \rangle}{2R_0}$$

MSRD$_\perp$





G. Dalba et al., PRB, **70**, 174301 (2004)

G. Dalba et al., PRL **82**, 4240 (1999)

Perpendicular MSRD

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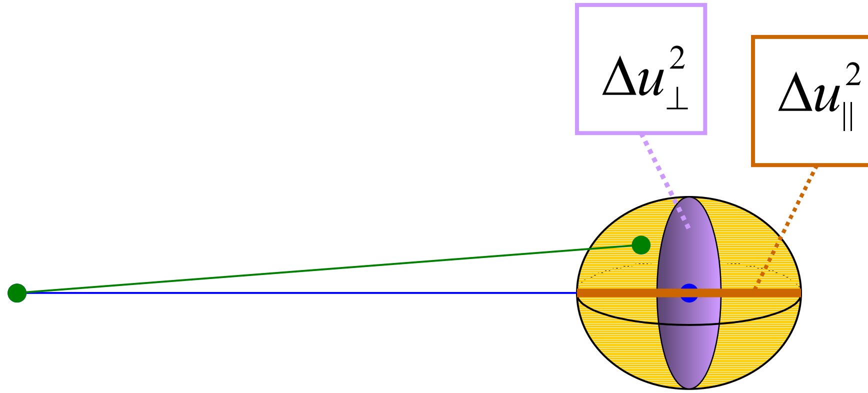
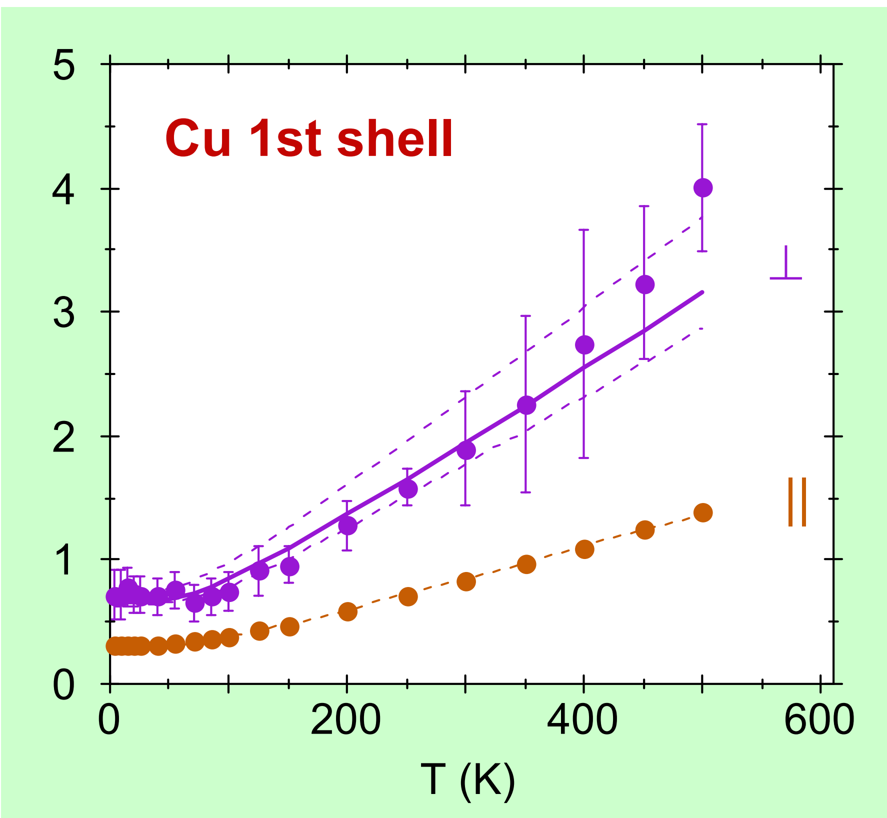
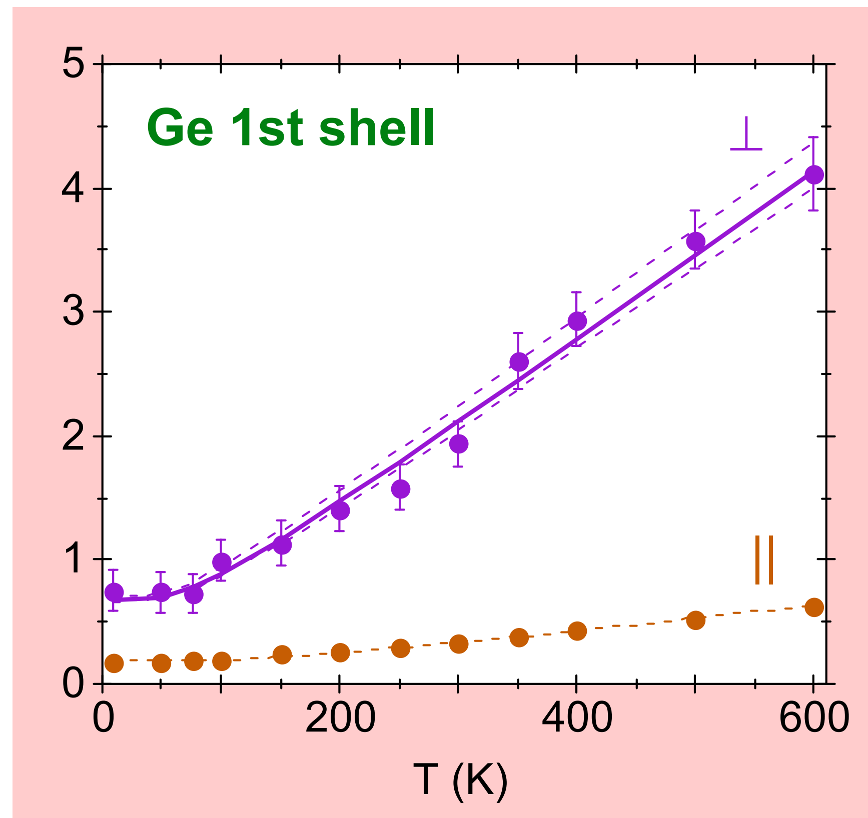
Einstein frequencies

	Cu	Ge	
⊥	4.57	4.12	THz
‖	4.96	7.55	THz







Third cumulant

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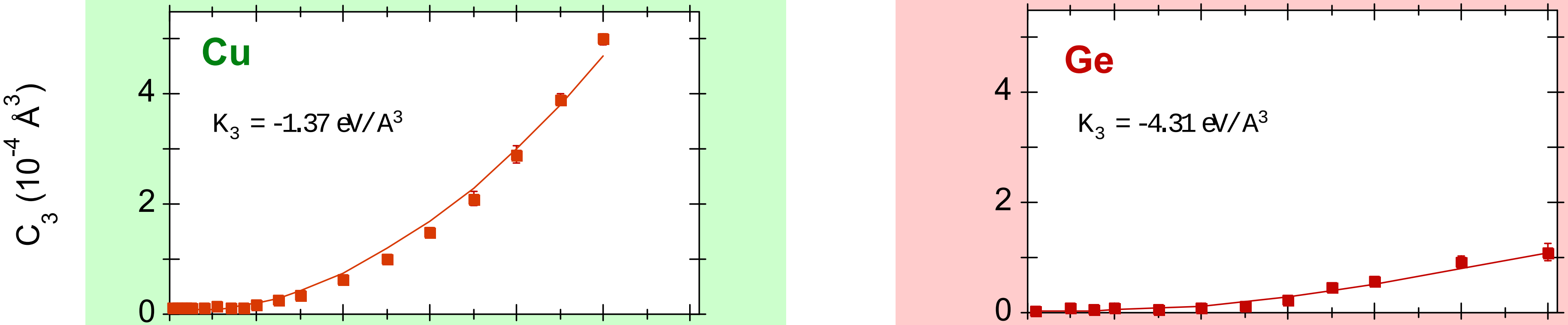
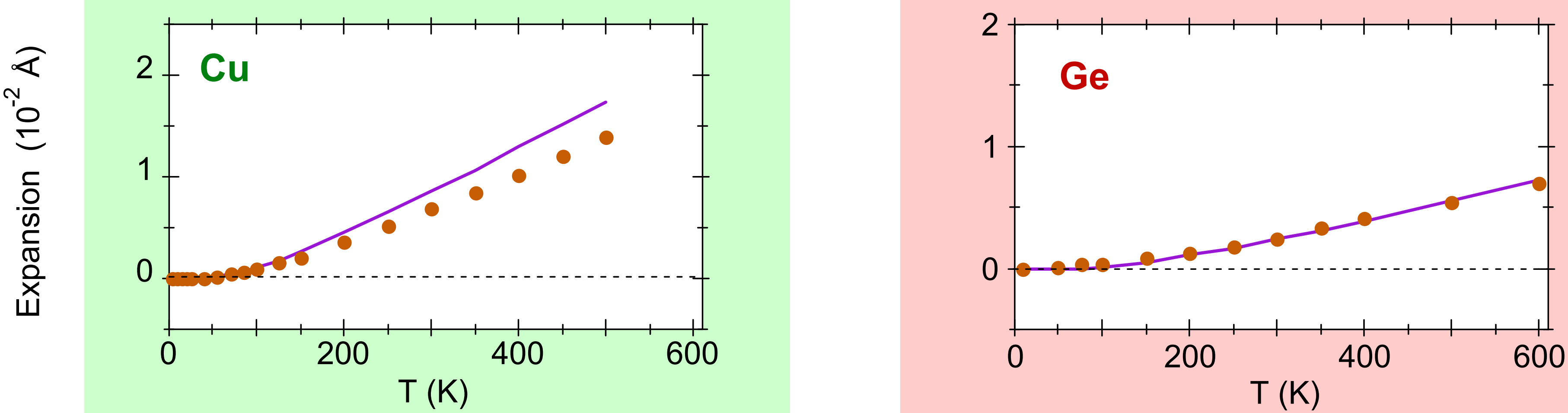
Effective potential asymmetry $$C_3^*(T) \approx -\frac{2k_3\sigma_0^4}{k_0}\,\frac{z^2+10z+1}{(1-z)^2}$$



Thermal expansion due to asymmetry $$-3k_3\,C_2^*/k_0$$



Germanium, comparison with theory

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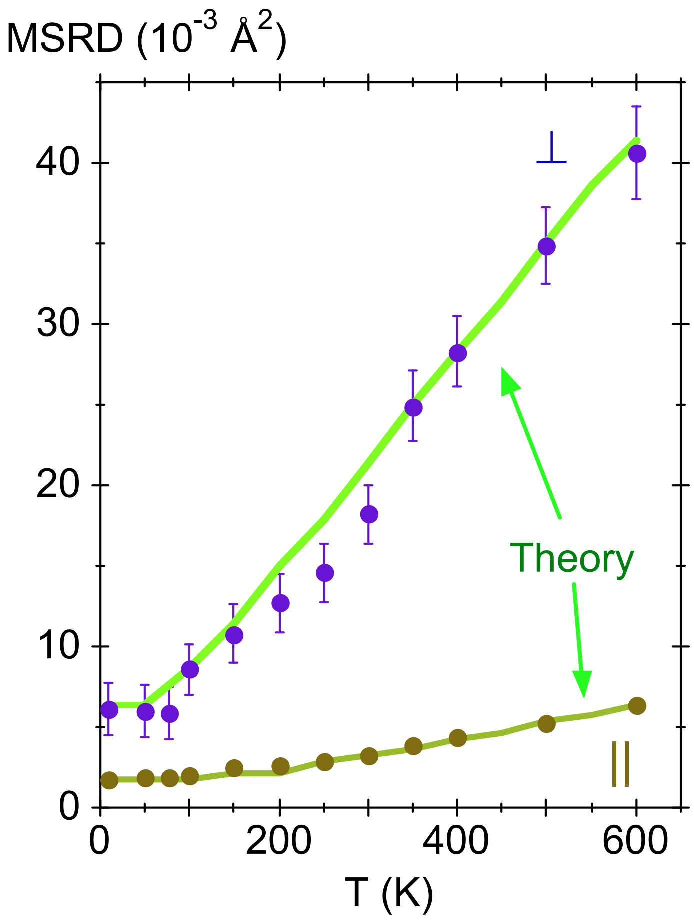
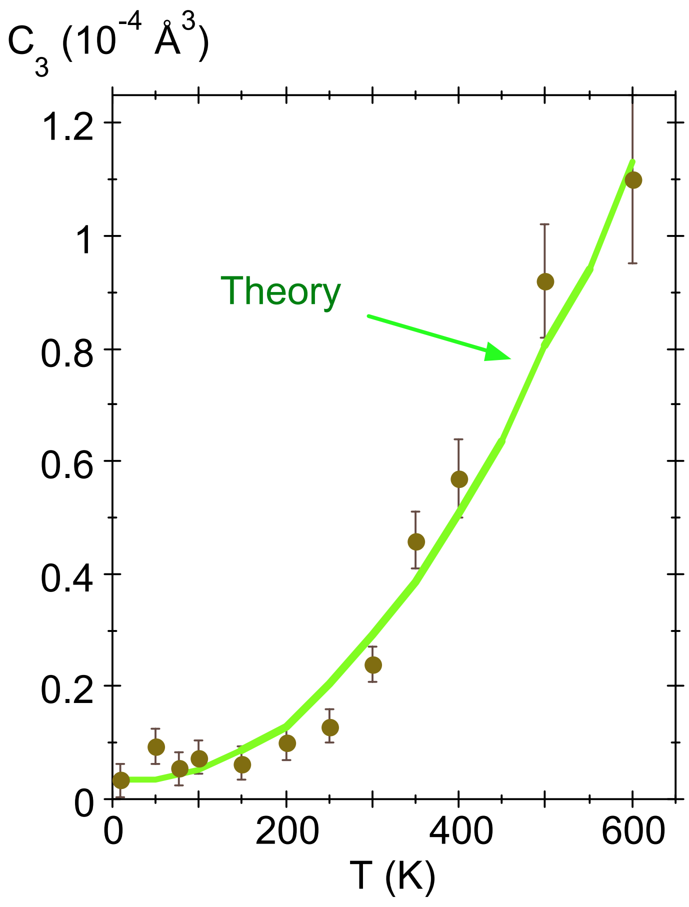
Ab-initio lattice dynamics + perturbative anharmonicity

D. Strauch et al.
private commun.



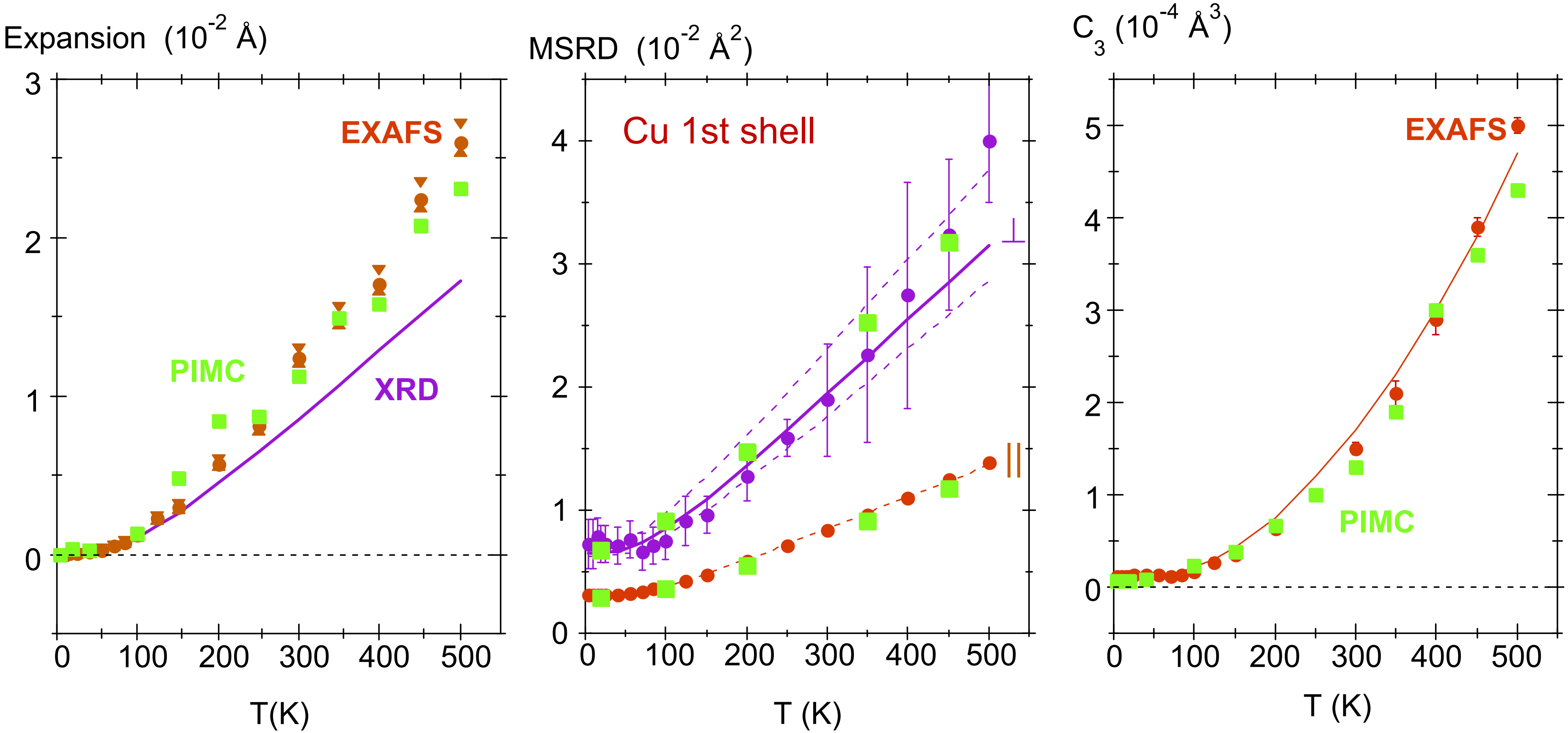


Copper, comparison with theory

Path Integral Monte Carlo calculations
(many-body potential)

- anharmonicity
- low-T quantum effects

S. a Beccara et al.
PRB 68, 140301 (2003)



Amorphous and crystalline Germanium

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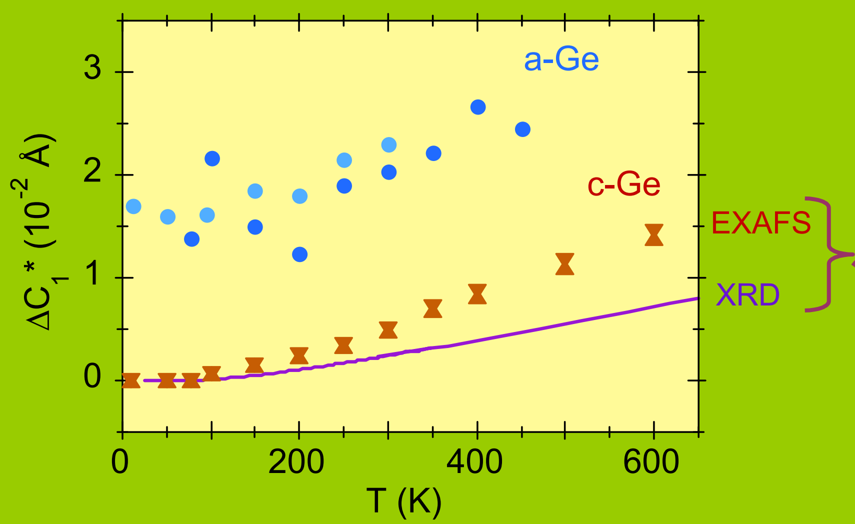
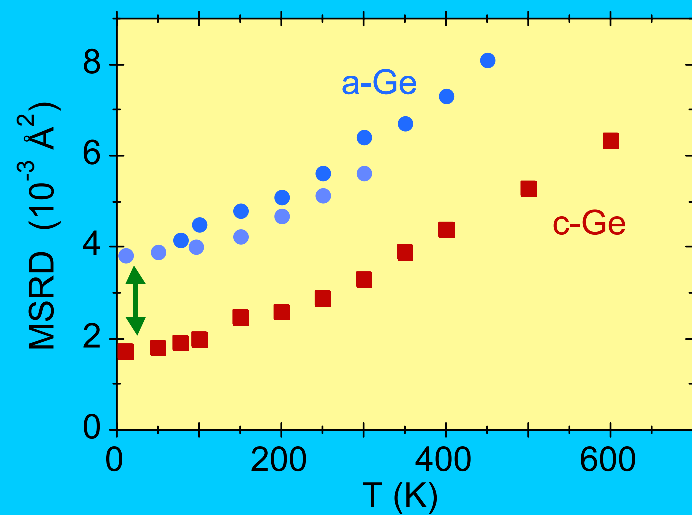
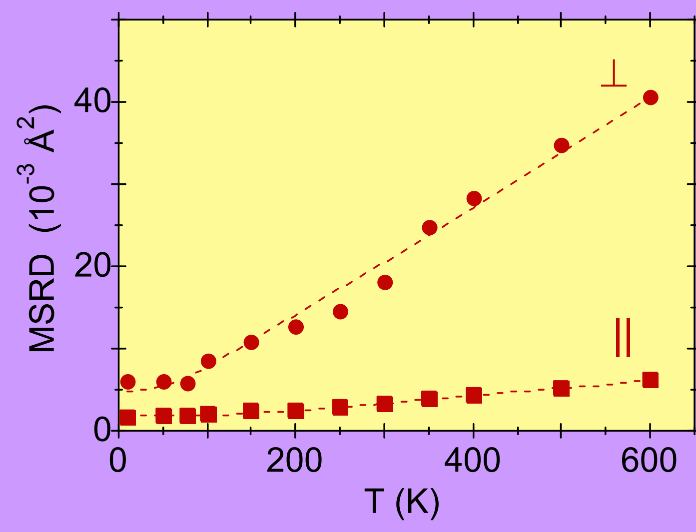
Nearest-neighbour distance



Parallel MSRD



Perpendicular MSRD



Effective potential and expansion

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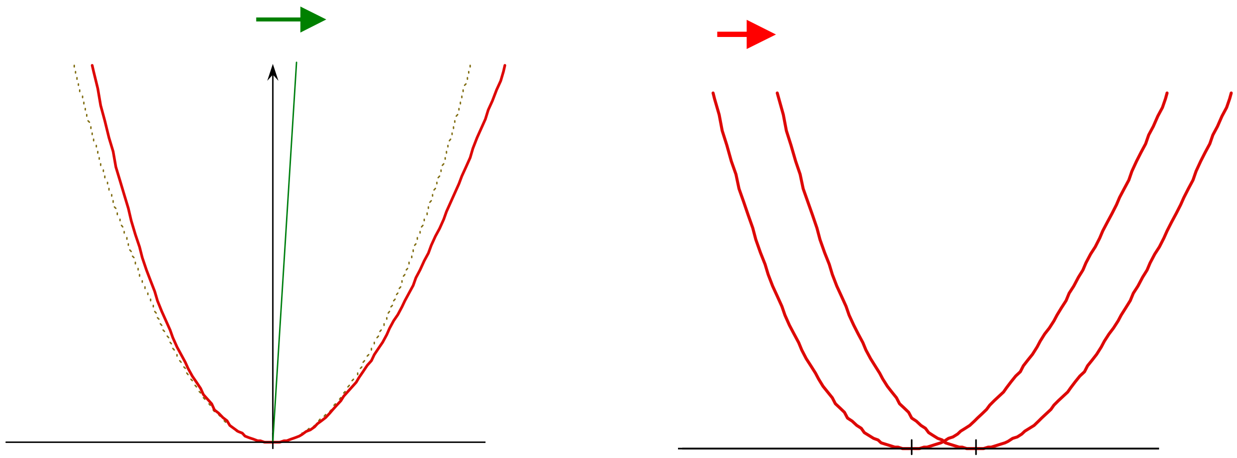
C_3 fitted by quantum model $\Rightarrow$ shape indep. of T



EXAFS expansion = Potential asymmetry + Potential shift

C_1^* → EXAFS expansion

Potential asymmetry → C_3

Potential shift → $\langle \Delta u_\perp^2 \rangle$, ?

MSRD in β-AgI

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