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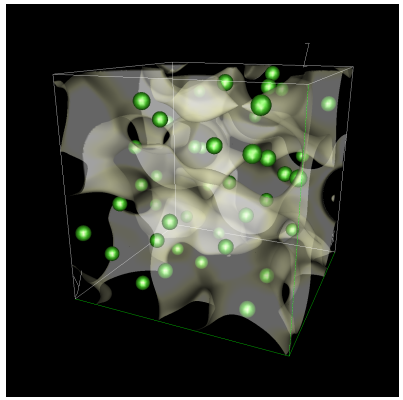
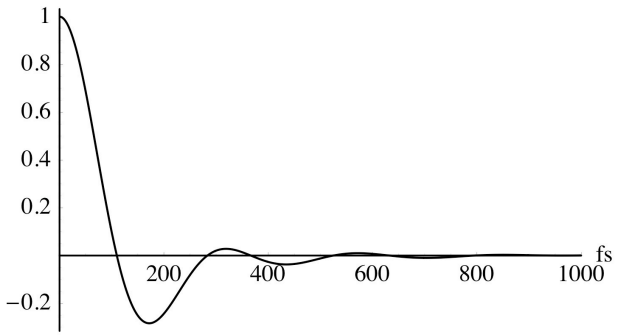
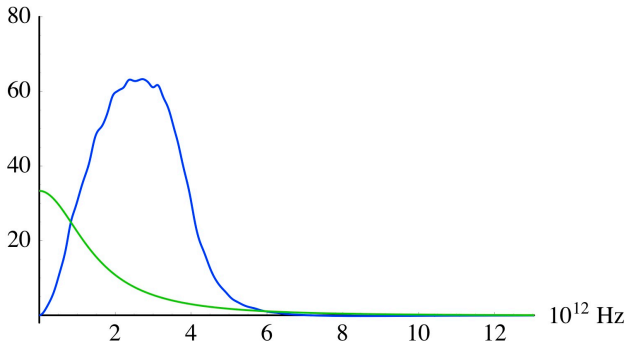
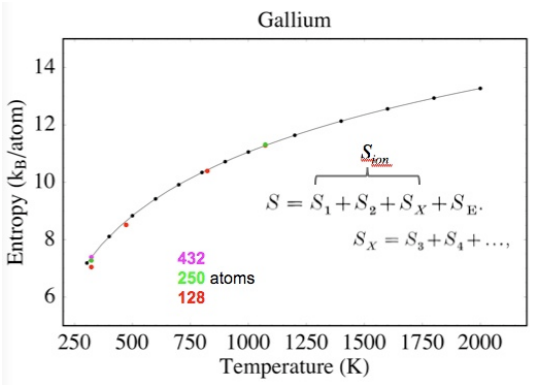






First-principles entropy calculations for liquid metals



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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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The calculation of entropy or free energy is a longstanding problem in molecular dynamics

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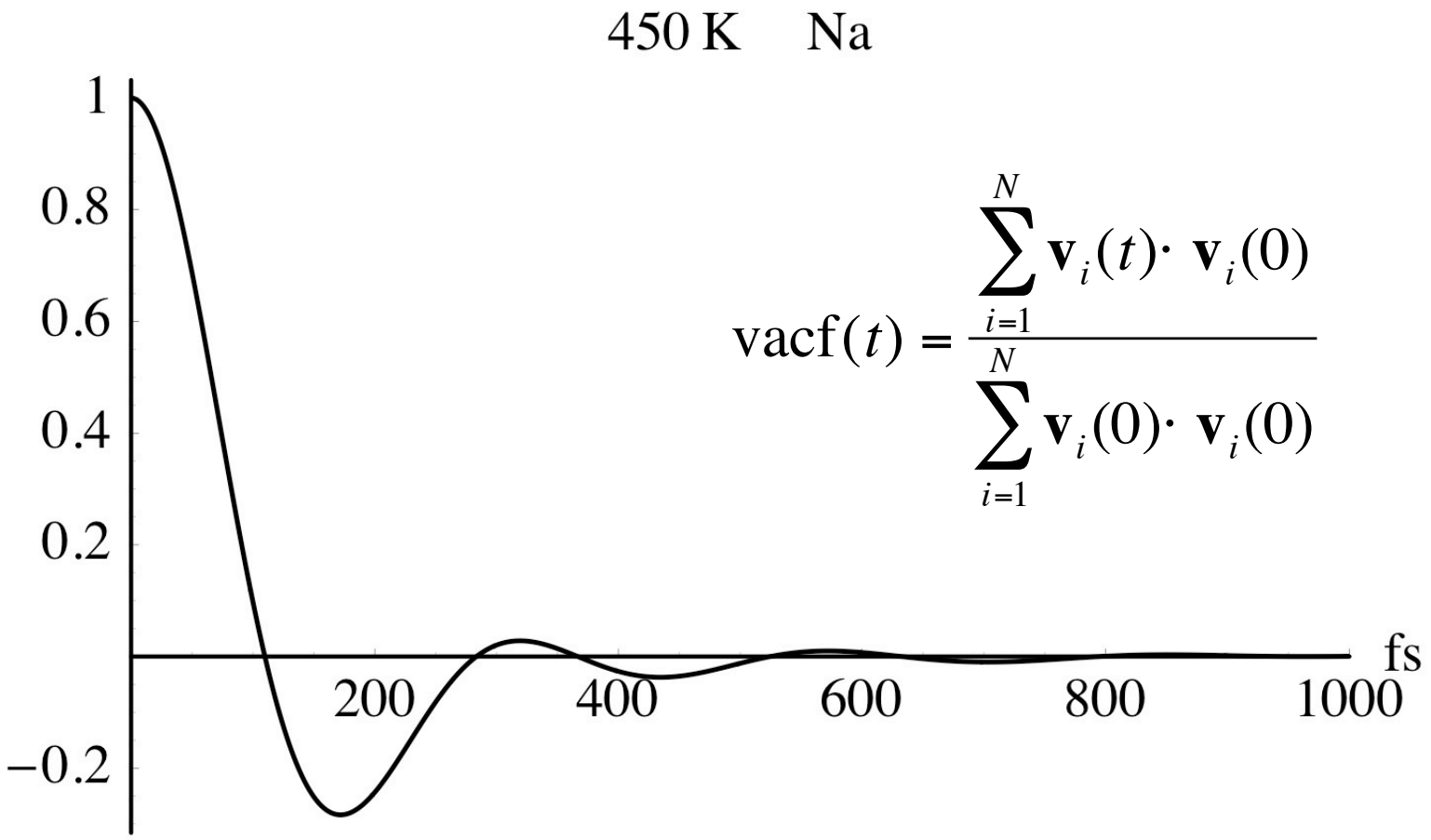
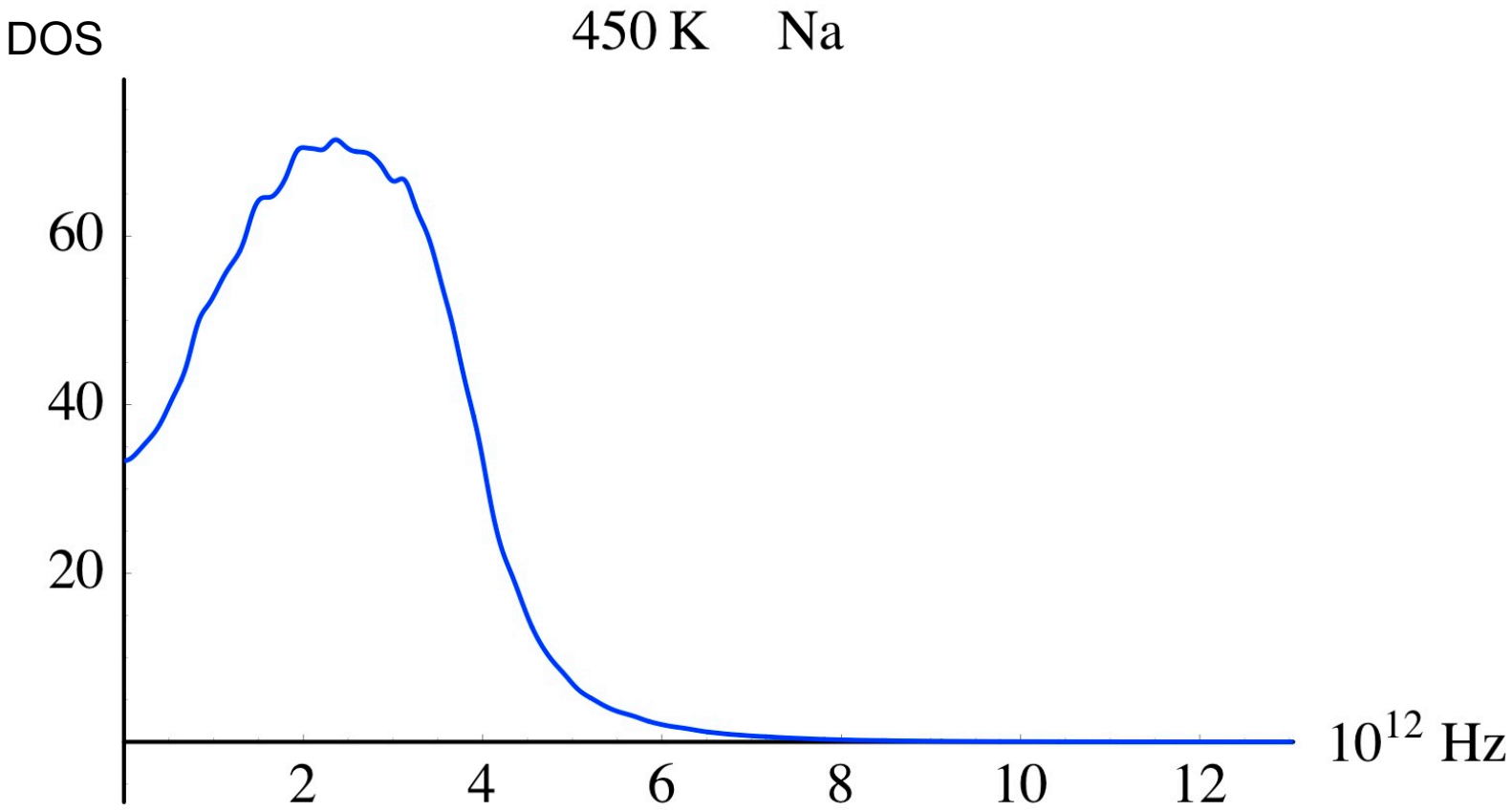
- Energy and Pressure are explicitly calculated in first-principles molecular dynamics codes
- Entropy is an implicit thermodynamic quantity, difficult to access
- This makes the computation of free energies or phase boundaries very time consuming (e.g. thermodynamic integration or coexistence of phase simulations)
- The two-phase method, introduced at Cal Tech, provides an interesting approach to calculating entropies for liquids

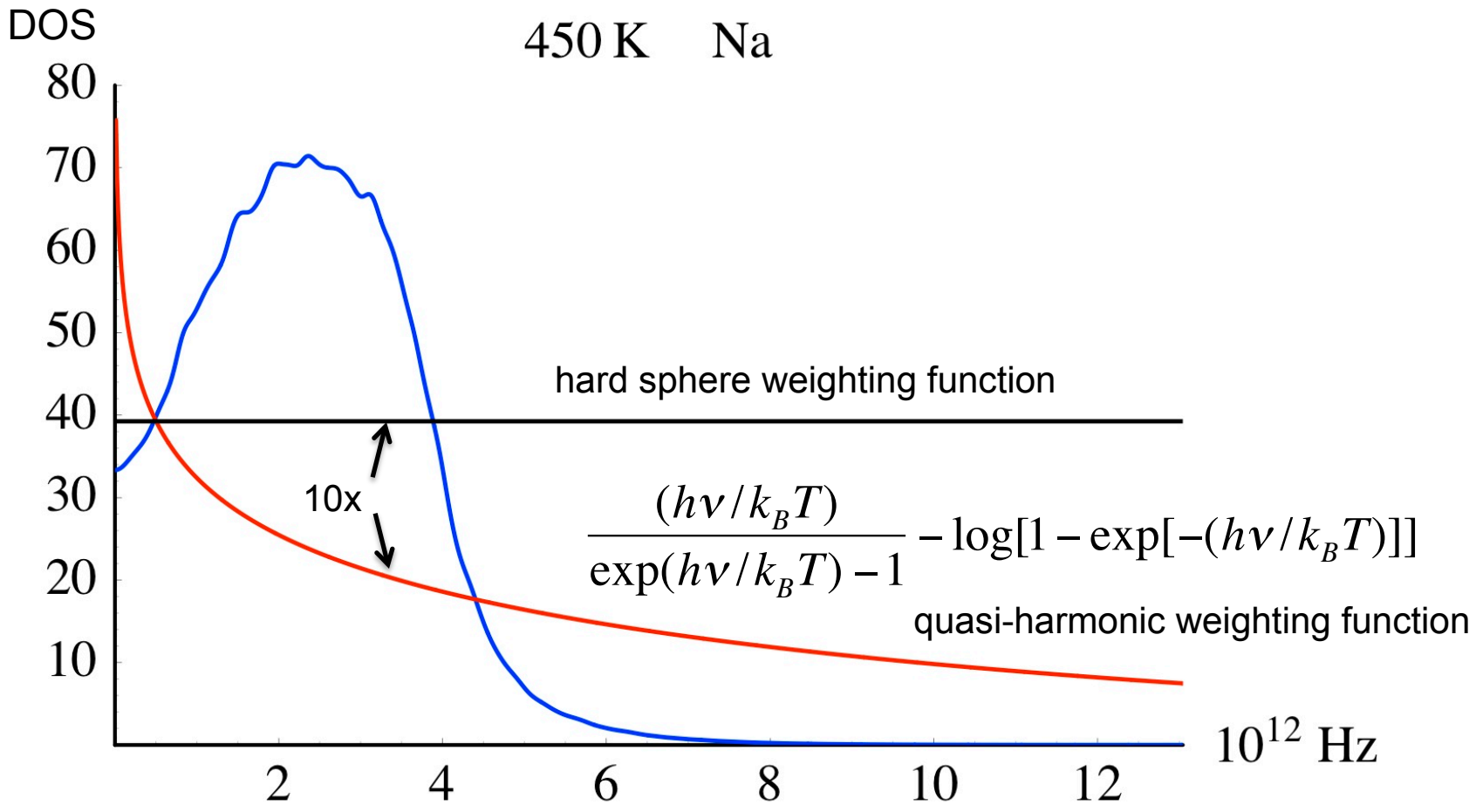
We compute the velocity autocorrelation function from the *ab initio* molecular dynamics



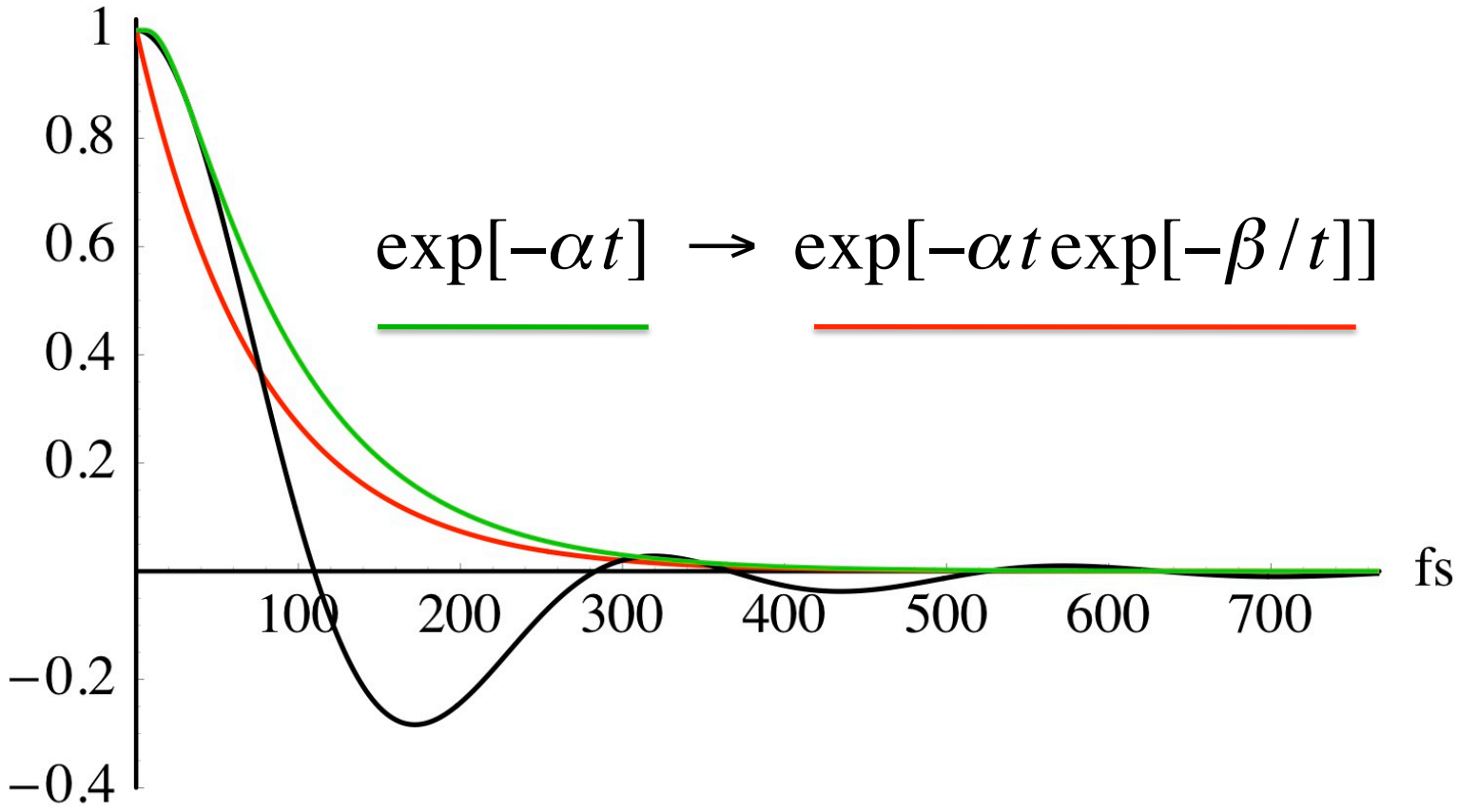
The Fourier transform of the autocorrelation function gives the mode spectrum density of states (DOS)



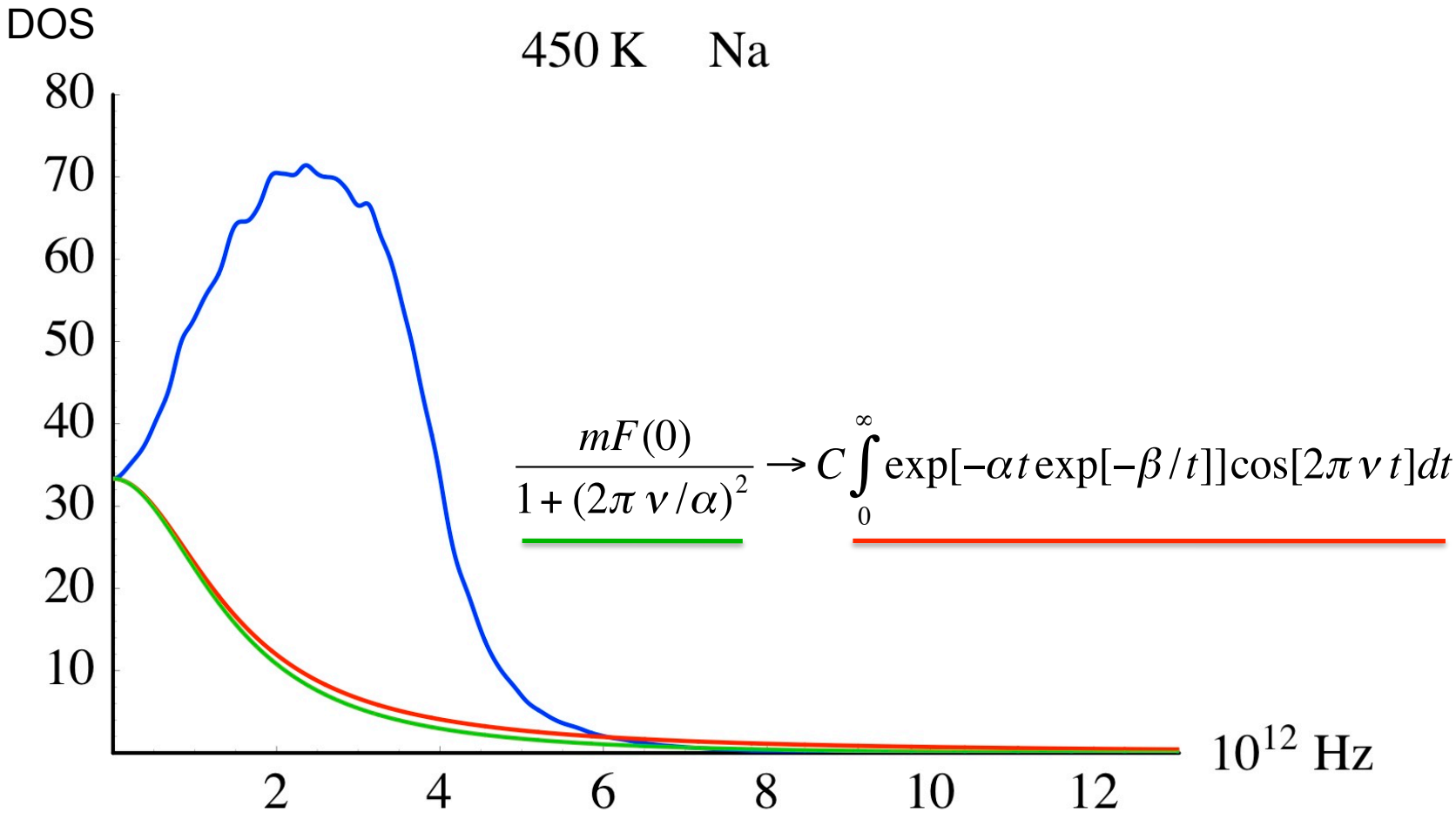
The quasi-harmonic weighting function diverges logarithmically at zero frequency



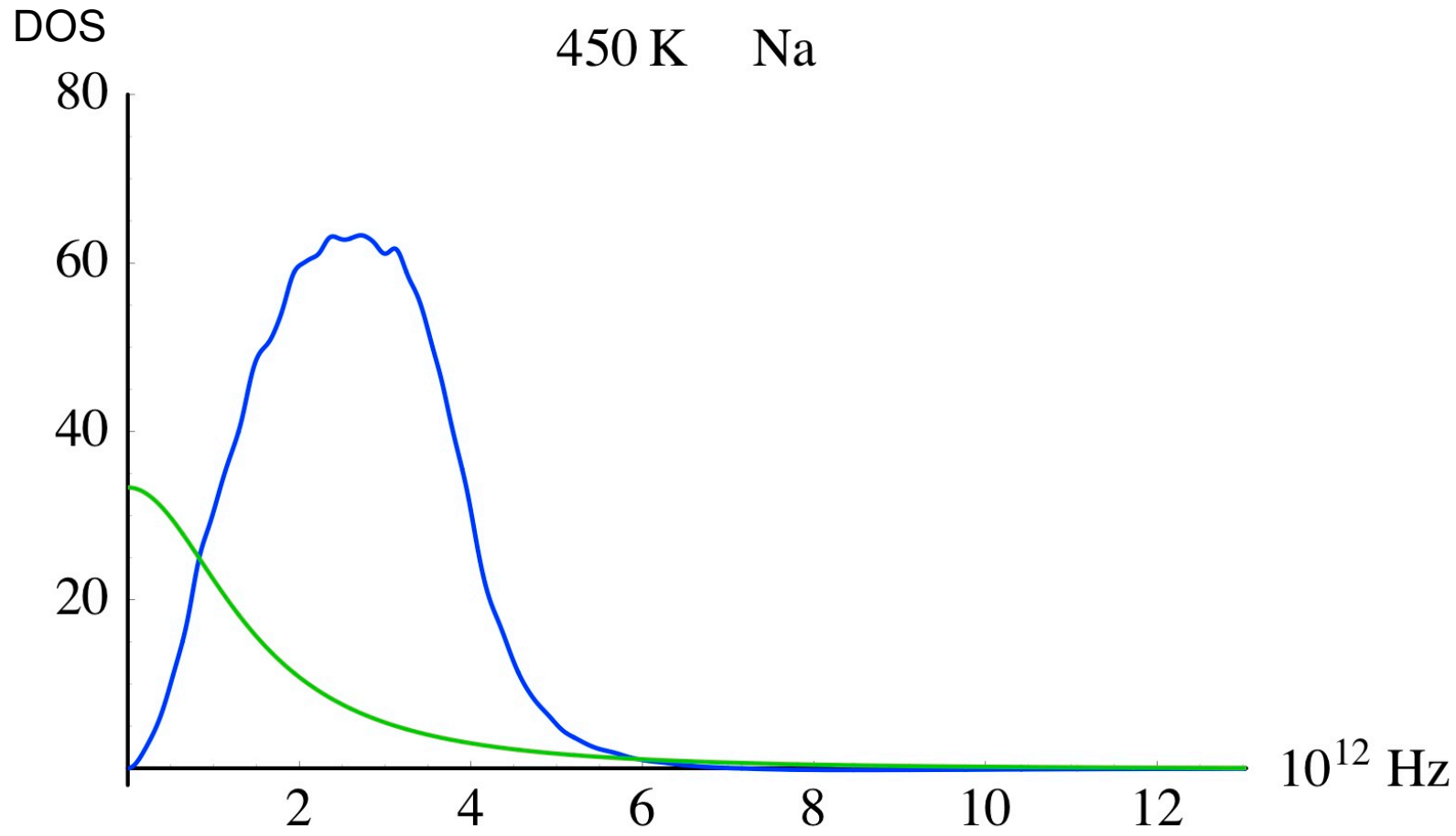
We use a quasi hard sphere autocorrelation that preserves the observed short time coherence



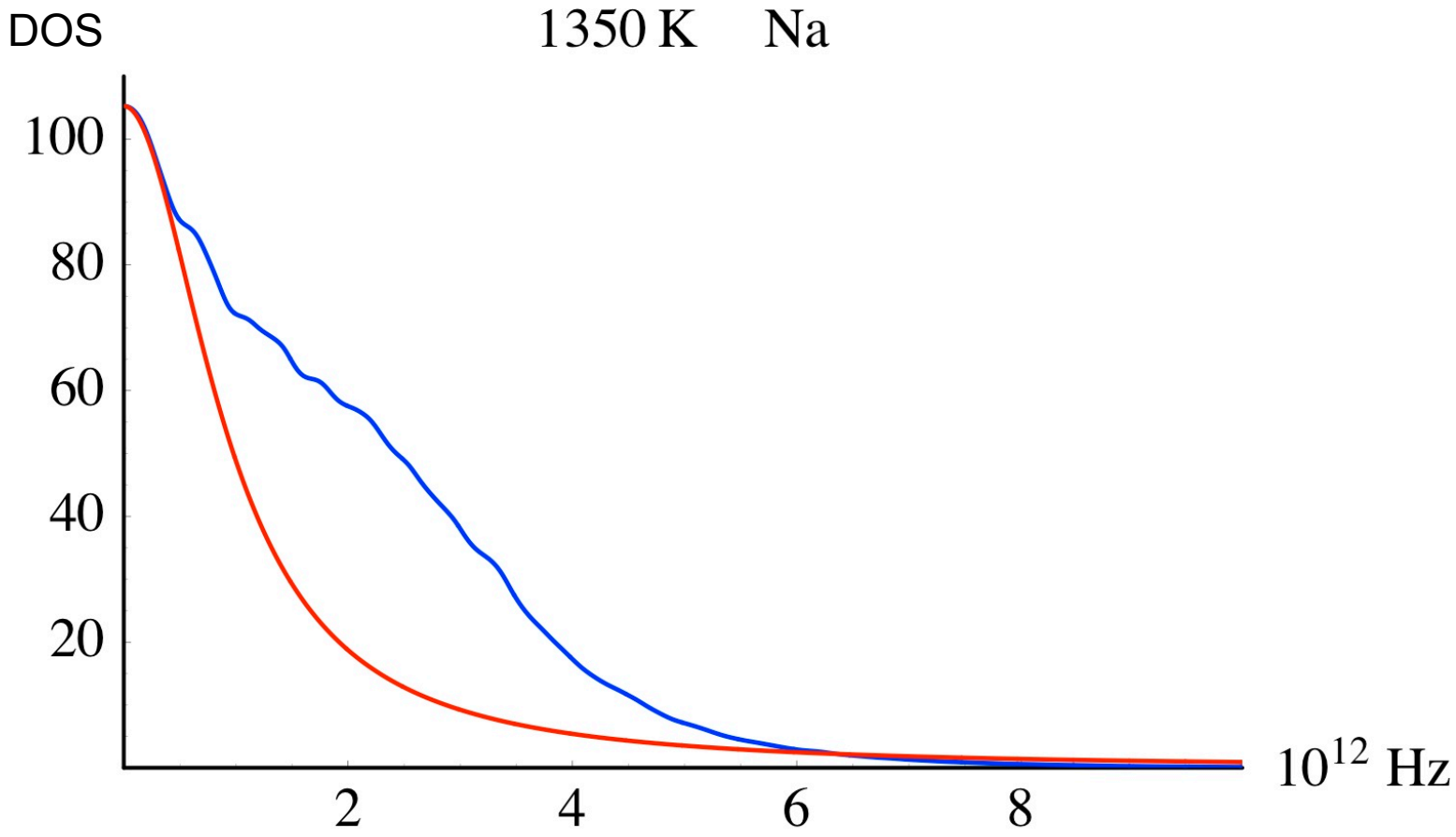
This removes the excess entropy associated with the high frequency tail



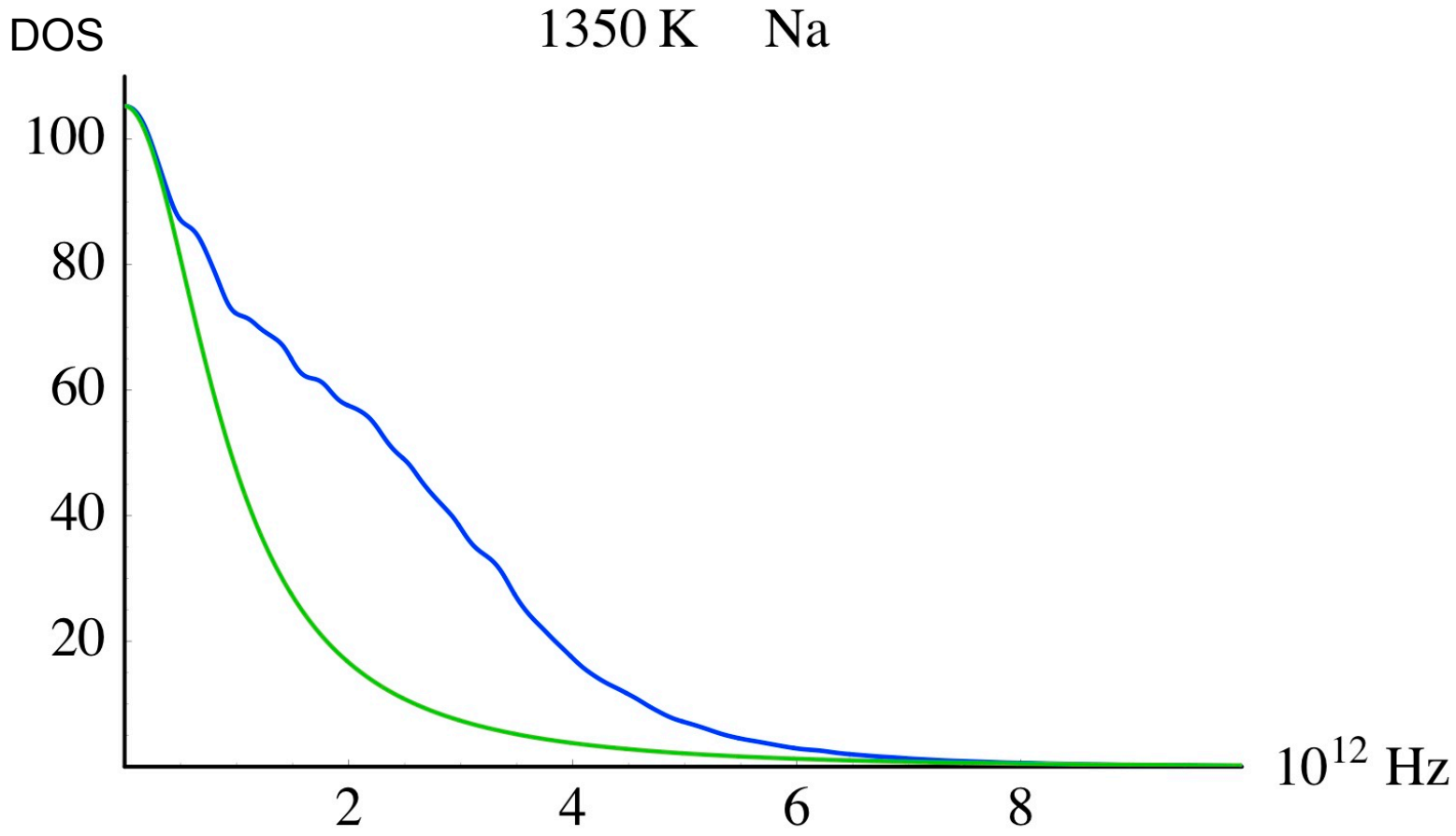
The mode spectrum is decomposed into a quasi-harmonic and an anharmonic (diffusive) component



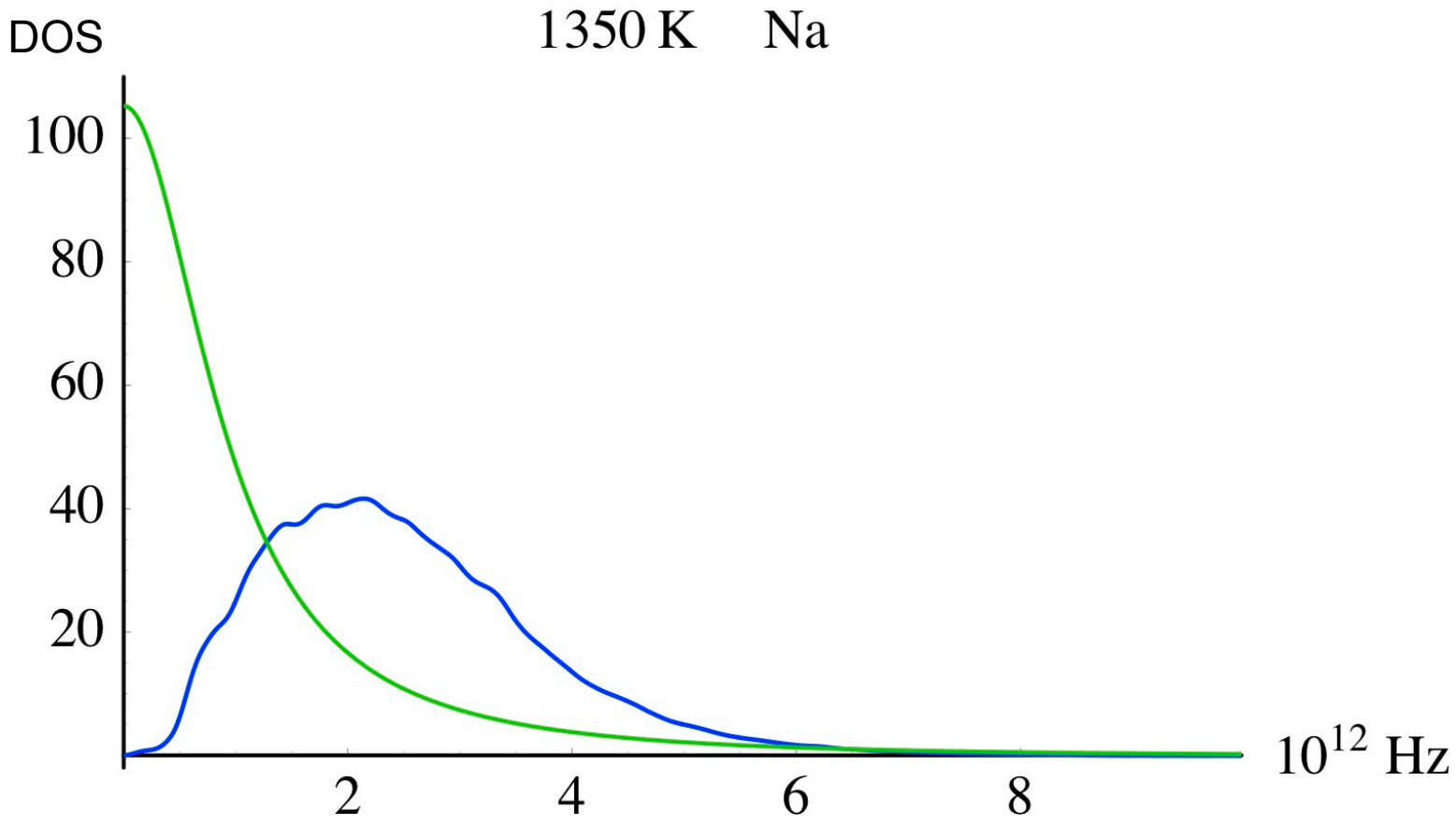
Similarly, for 1350 K, the hard sphere component generates a high entropy tail



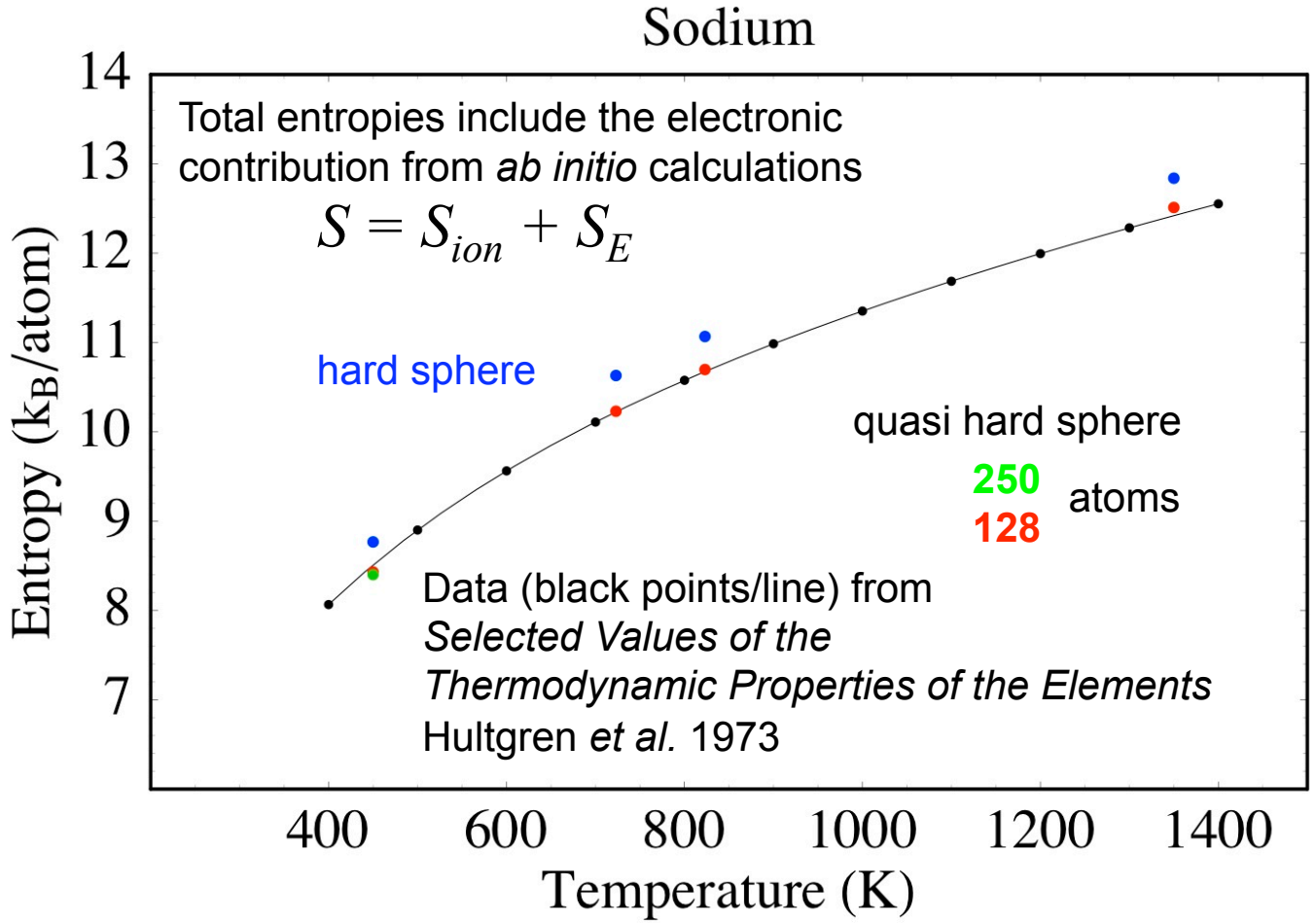
The quasi-hard-sphere treatment corrects the excessive high frequency tail



The anharmonic or diffusive component is much larger at 1350 K

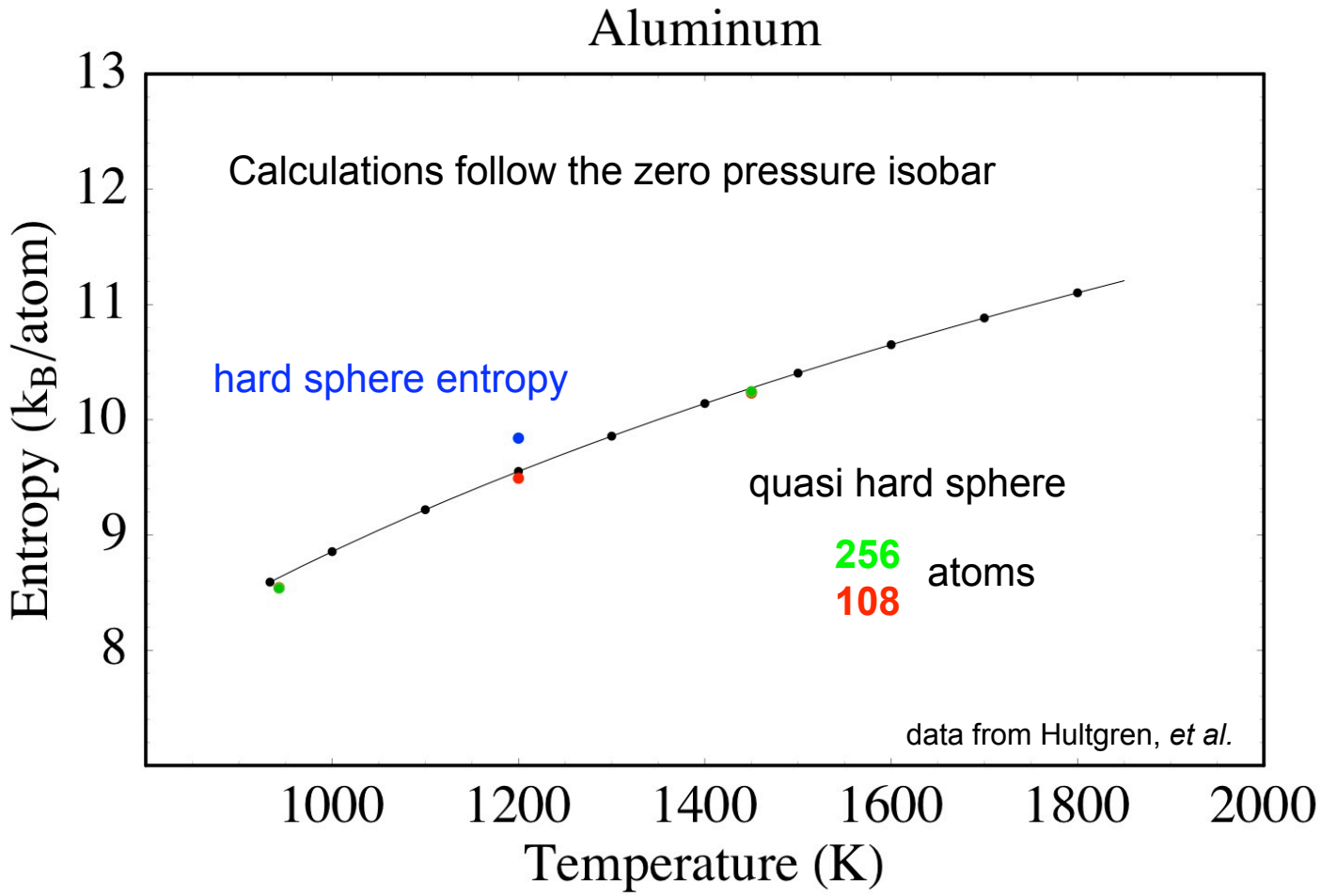


The calculated entropies agree with data to within ~ 1% with the quasi hard sphere treatment

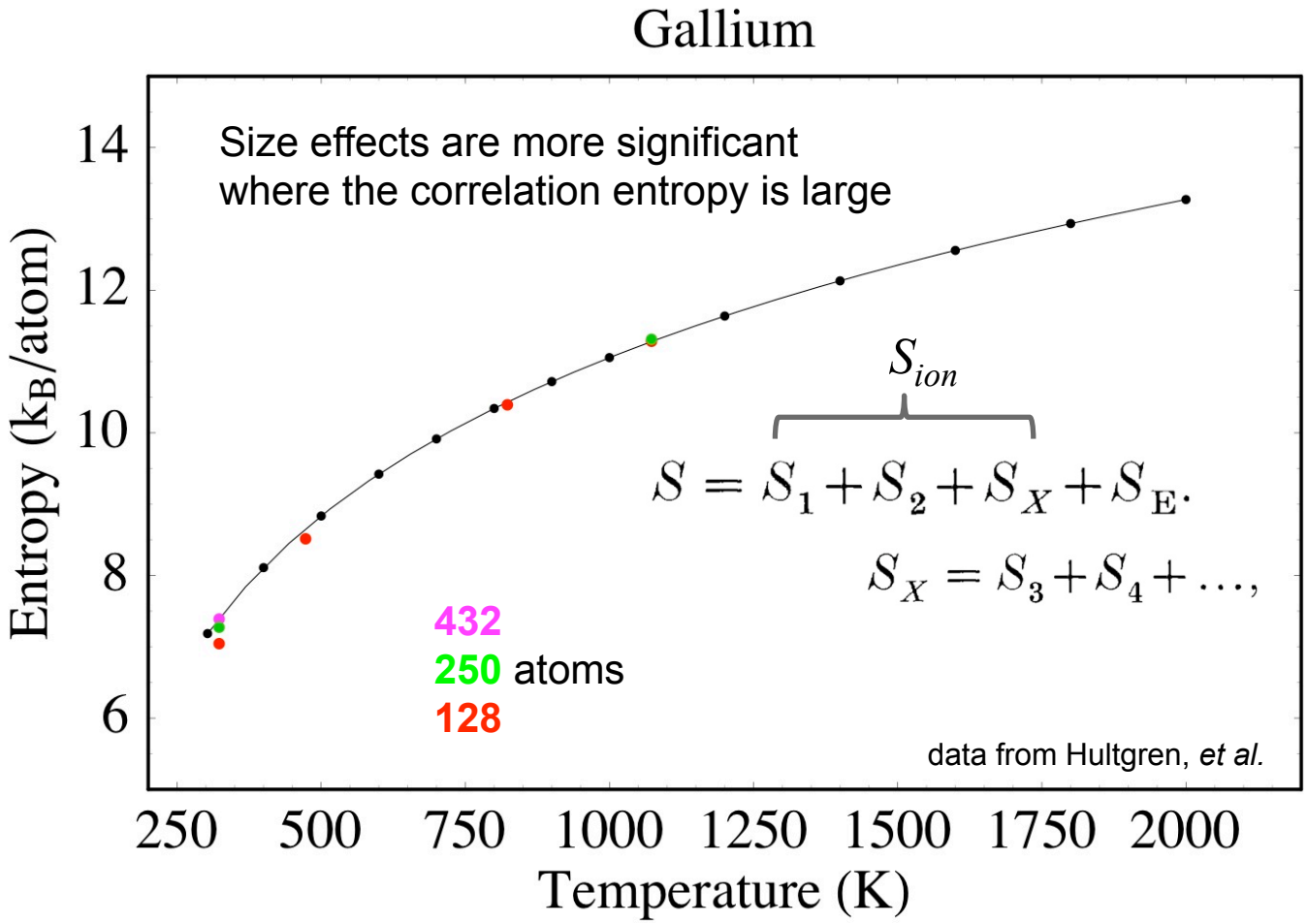


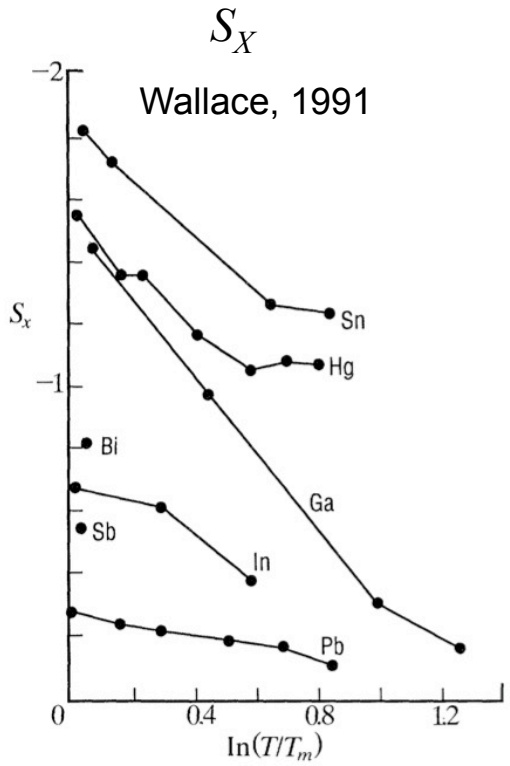
Symbol widths for calculations represent ~ 1%

We find similarly good results for aluminum



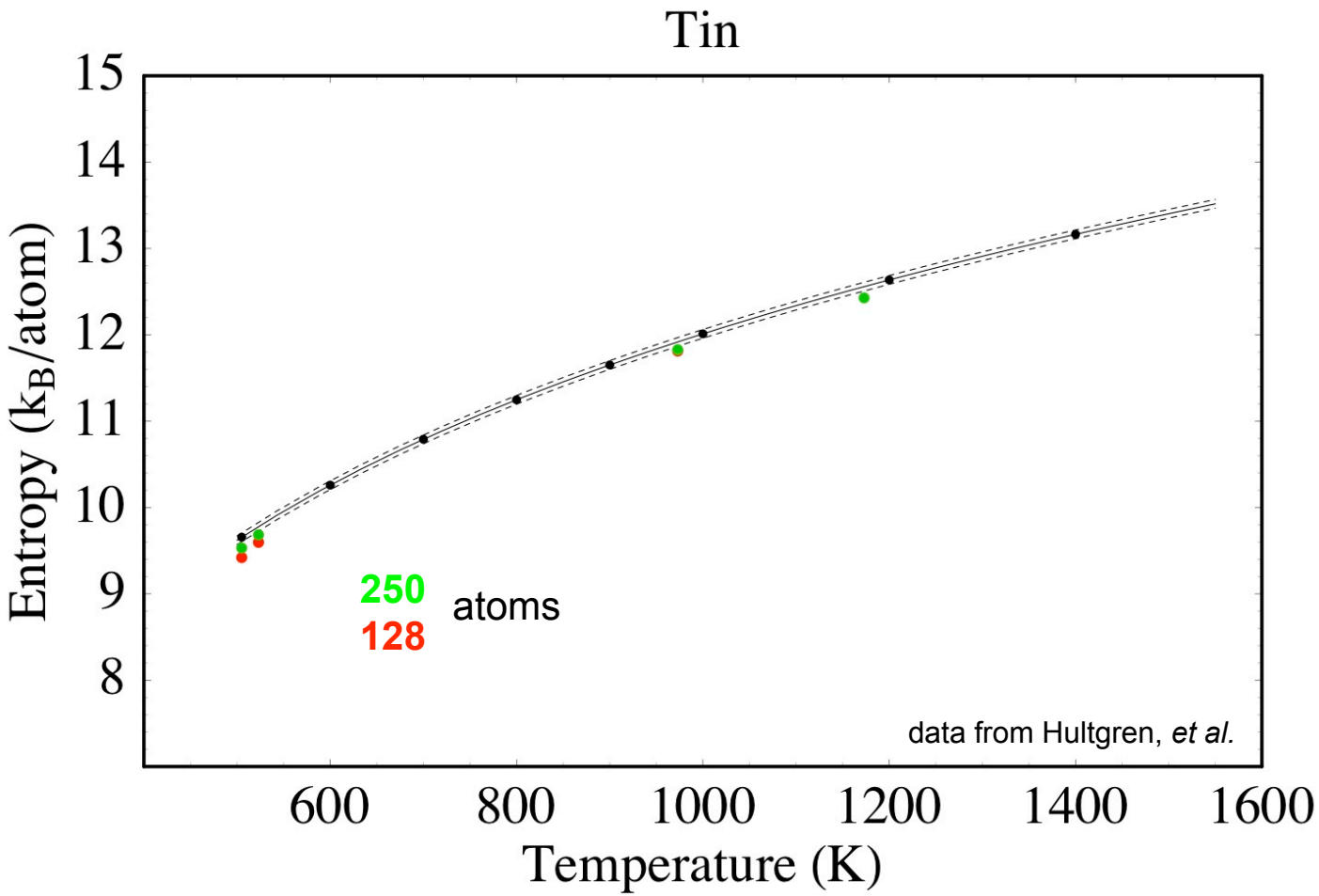
Gallium has very high correlation entropy near melt*



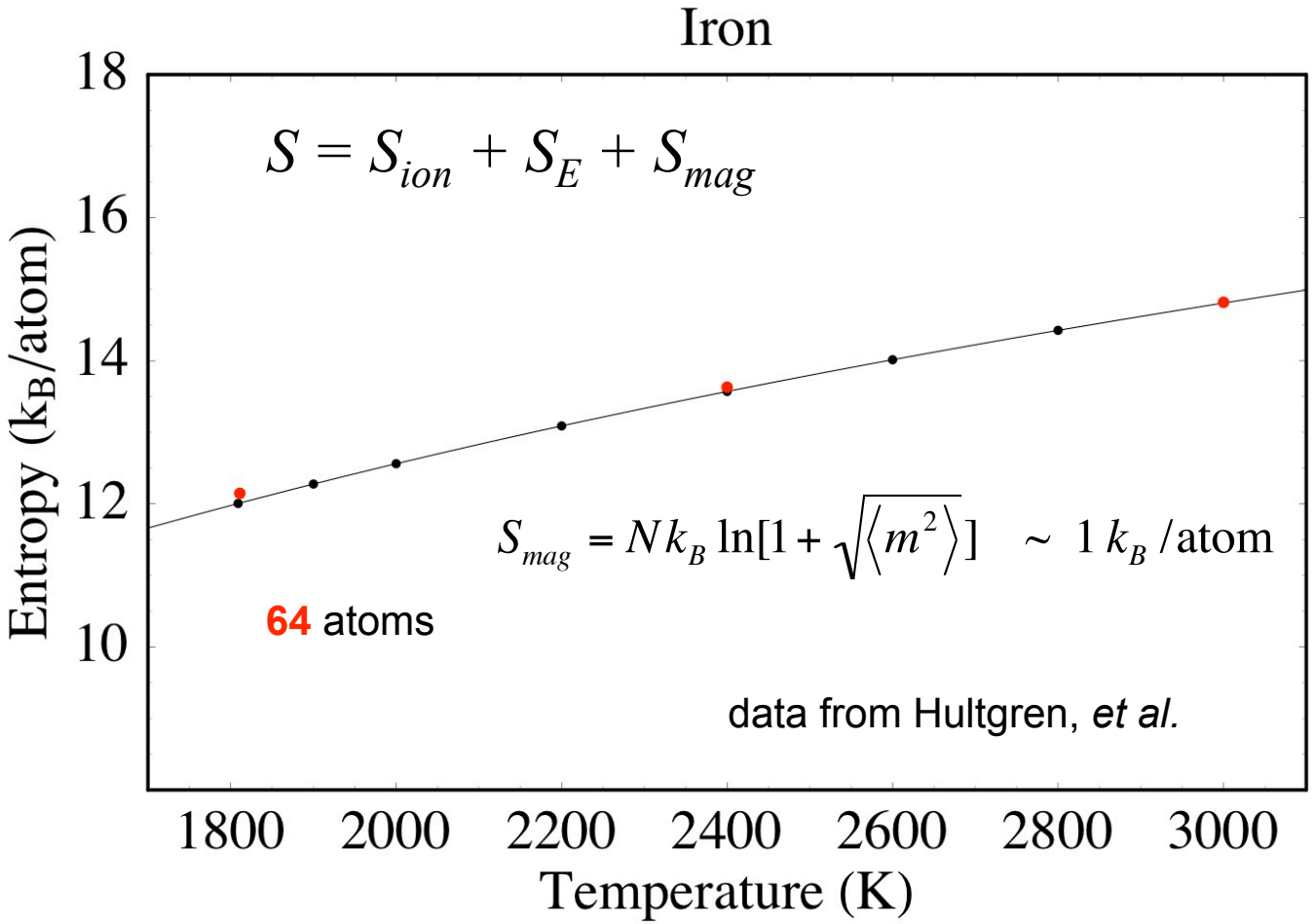


* Wallace, *Entropy of Liquid Metals*, Proc. R. Soc. Lond. A (1991) **433**, 615-630

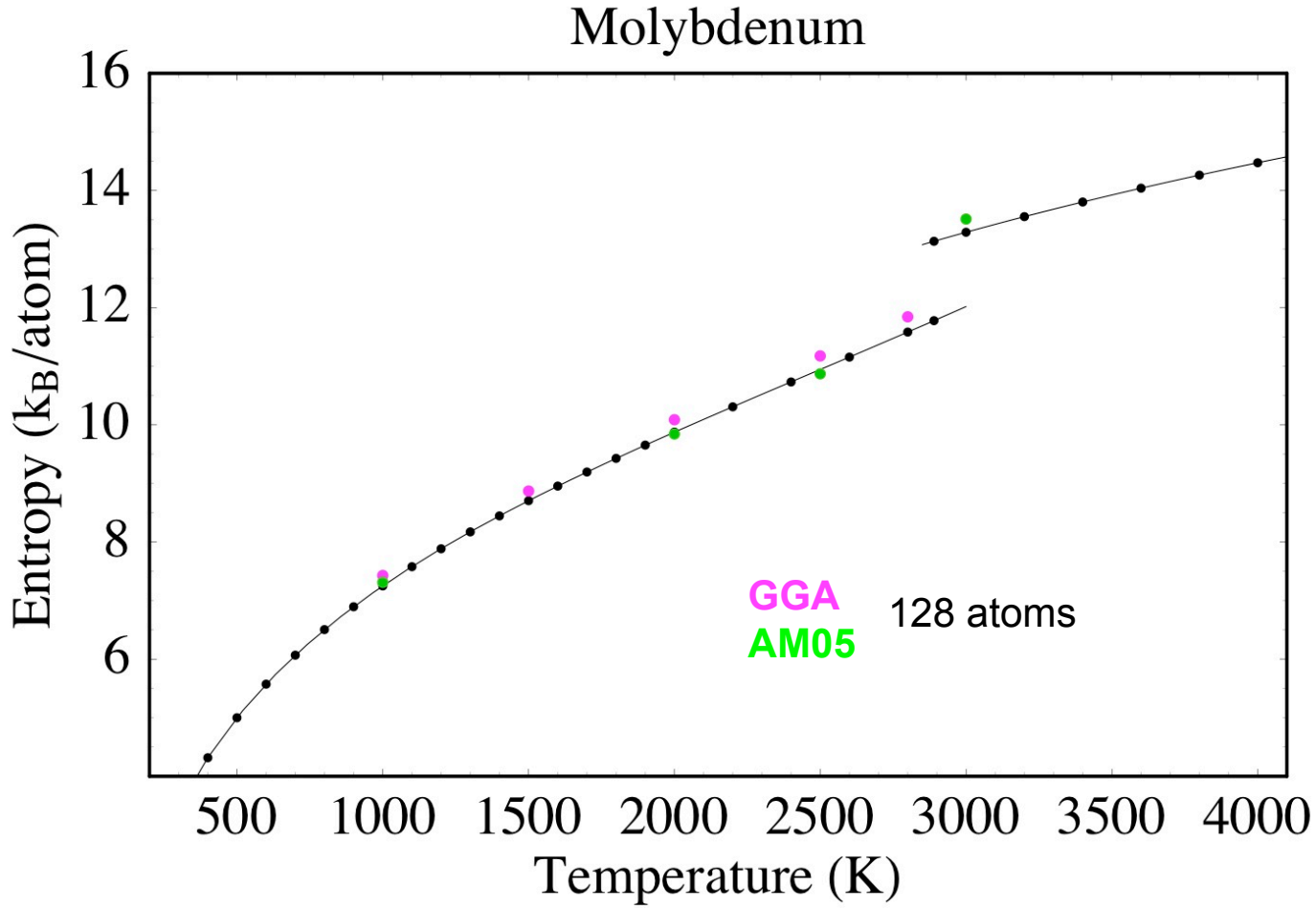
Tin also has high correlation entropy



Accurate treatment of iron requires accounting for the magnetic entropy due to spin fluctuations in the liquid



Despite molybdenum's reportedly high anharmonic entropy in the solid phase, the entropy is reproduced well



Summary

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- The two phase method of computing liquid entropies systematically overestimates the entropy for liquid metal
- A quasi hard sphere autocorrelation component, using only information from the total autocorrelation function, eliminates the source of the excess entropy
- The approach is validated against experimental data for several elements
- The calculation of free energies and phase boundaries is greatly simplified with this approach