

White dwarf cooling: electron-phonon coupling and the metallization of solid helium

Bartomeu Monserrat

University of Cambridge

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Outline

White dwarf stars overview

Theoretical background

Anharmonic energy

Phonon expectation values

Results

Conclusions

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White dwarf stars overview

Theoretical background

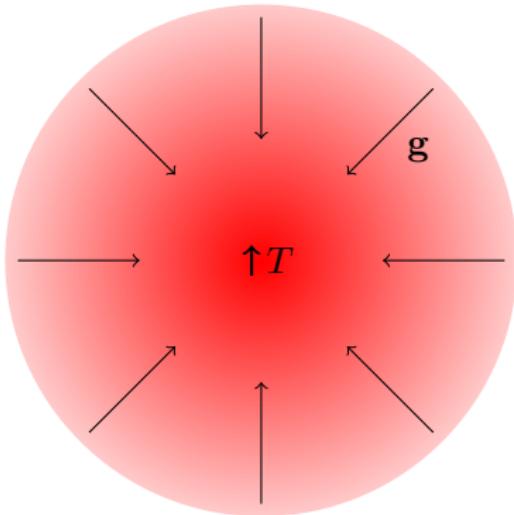
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Star formation

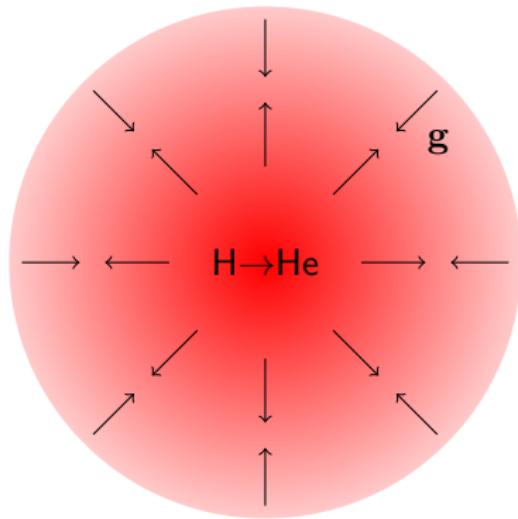


- ▶ Virial theorem: $K = -1/2 V_g$.
- ▶ Energy expressions:

$$K \propto Nk_B T \quad \text{and} \quad V_g \propto -\frac{GM^2}{R}$$

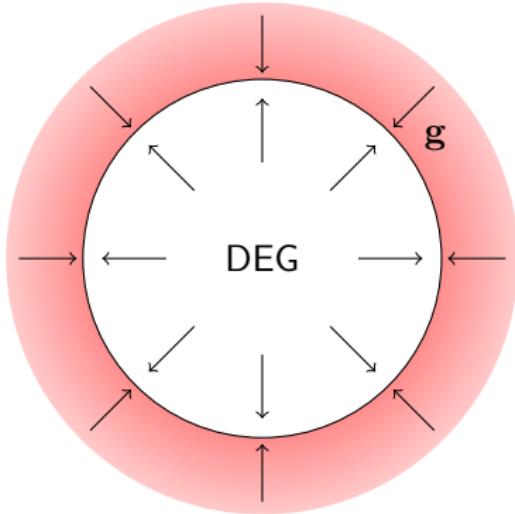
- ▶ Temperature **increases** as the star gravitationally **collapses**.

Main sequence star



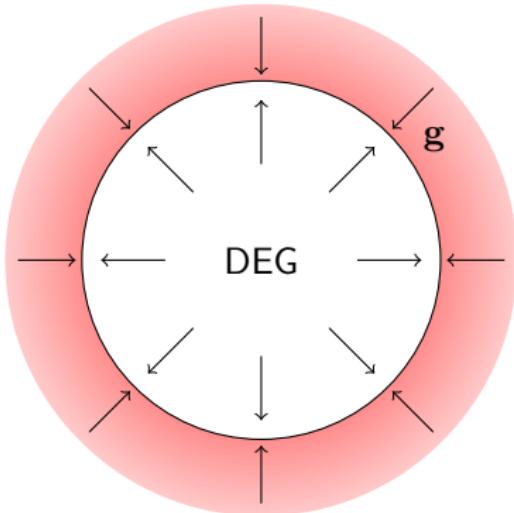
- ▶ Thermonuclear reactions: hydrogen burning.
- ▶ Gravitation balanced by nuclear reactions.
- ▶ Main sequence star (e.g. the Sun).

White dwarf formation



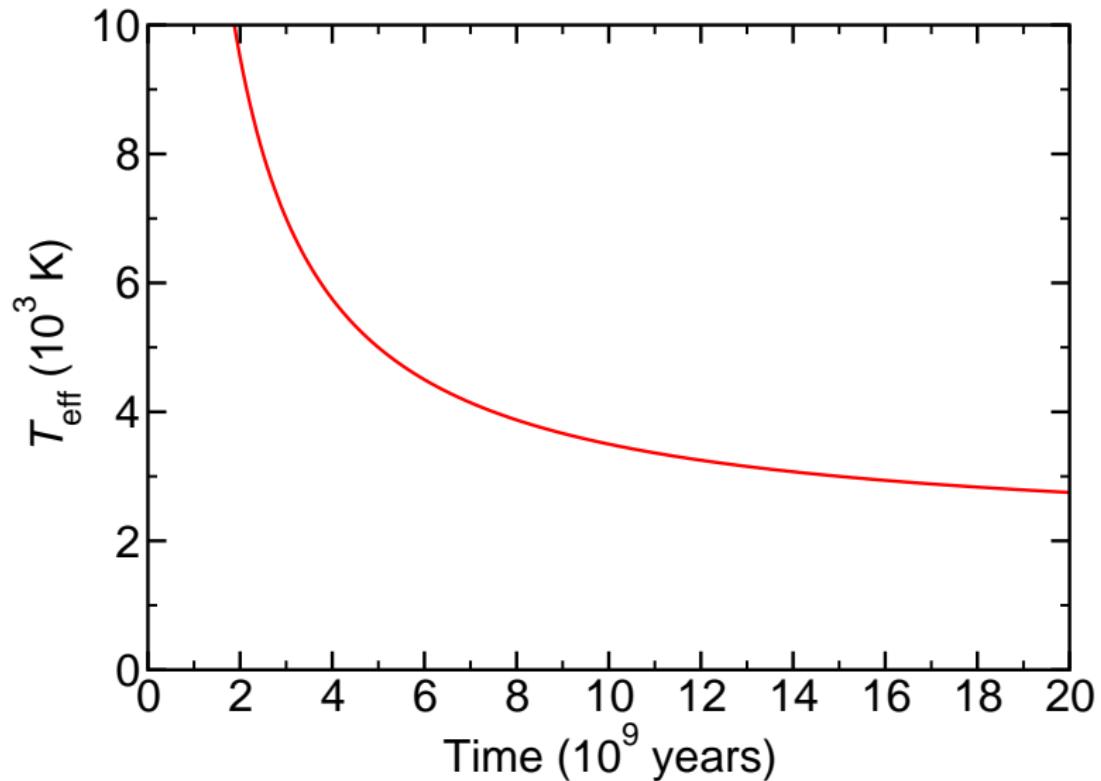
- ▶ Burning material exhausted.
- ▶ Gravitational contraction resumes.
- ▶ High density leads to degenerate electron gas (DEG).
- ▶ White dwarf star balanced by DEG.
- ▶ Complications: mass loss (red giant), further burning cycles, ...

White dwarf structure

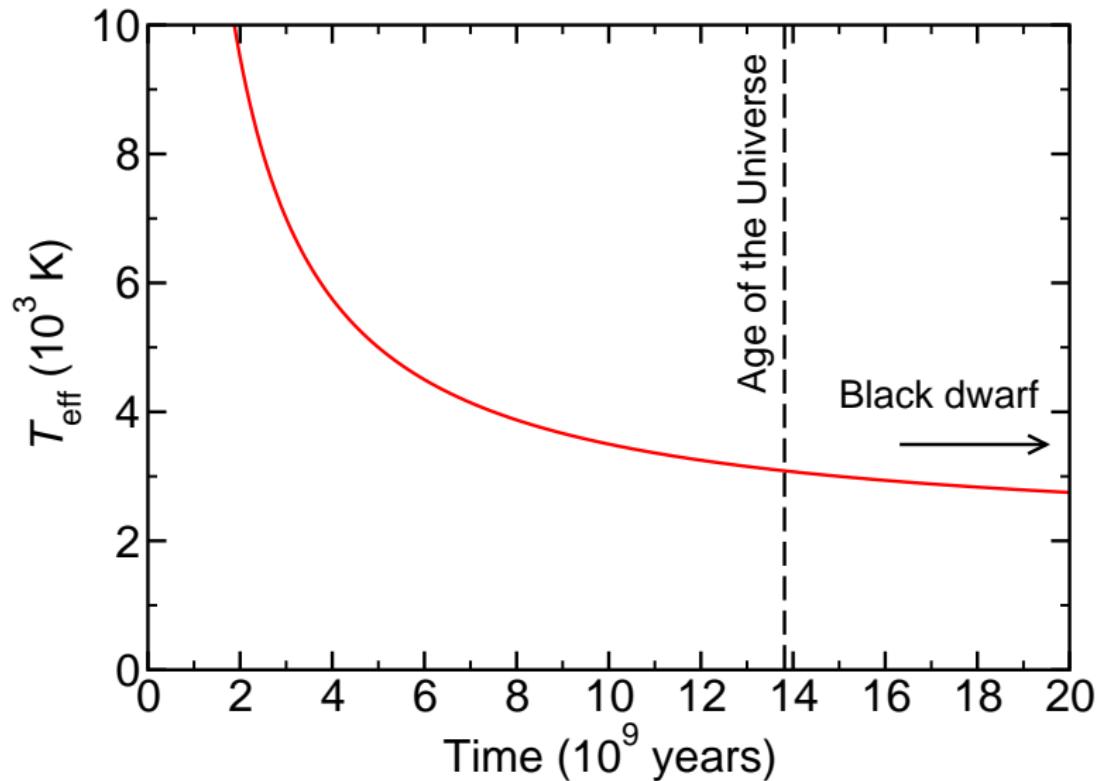


- ▶ Degenerate core: He or C/O.
- ▶ Atmosphere: H, He and traces of other elements.
- ▶ Atmosphere represents $10^{-4} - 10^{-2}$ of the total mass.
- ▶ Atmosphere stratification due to strong gravity.
- ▶ Weak energy sources: crystallization, ...
- ▶ Energy transport: conduction, radiation and convection.

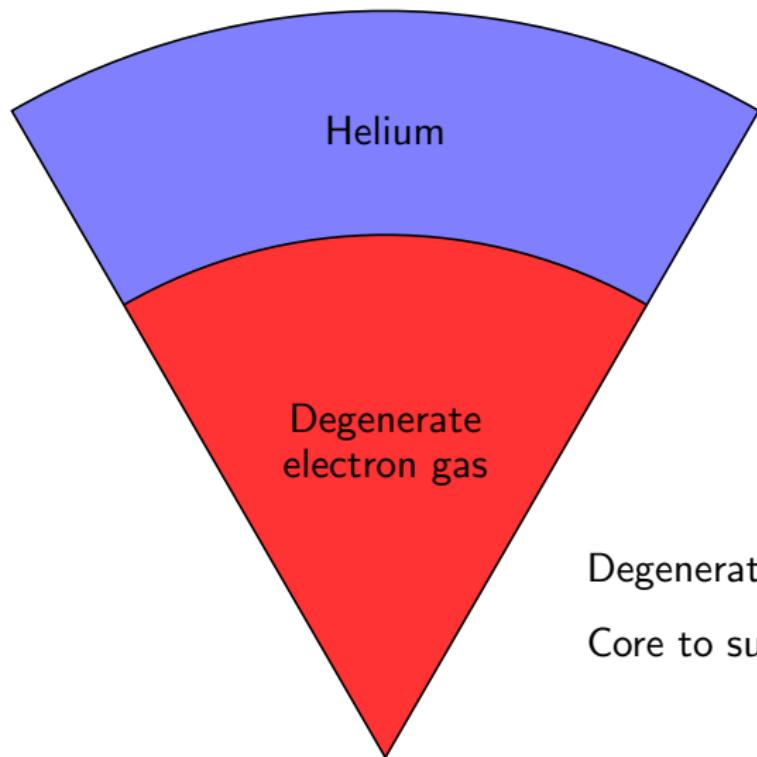
White dwarf cooling



White dwarf cooling



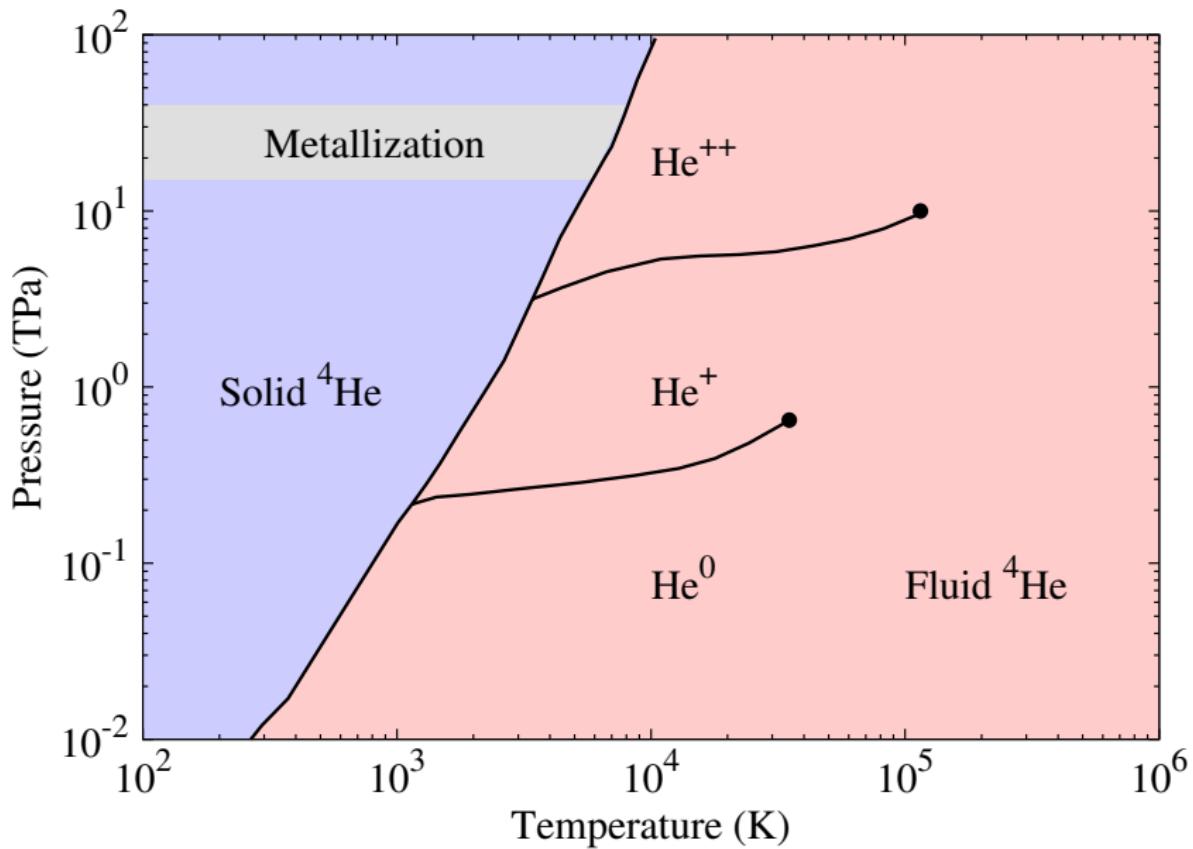
White dwarf cooling: metallization of solid helium (I)



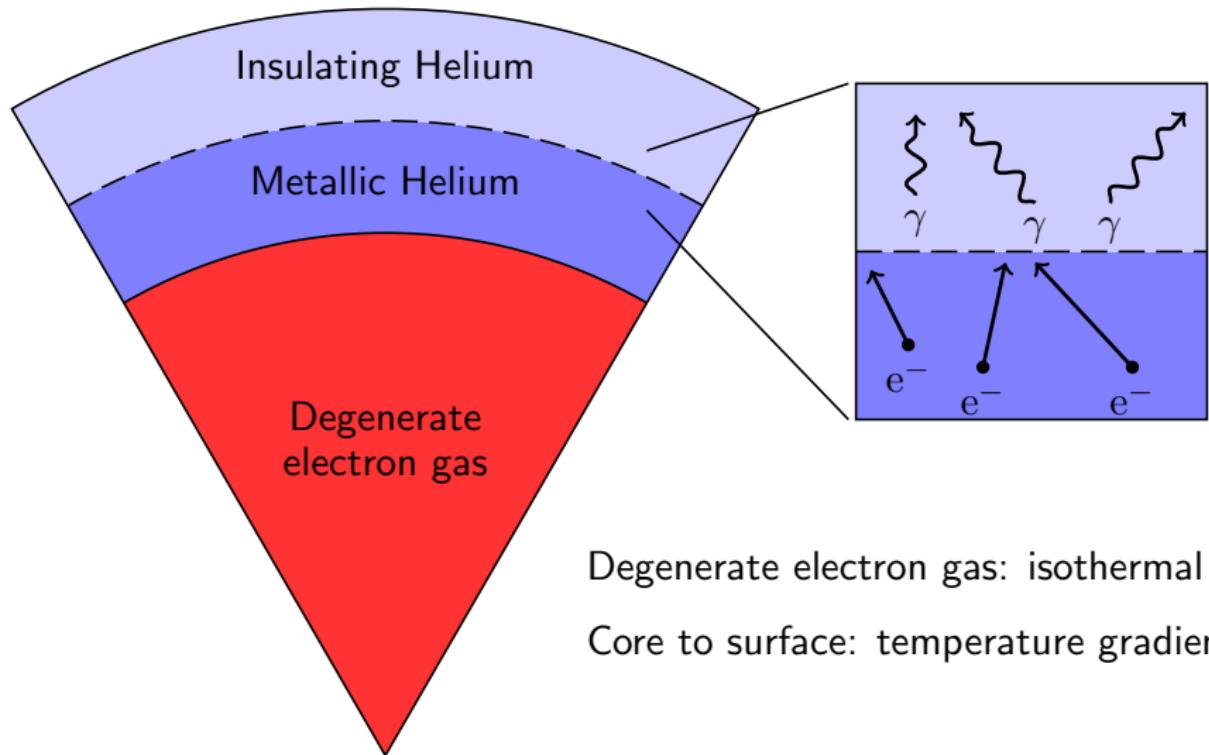
Degenerate electron gas: isothermal

Core to surface: temperature gradient

Helium phase diagram



White dwarf cooling: metallization of solid helium (II)



Metallization pressure

- ▶ DFT: 17 TPa at zero temperature.
- ▶ DMC and *GW*: 25.7 TPa at zero temperature.
- ▶ Electron-phonon coupling: ?

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Harmonic approximation

- ▶ Vibrational Hamiltonian in $\{\mathbf{r}_\alpha\}$ (or $\{\mathbf{u}_\alpha\}$):

$$\hat{H}_{\text{vib}} = -\frac{1}{2} \sum_{\mathbf{R}_p, \alpha} \frac{1}{m_\alpha} \nabla_{p\alpha}^2 + \frac{1}{2} \sum_{\mathbf{R}_p, \alpha; \mathbf{R}_{p'}, \beta} \mathbf{u}_{p\alpha} \Phi_{p\alpha; p'\beta} \mathbf{u}_{p'\beta}$$

- ▶ Normal mode analysis: $\{\mathbf{u}_{p\alpha}\} \longrightarrow \{q_{\mathbf{k}s}\}$

$$\begin{aligned} u_{p\alpha; i} &= \frac{1}{\sqrt{N_0 m_\alpha}} \sum_{\mathbf{k}, s} q_{\mathbf{k}s} e^{i \mathbf{k} \cdot \mathbf{R}_p} w_{\mathbf{k}s; i\alpha} \\ q_{\mathbf{k}s} &= \frac{1}{\sqrt{N_0}} \sum_{\mathbf{R}_p, \alpha, i} \sqrt{m_\alpha} u_{p\alpha; i} e^{-i \mathbf{k} \cdot \mathbf{R}_p} w_{-\mathbf{k}s; i\alpha} \end{aligned}$$

- ▶ Vibrational Hamiltonian in $\{q_{\mathbf{k}s}\}$:

$$\hat{H}_{\text{vib}} = \sum_{\mathbf{k}, s} \left(-\frac{1}{2} \frac{\partial^2}{\partial q_{\mathbf{k}s}^2} + \frac{1}{2} \omega_{\mathbf{k}s}^2 q_{\mathbf{k}s}^2 \right)$$

Principal axes approximation to the BO energy surface

$$V(\{q_{\mathbf{k}s}\}) = \textcolor{teal}{V(0)} + \sum_{\mathbf{k}, s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum'_{\mathbf{k}', s'} V_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$

- ▶ **Static lattice** DFT total energy
- ▶ DFT total energy along frozen **independent phonon**
- ▶ DFT total energy along frozen **coupled phonons**

Vibrational self-consistent field equations

- ▶ Phonon Schrödinger equation:

$$\left(\sum_{\mathbf{k},s} -\frac{1}{2} \frac{\partial^2}{\partial q_{\mathbf{k}s}^2} + V(\{q_{\mathbf{k}s}\}) \right) \Phi(\{q_{\mathbf{k}s}\}) = E \Phi(\{q_{\mathbf{k}s}\})$$

- ▶ Ground state ansatz: $\Phi(\{q_{\mathbf{k}s}\}) = \prod_{\mathbf{k},s} \phi_{\mathbf{k}s}(q_{\mathbf{k}s})$
- ▶ Self-consistent equations:

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial q_{\mathbf{k}s}^2} + \bar{V}_{\mathbf{k}s}(q_{\mathbf{k}s}) \right) \phi_{\mathbf{k}s}(q_{\mathbf{k}s}) = \lambda_{\mathbf{k}s} \phi_{\mathbf{k}s}(q_{\mathbf{k}s})$$

$$\bar{V}_{\mathbf{k}s}(q_{\mathbf{k}s}) = \left\langle \prod'_{\mathbf{k}',s'} \phi_{\mathbf{k}'s'}(q_{\mathbf{k}'s'}) \middle| V(\{q_{\mathbf{k}''s''}\}) \middle| \prod'_{\mathbf{k}',s'} \phi_{\mathbf{k}'s'}(q_{\mathbf{k}'s'}) \right\rangle$$

Vibrational self-consistent field equations (II)

- ▶ Approximate vibrational excited states:

$$|\Phi^{\mathbf{S}}(\mathbf{Q})\rangle = \prod_{\mathbf{k},s} |\phi_{\mathbf{k}s}^{S_{\mathbf{k}s}}(q_{\mathbf{k}s})\rangle$$

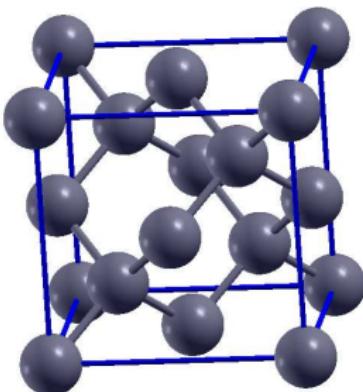
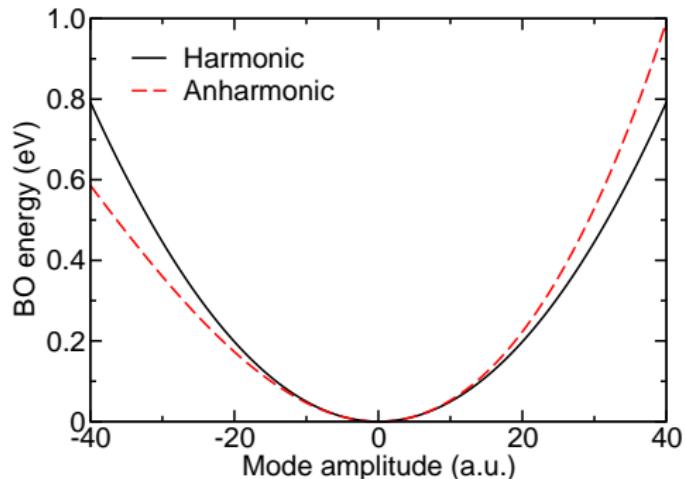
where \mathbf{S} is a vector with elements $S_{\mathbf{k}s}$.

- ▶ Anharmonic free energy:

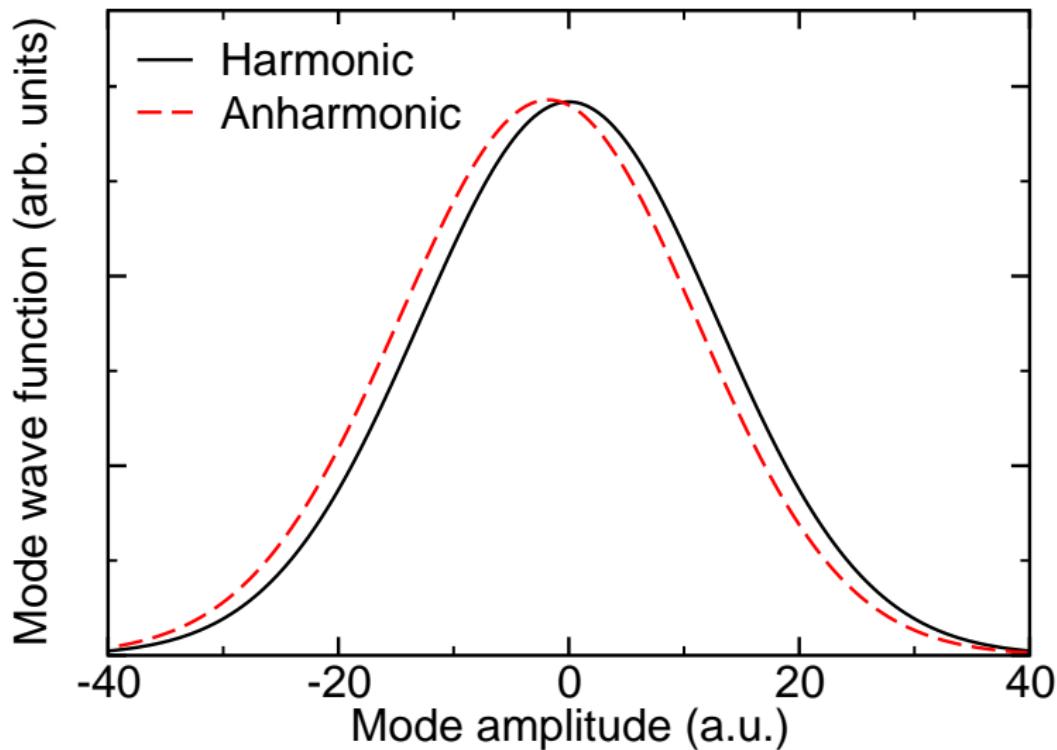
$$F = -\frac{1}{\beta} \ln \sum_{\mathbf{S}} e^{-\beta E_{\mathbf{S}}}$$

Diamond independent phonon term (I)

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k}, s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum'_{\mathbf{k}', s'} V_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$

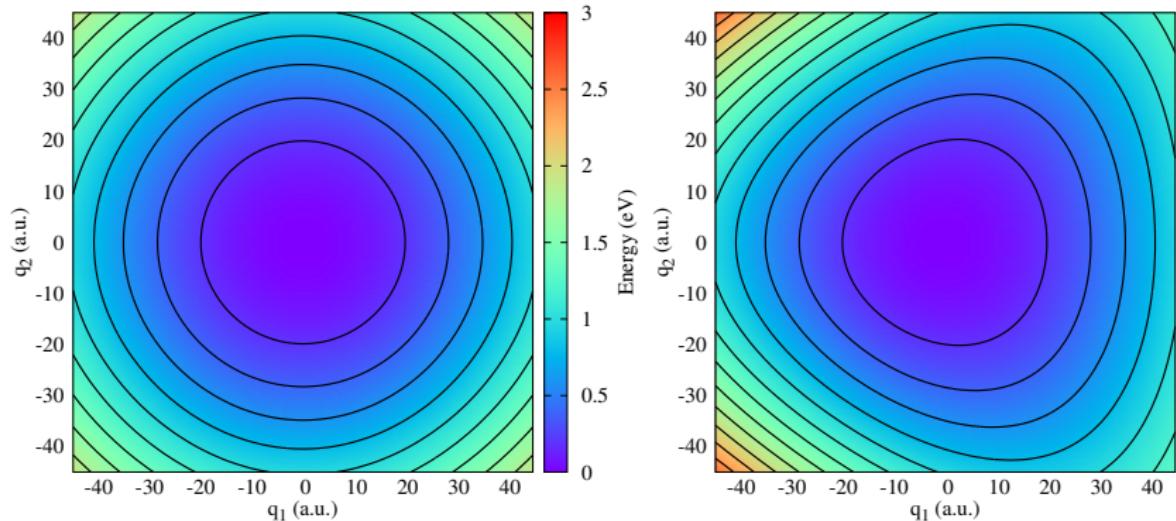


Diamond independent phonon term (II)



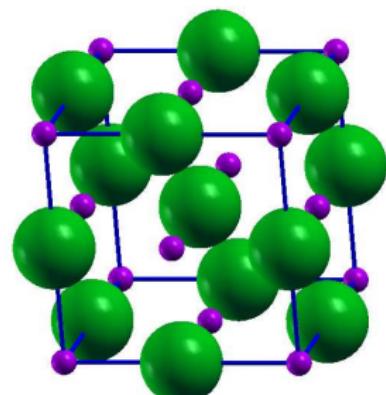
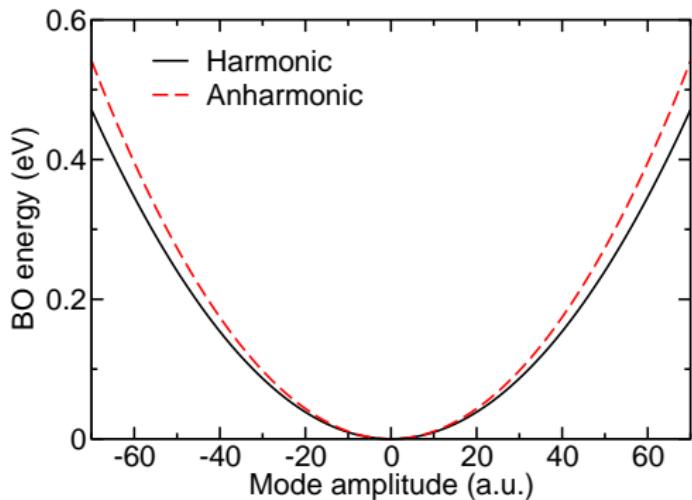
Diamond coupled phonons term

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k}, s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum'_{\mathbf{k}', s'} V_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$

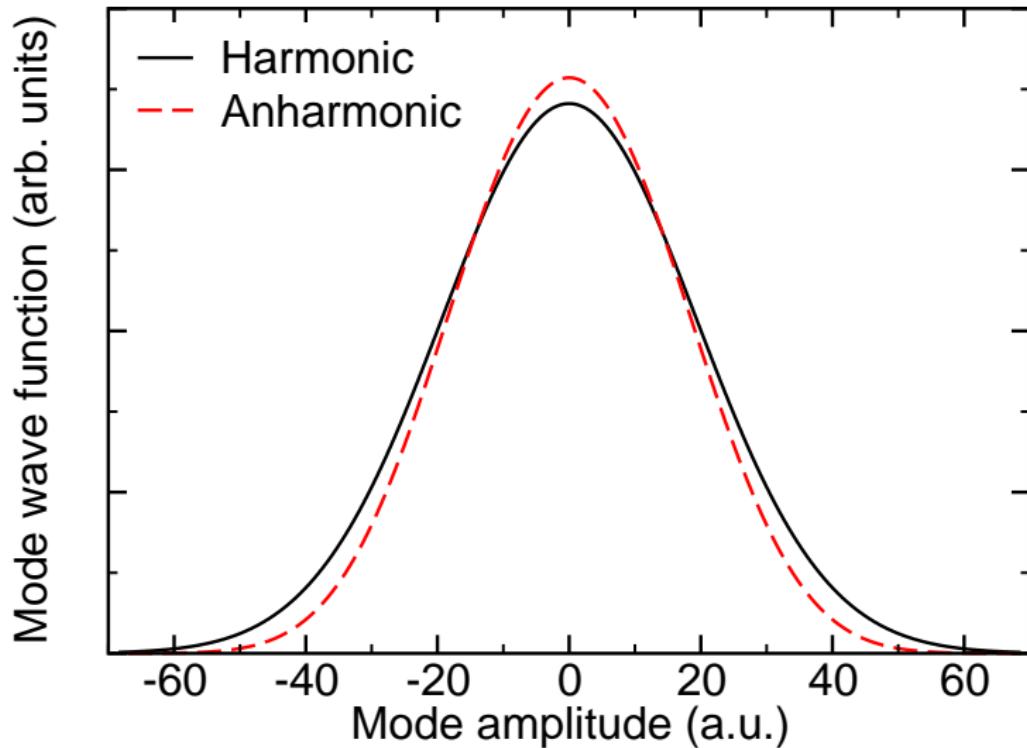


LiH independent phonon term (I)

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k}, s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum'_{\mathbf{k}', s'} V_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$

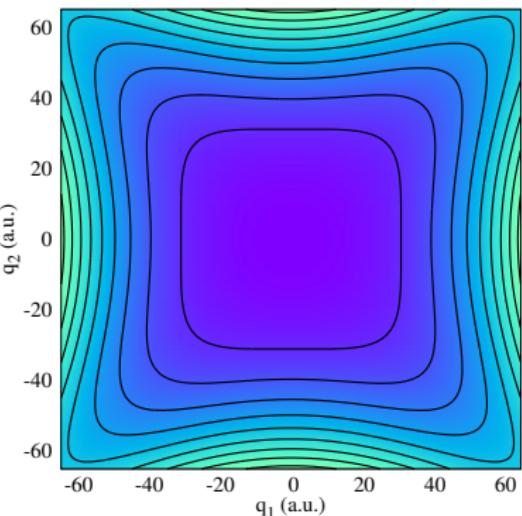
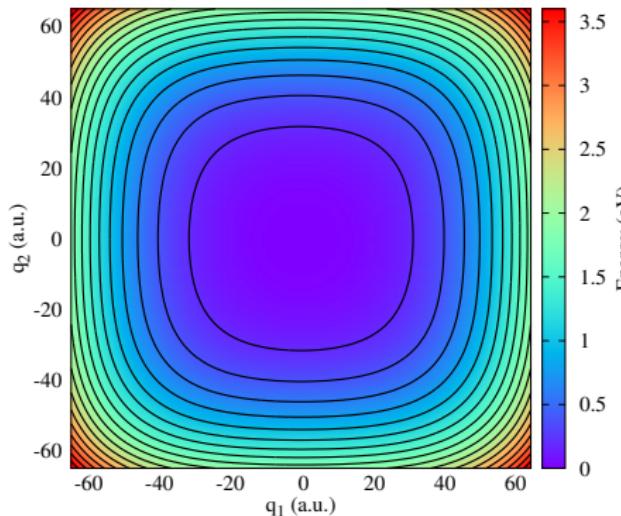


LiH independent phonon term (II)

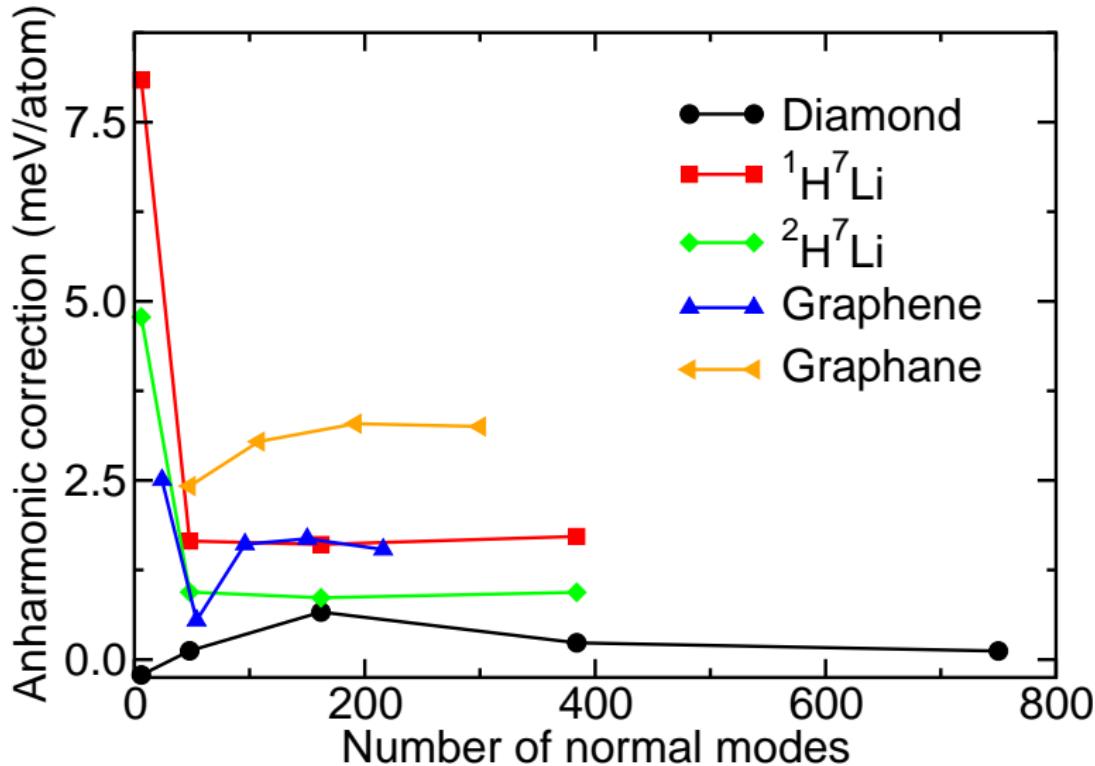


LiH coupled phonons term

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k}, s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum' V_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$



Anharmonic ZPE correction



General phonon expectation value

- ▶ Phonon expectation value at inverse temperature β :

$$\langle \hat{O}(\mathbf{Q}) \rangle_{\Phi, \beta} = \frac{1}{Z} \sum_{\mathbf{S}} \langle \Phi^{\mathbf{S}}(\mathbf{Q}) | \hat{O}(\mathbf{Q}) | \Phi^{\mathbf{S}}(\mathbf{Q}) \rangle e^{-\beta E_{\mathbf{S}}}$$

- ▶ Evaluation:

- ▶ Standard theories (Allen-Heine, Grüneisen):

$$\hat{O}(\mathbf{Q}) = \hat{O}(\mathbf{0}) + \sum_{\mathbf{k}, s} a_{\mathbf{k}s} q_{\mathbf{k}s}^2$$

- ▶ Principal axes expansion:

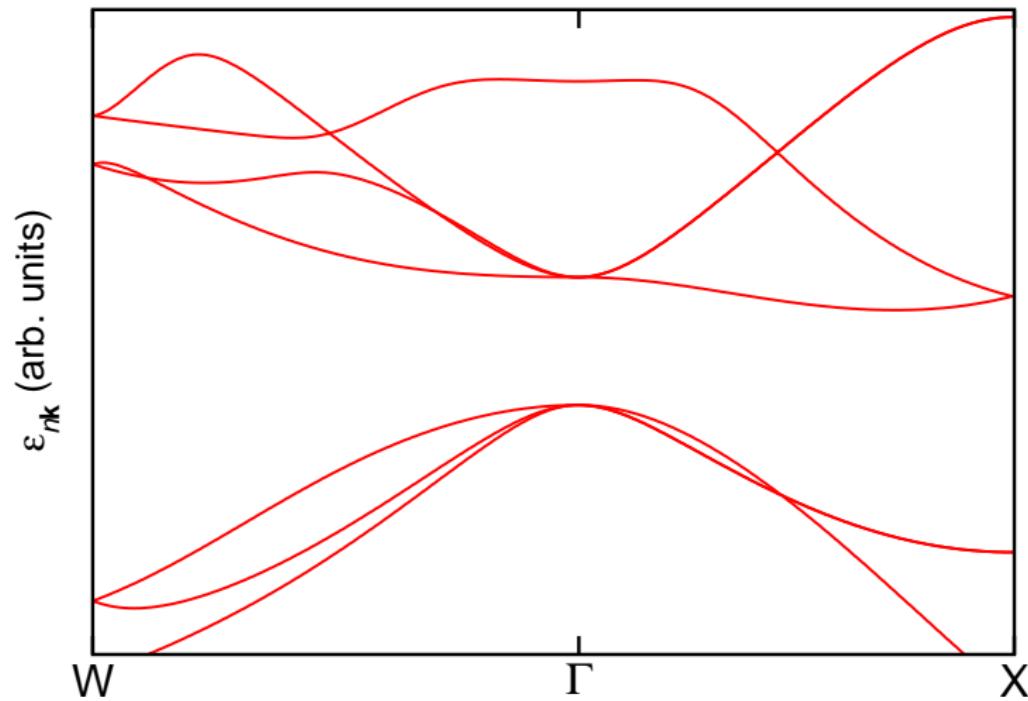
$$\hat{O}(\mathbf{Q}) = \hat{O}(\mathbf{0}) + \sum_{\mathbf{k}, s} \hat{O}_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k}, s} \sum'_{\mathbf{k}', s'} \hat{O}_{\mathbf{k}s; \mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \dots$$

- ▶ Monte Carlo sampling

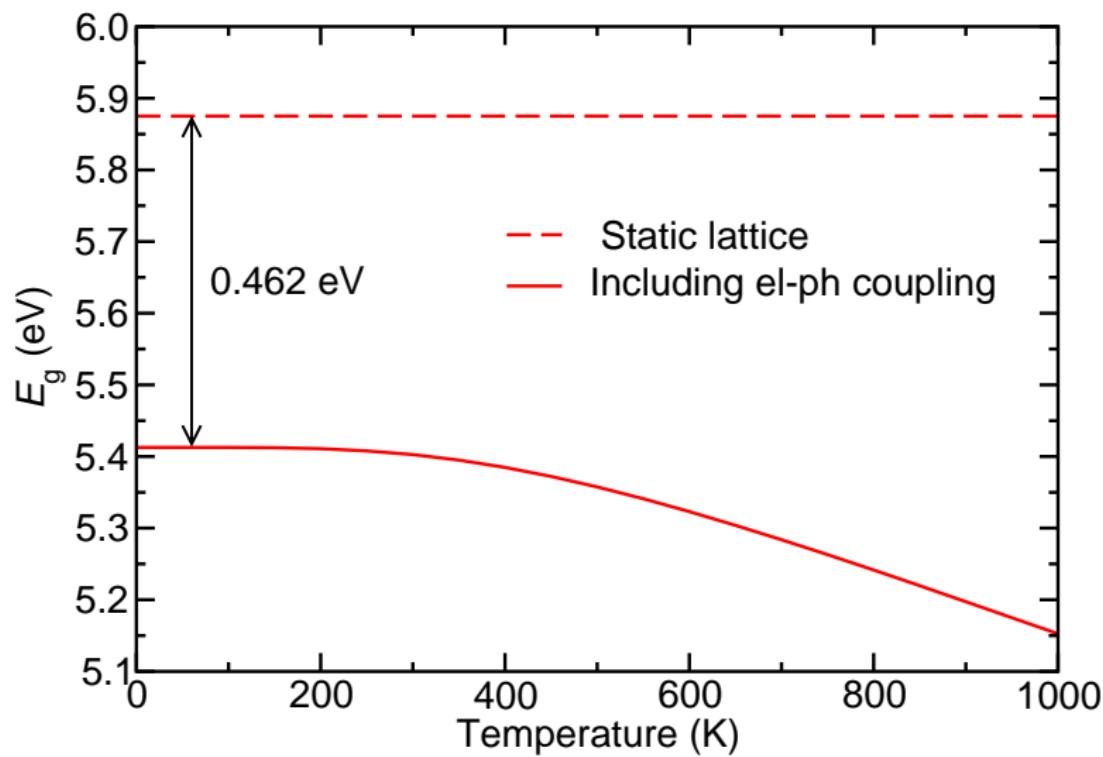
Band gap renormalization

- ▶ Band gap problem (LDA, PBE, ...): underestimation of gaps.
- ▶ Caused by the lack of a discontinuity in approximate xc -functionals with respect to particle number: correction Δ_{xc} to band gap.
- ▶ Approximate systematic shift in *all* displaced configurations.
- ▶ Error disappears in *change* in band gap.

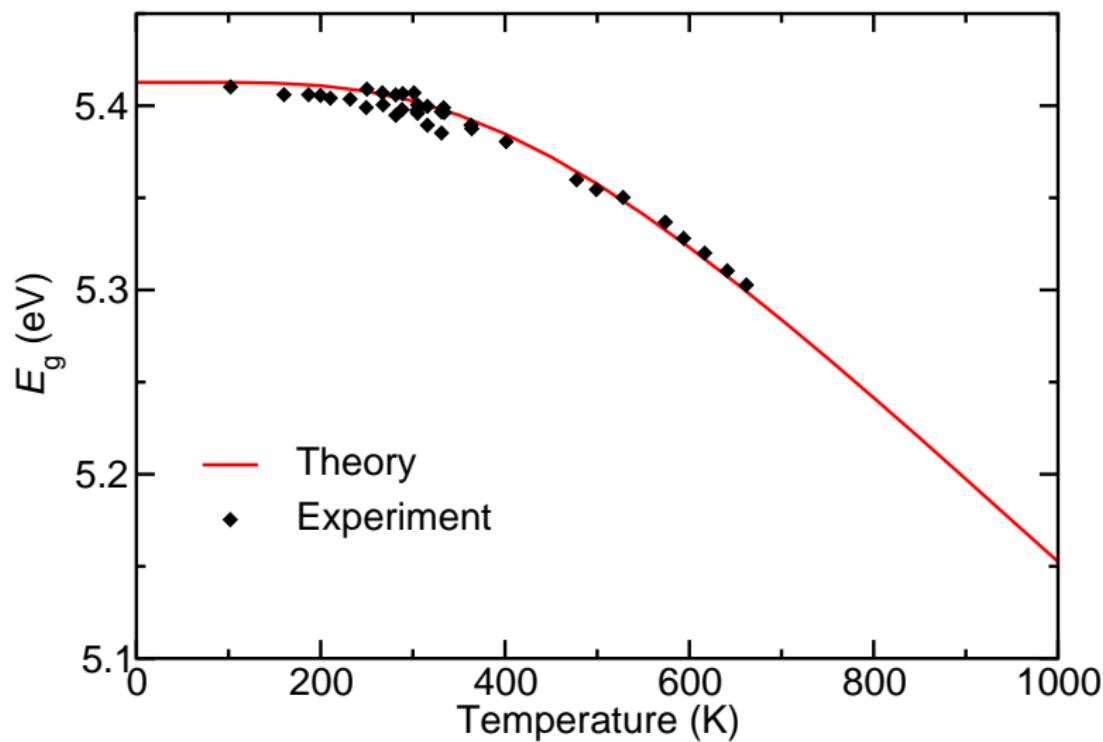
Diamond thermal band gap (I)



Diamond thermal band gap (II)



Diamond thermal band gap (III)



Experimental data from Proc. R. Soc. London, Ser. A **277**, 312 (1964)

Thermal expansion (I)

- ▶ Gibbs free energy:

$$dG = dF_{el} + dF_{vib} - \Omega \sum_{i,j} \sigma_{ij}^{\text{ext}} d\epsilon_{ij}$$

- ▶ Vibrational stress:

$$dF_{vib} = -\Omega \sum_{i,j} \sigma_{ij}^{\text{vib}} d\epsilon_{ij}$$

- ▶ Effective stress:

$$dG = dF_{el} - \Omega \sum_{i,j} \sigma_{ij}^{\text{eff}} d\epsilon_{ij}$$

where $\sigma_{ij}^{\text{eff}} = \sigma_{ij}^{\text{ext}} + \sigma_{ij}^{\text{vib}}$.

Thermal expansion (II)

- ▶ Potential part of vibrational stress tensor:

$$\sigma_{ij}^{\text{vib},V} = \langle \Phi(\mathbf{Q}) | \sigma_{ij}^{\text{el}} | \Phi(\mathbf{Q}) \rangle$$

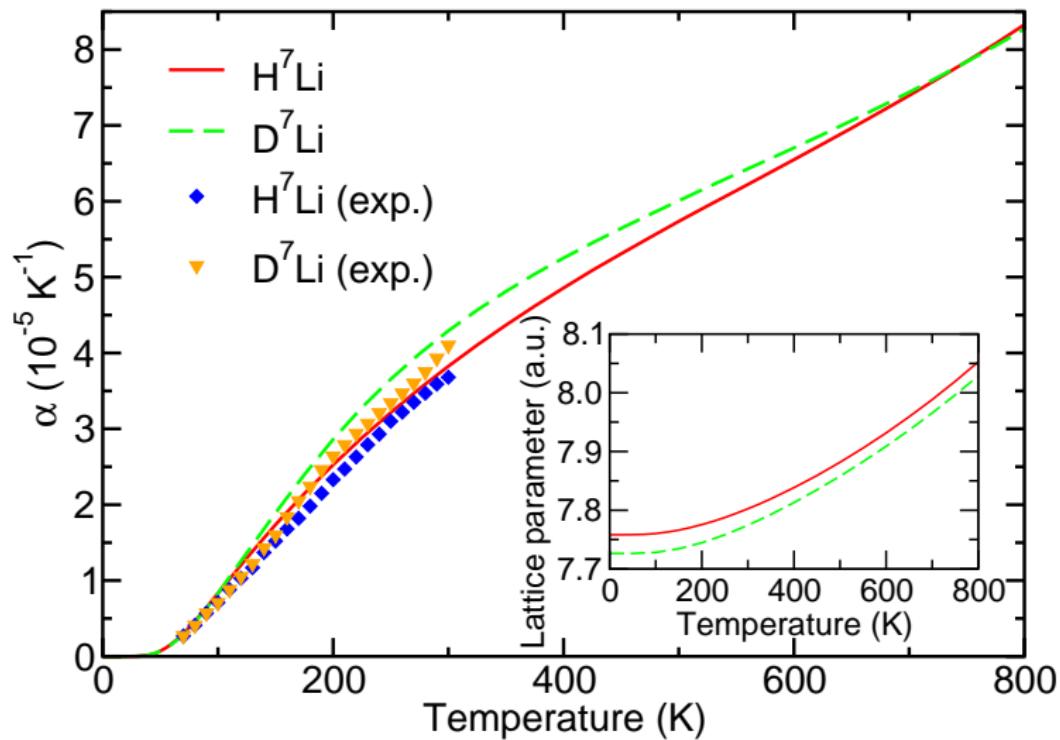
- ▶ Kinetic part of vibrational stress tensor:

$$\sigma_{ij}^{\text{vib},T} = -\frac{1}{\Omega} \left\langle \Phi \left| \sum_{\mathbf{R}_p, \alpha} m_\alpha \dot{u}_{p\alpha;i} \dot{u}_{p\alpha;j} \right| \Phi \right\rangle$$

- ▶ Total vibrational stress tensor:

$$\sigma_{ij}^{\text{vib}} = \sigma_{ij}^{\text{vib},V} + \sigma_{ij}^{\text{vib},T}$$

LiH and LiD thermal expansion coefficient



Experimental data from J. Phys. C **15**, 6321 (1982)

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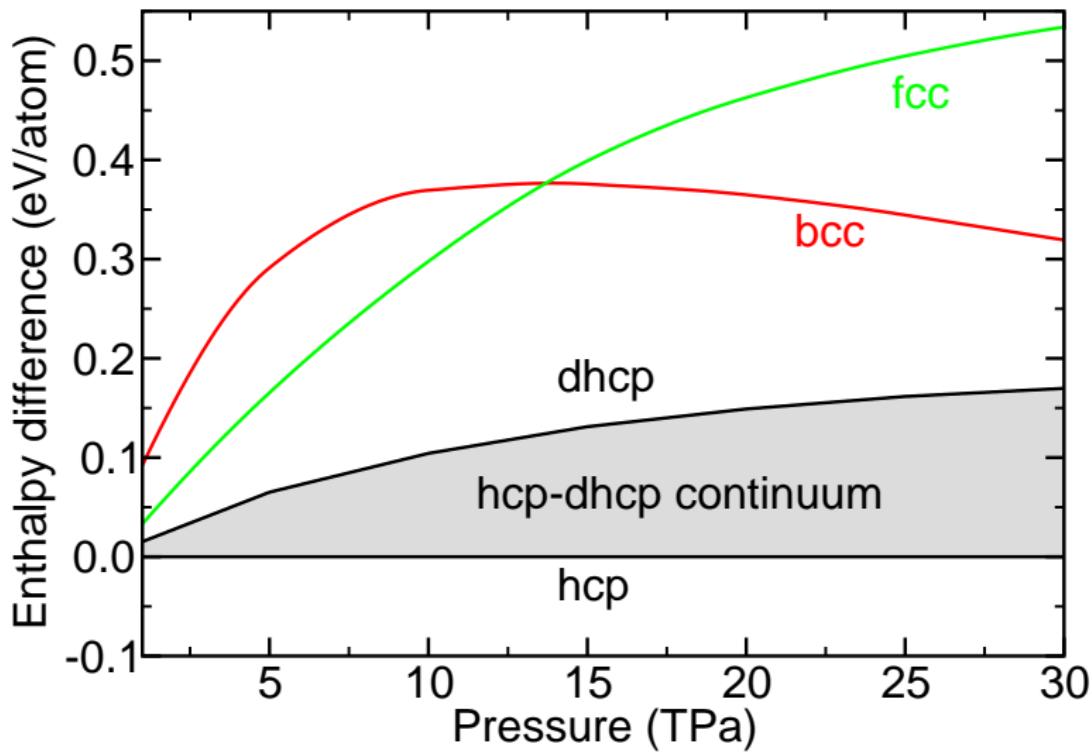
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Phonon expectation values

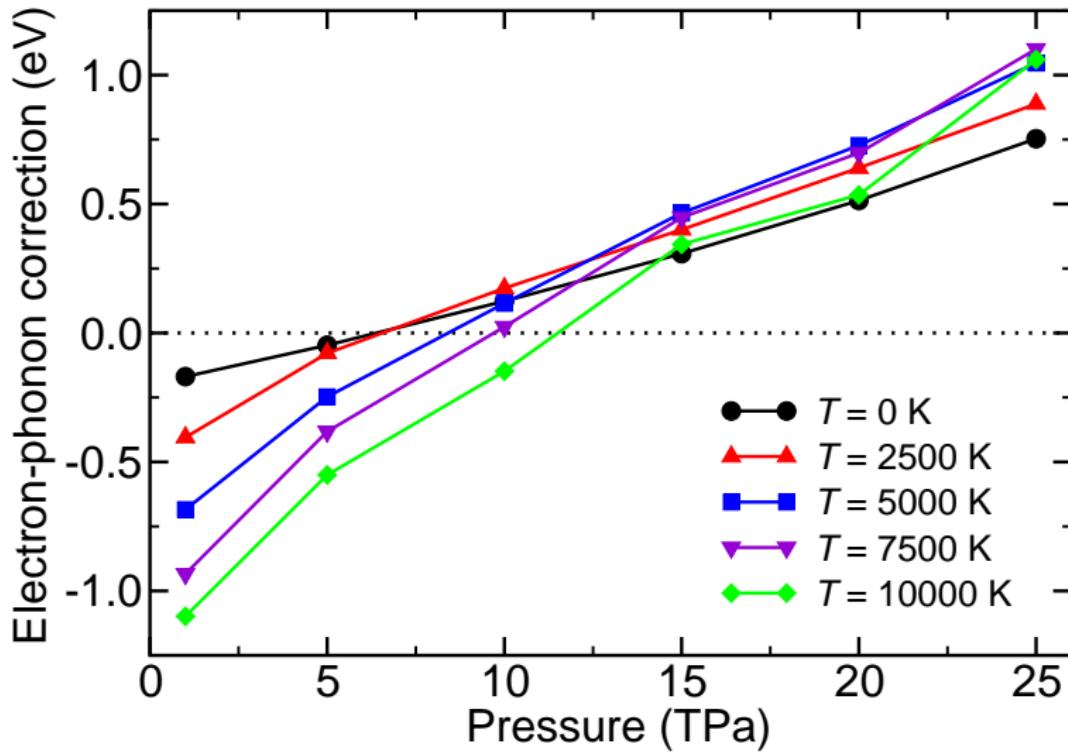
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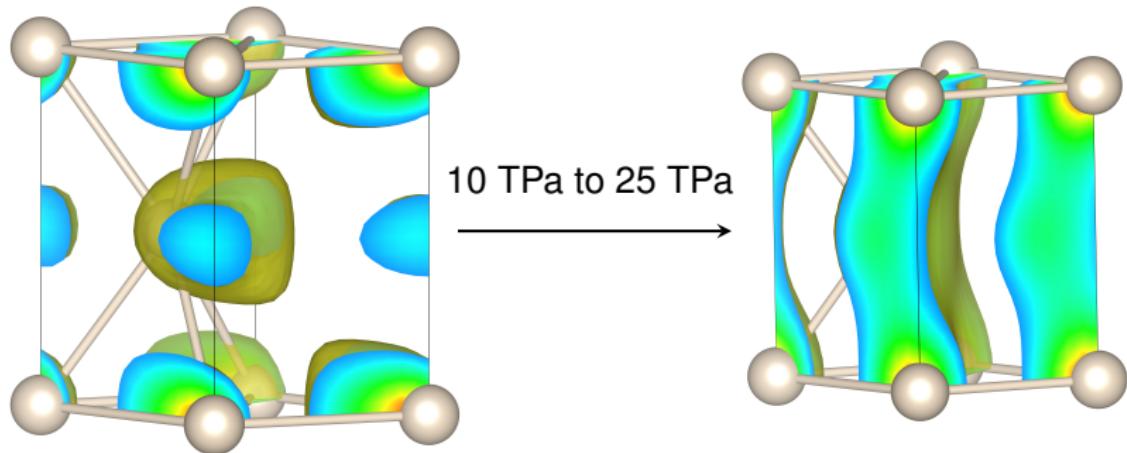
Solid helium structural phase diagram



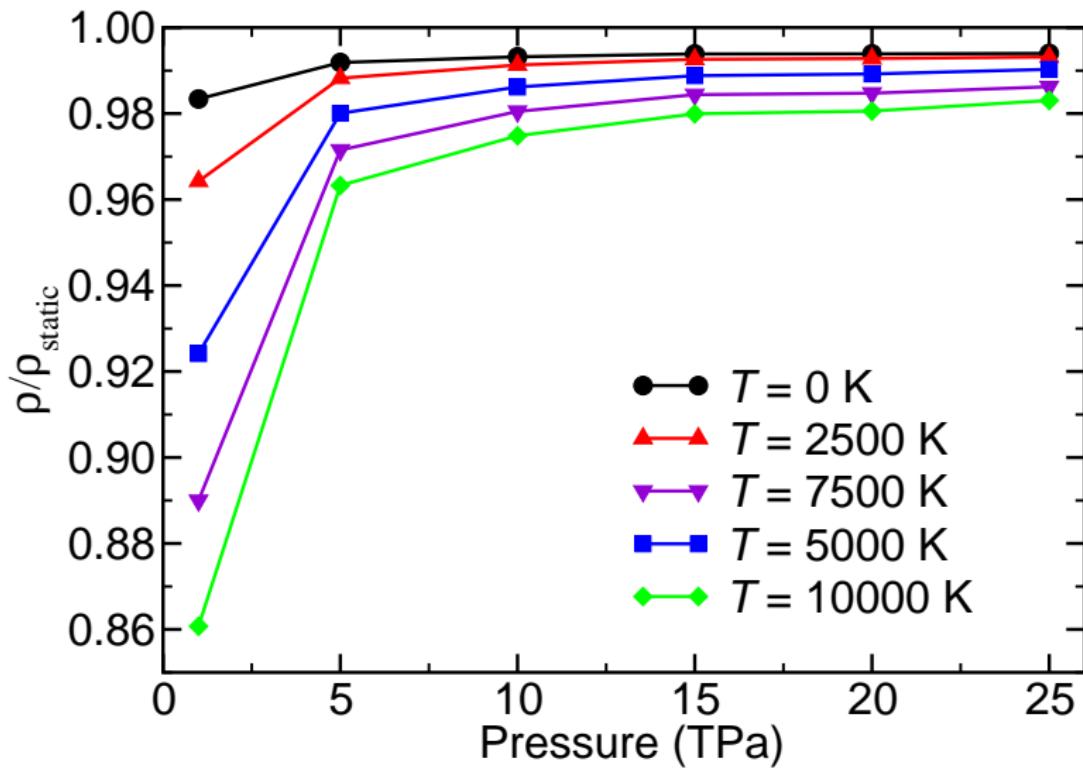
Solid helium electron-phonon gap correction (I)



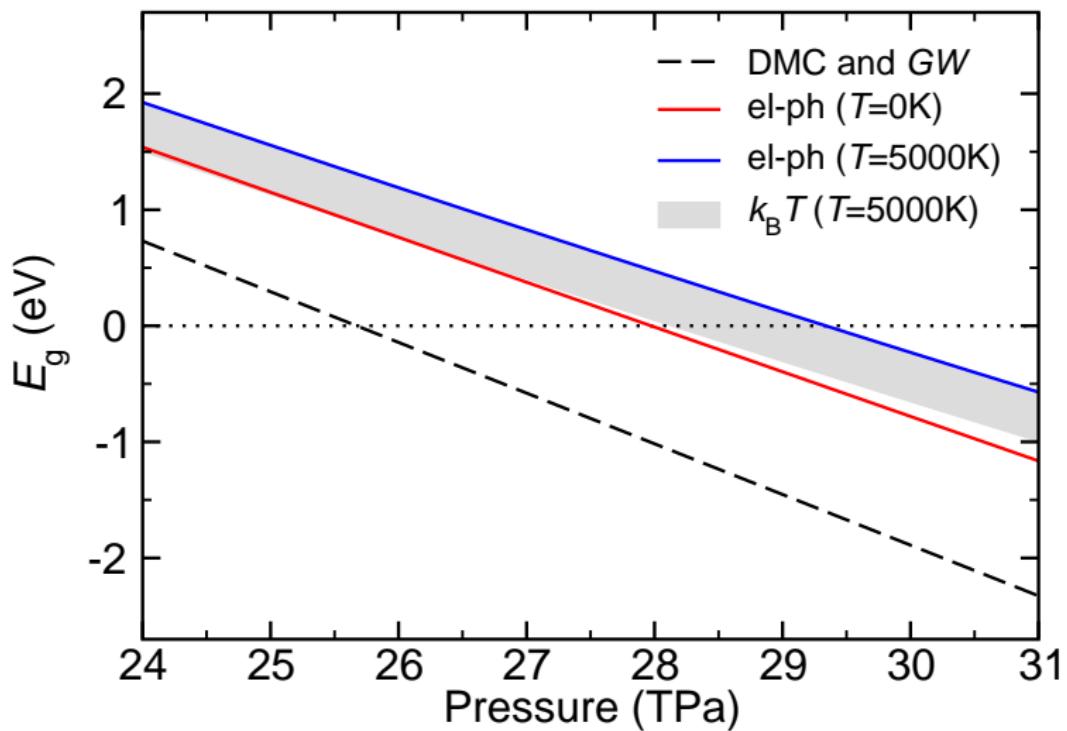
Solid helium electron-phonon gap correction (II)



Solid helium equilibrium density

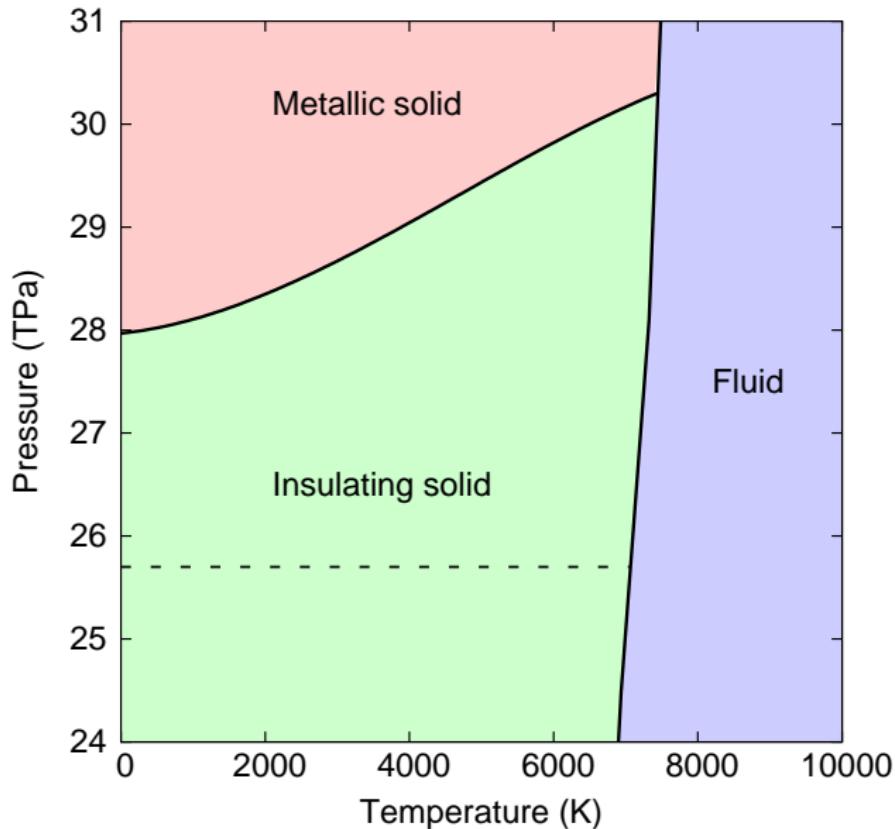


Solid helium metallization pressure



DMC and GW from PRL **101**, 106407 (2008)

Helium phase diagram revisited



White dwarf cooling revisited: metallization of solid helium

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Conclusions

- ▶ Theory for anharmonic vibrational energy of solids.
- ▶ General framework for phonon-dependent expectation values.
- ▶ Metallization of solid helium.
- ▶ White dwarf energy transport and cooling.

- ▶ Acknowledgements:
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 - ▶ Dr Neil D. Drummond
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 - ▶ Prof. Chris J. Pickard
 - ▶ TCM group
 - ▶ EPSRC

- ▶ References:
 - ▶ B. Monserrat, N.D. Drummond, R.J. Needs
Physical Review B **87**, 144302 (2013)
 - ▶ B. Monserrat, N.D. Drummond, C.J. Pickard, R.J. Needs
Helium paper, in preparation (2013)