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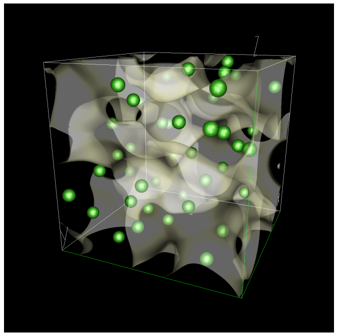
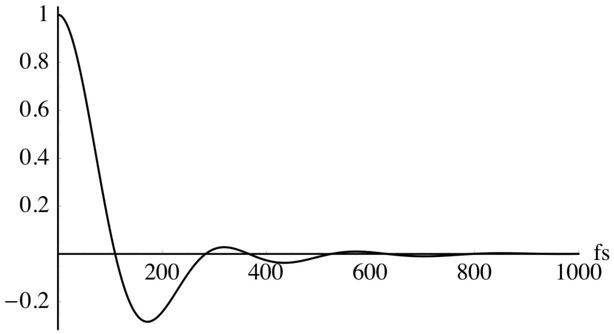
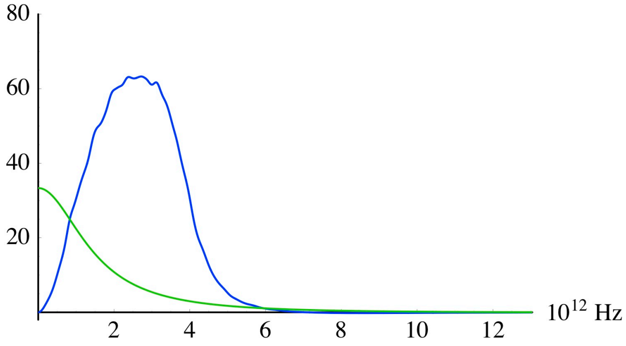
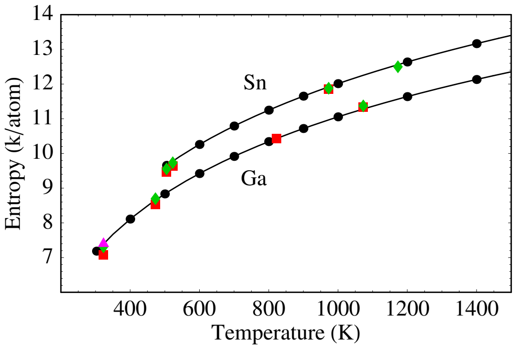






First-principles entropy calculations for liquid metals and warm dense matter



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SCCM/AIRAPT 2013 Seattle

U.S. DEPARTMENT OF ENERGY

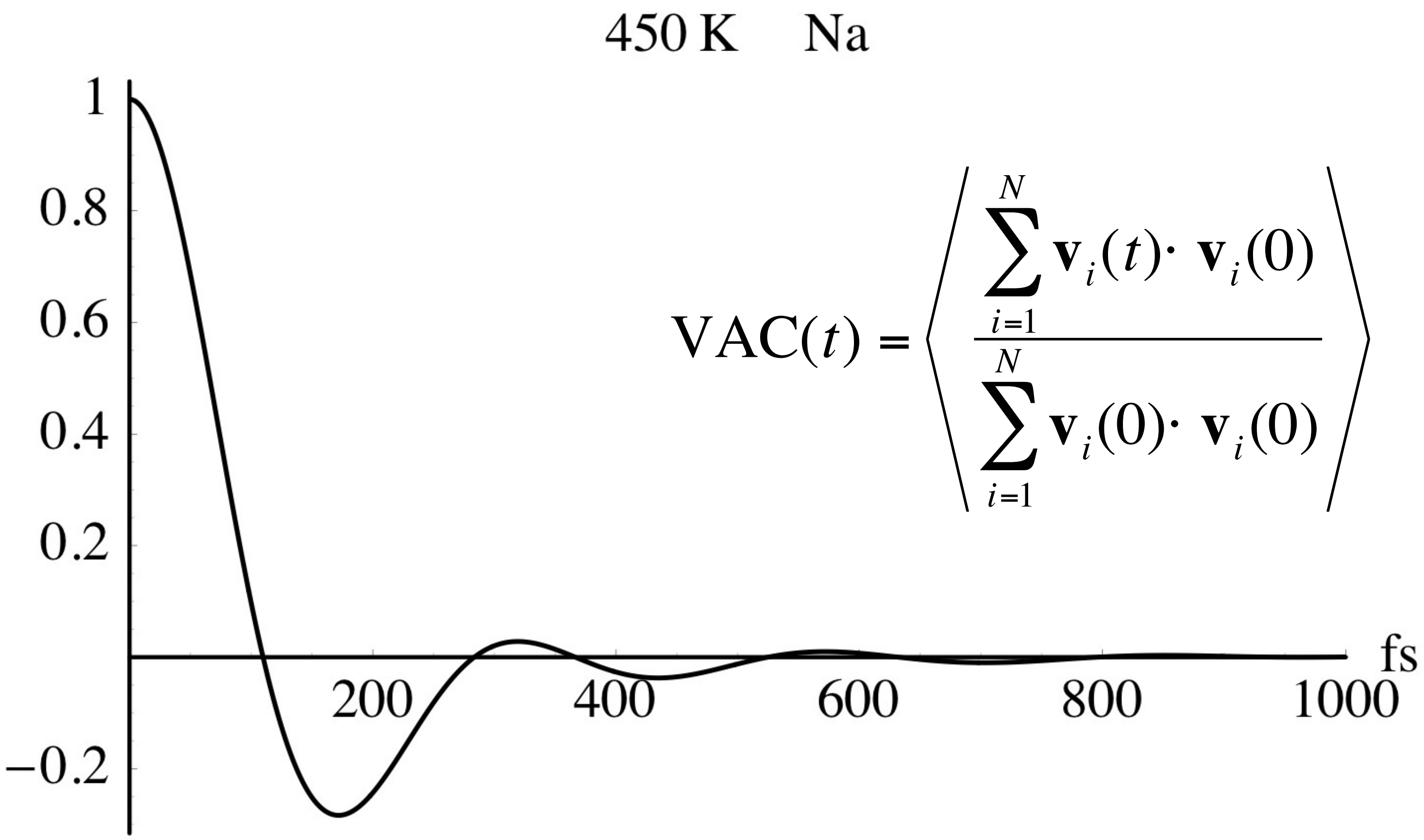
NNSA National Nuclear Security Administration

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

- Energy and Stress 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 thermodynamic method (2PT)[1], developed at Caltech, provides a novel approach to calculating entropies for liquids

[1] Lin, Blanco, and Goddard, J. Chem. Phys. **119**, 11792 (2003)

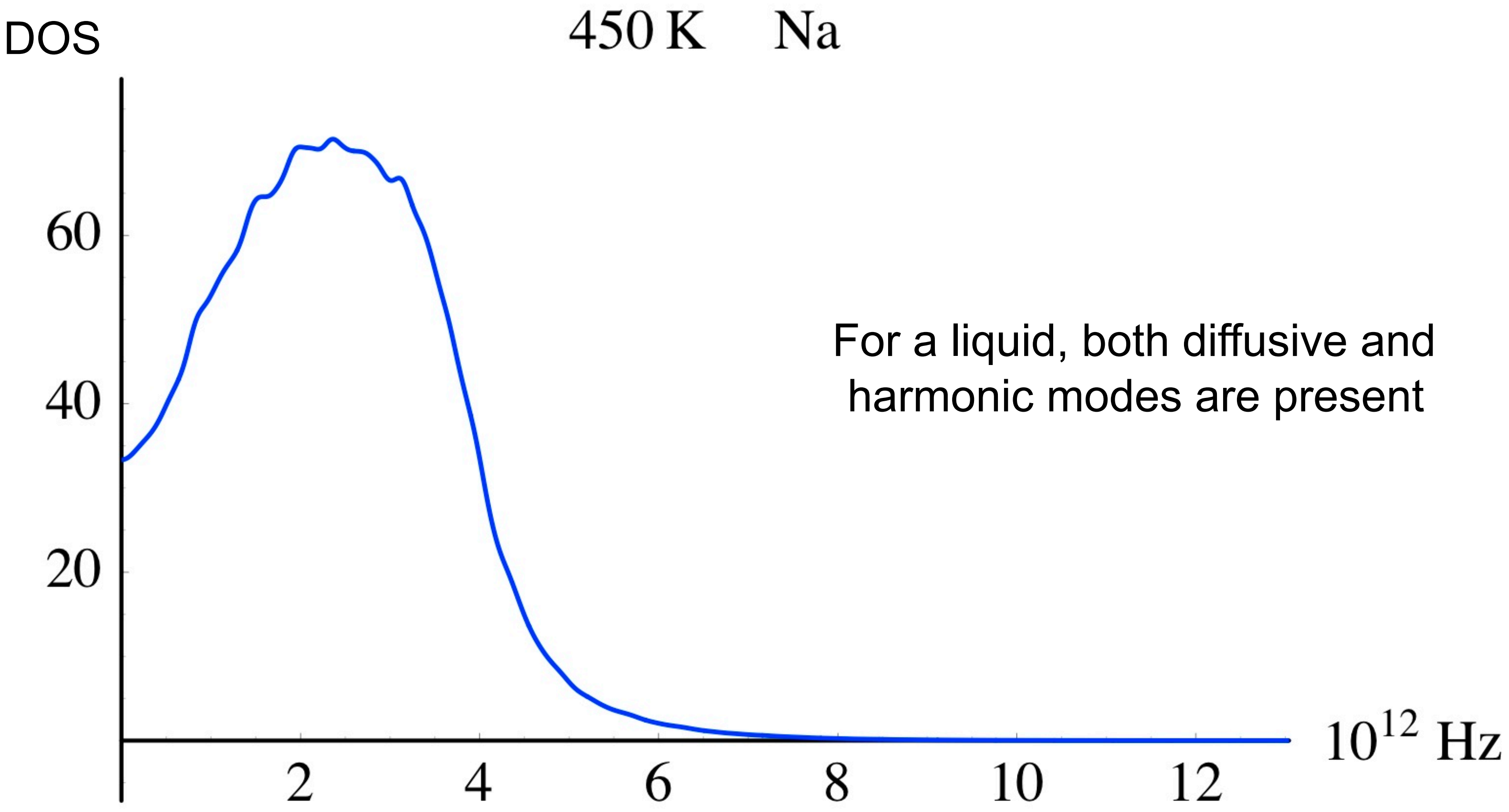
The starting point for the 2PT approach is the velocity autocorrelation function



$$\mathrm{VAC}(t) = \left\langle \frac{\sum_{i=1}^{N} \mathbf{v}_i(t)\cdot\, \mathbf{v}_i(0)}{\sum_{i=1}^{N} \mathbf{v}_i(0)\cdot\, \mathbf{v}_i(0)} \right\rangle$$

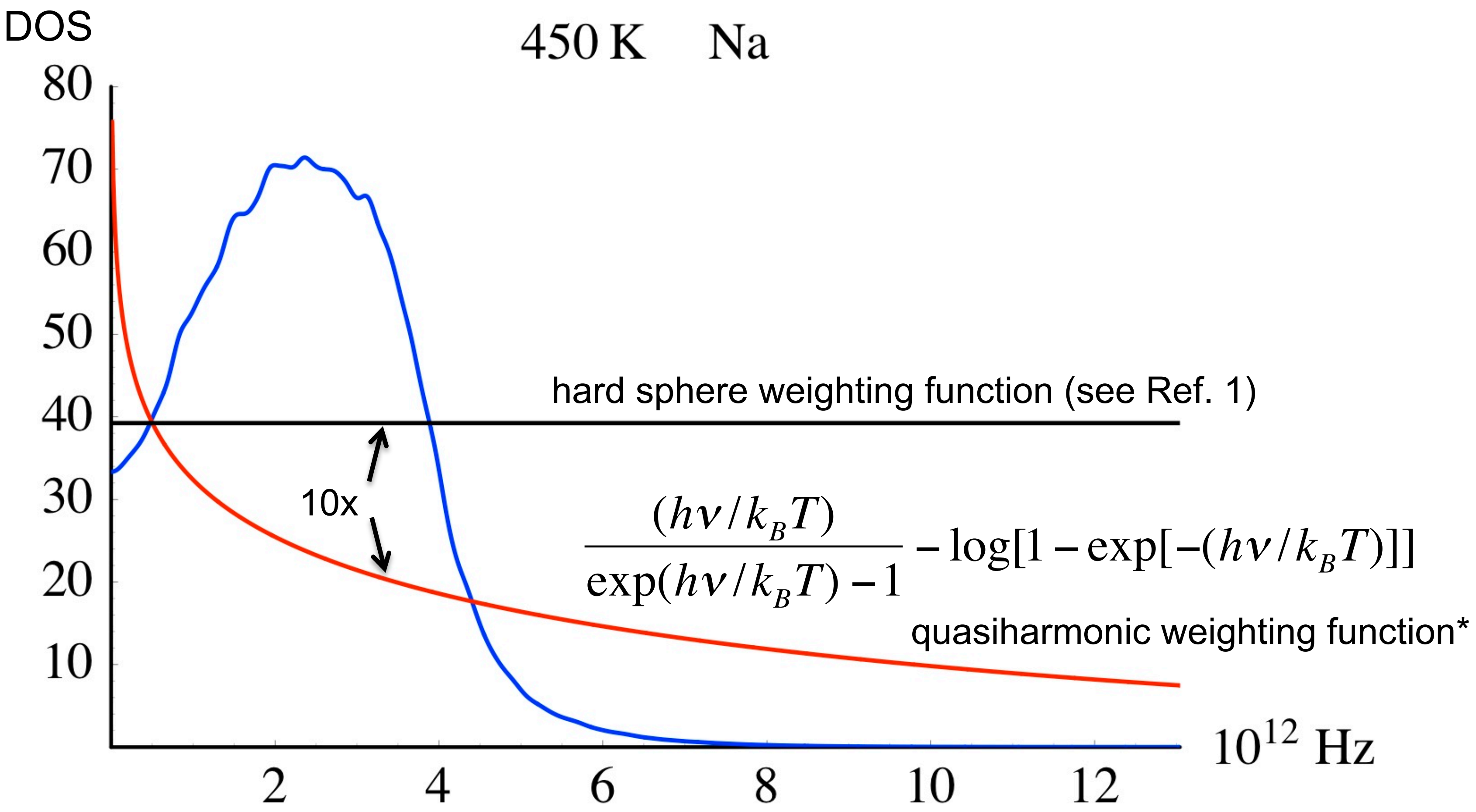
All calculations presented here are first-principles molecular dynamics (FPMD) performed with VASP

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



For a liquid, both diffusive and harmonic modes are present

The quasiharmonic spectral weighting function for the entropy diverges logarithmically at zero frequency



hard sphere weighting function (see Ref. 1)

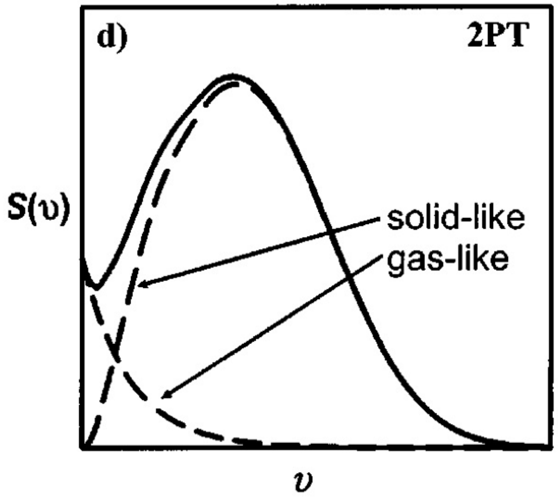
$$\frac{(h\nu/k_BT)}{\exp(h\nu/k_BT)-1}-\log[1-\exp[-(h\nu/k_BT)]]$$

quasiharmonic weighting function*

*More general than simple non-interacting harmonic motion (e.g. interacting, anharmonic)
Werthamer (1969), Hui and Allen (1975), Wallace in *Thermodynamics of Crystals*

The key element of the 2PT approach is to decompose the density of states into gas-like and solid-like components

- The diffusive (gas-like) component is modeled as a hard sphere gas, which removes the divergent behavior
- The remaining portion is treated as a solid and the entropy is computed with the quasiharmonic weighting function

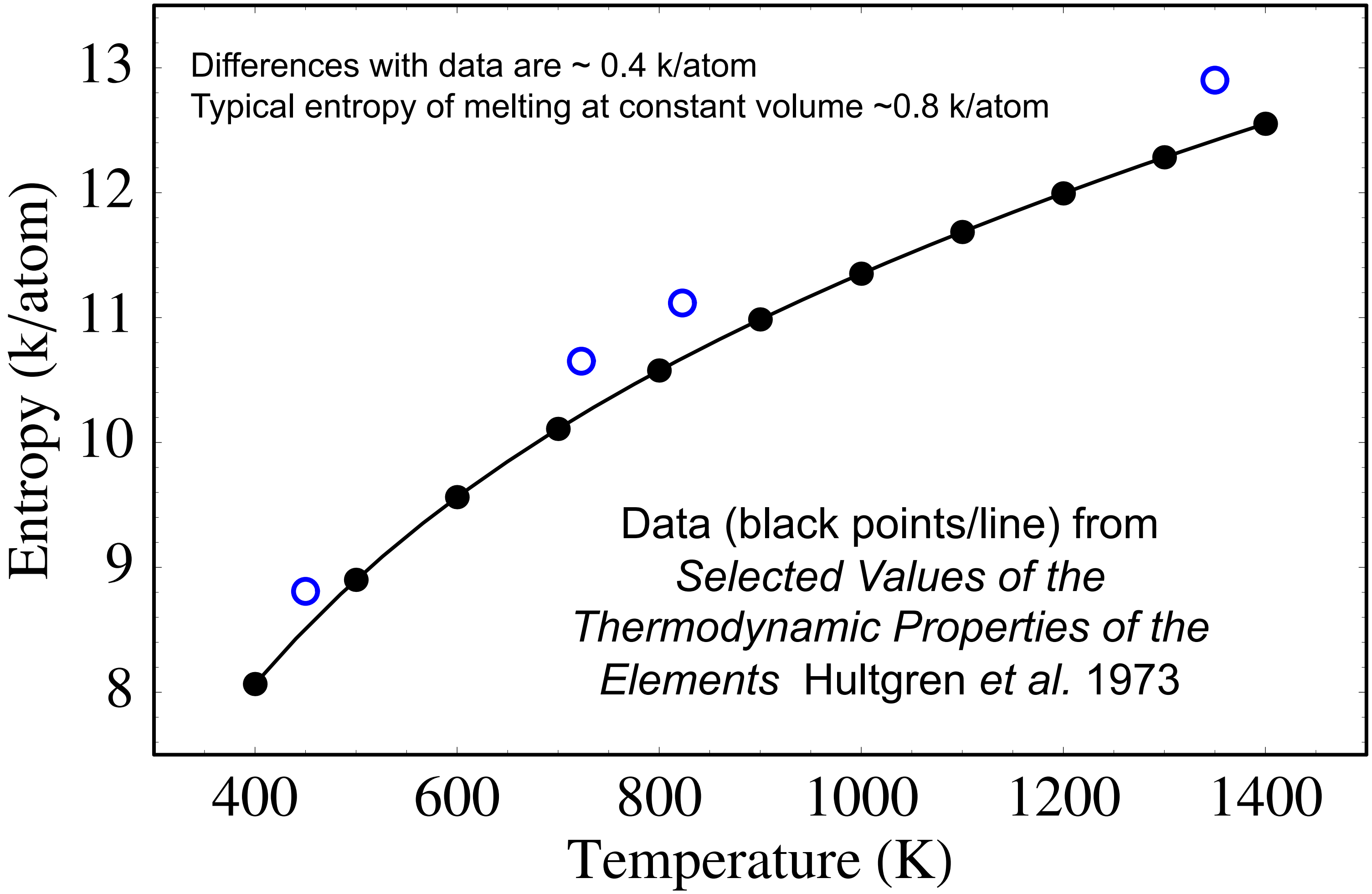


From Ref. 1

$$\Phi(t) = (1 - f_g)\Phi_s(t) + f_g\Phi_g(t)$$

$$F(\nu) = (1 - f_g)F_s(\nu) + f_gF_g(\nu)$$

The 2PT method gives the right trend, but systematically overestimates the total entropy for liquid sodium

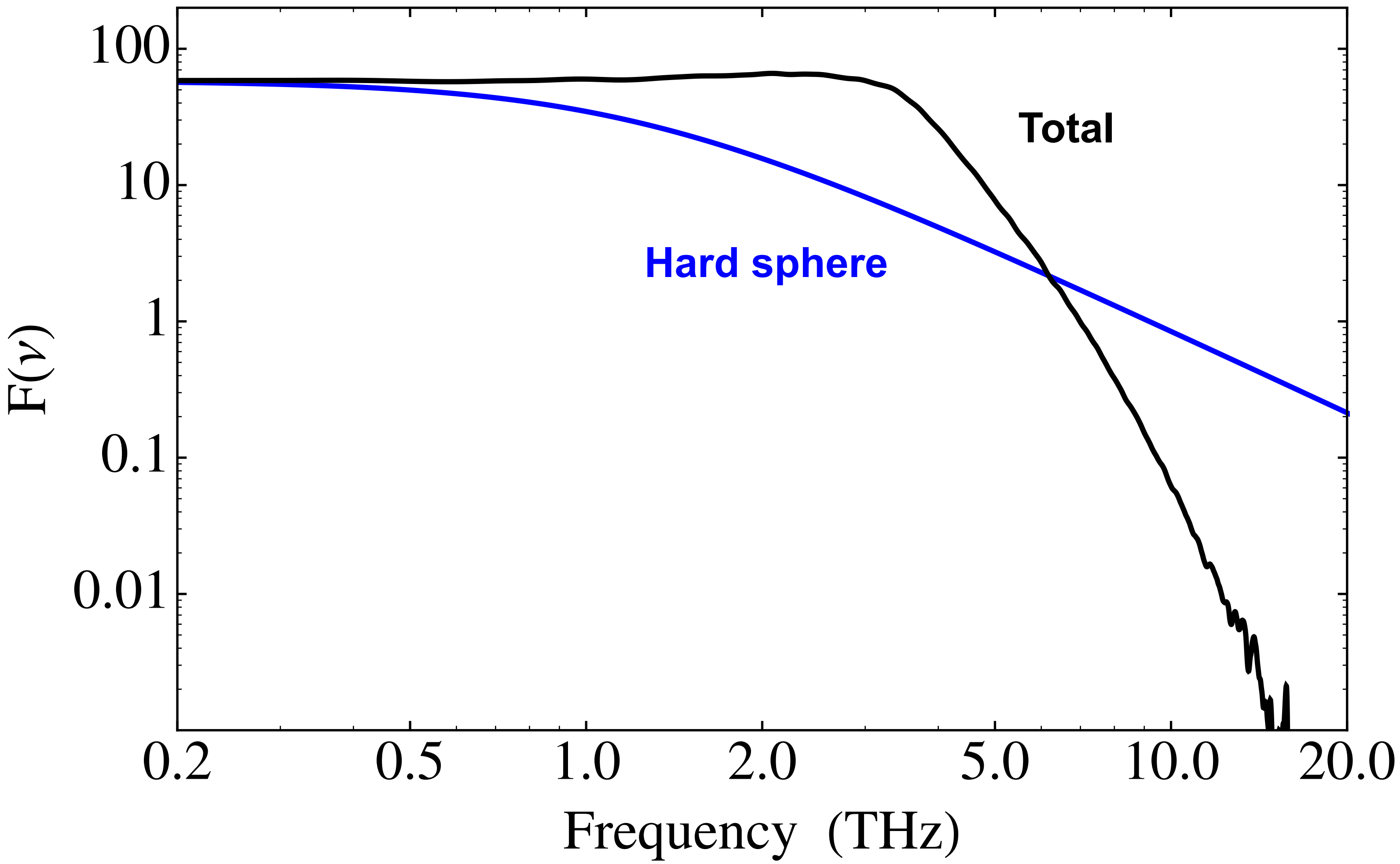


Differences with data are ~ 0.4 k/atom
Typical entropy of melting at constant volume ~0.8 k/atom

Data (black points/line) from *Selected Values of the Thermodynamic Properties of the Elements* Hultgren *et al.* 1973

Similar results for sodium were found using the 2PT method by Teweldeberhan and Bonev, Phys. Rev. B **83**, 134120 (2011)
[the first application of 2PT with *ab initio* tools, that I'm aware of]

The hard sphere model contributes a Lorentzian tail that exceeds the total density of states



The Lorentzian tail and excess entropy derive from the exponential decay of correlations in the hard sphere model

We use a Memory Function* representation to derive a consistent and realistic model for the diffusive component

$$\frac{d\Phi_g(t)}{dt} = -\int_0^t K_g(\tau)\Phi_g(t-\tau)d\tau$$

* Tjon, 1966
Singwi and Tosi, 1967

The frequency spectrum is given by

$$F_g(\nu) = \frac{1}{2}\left[\frac{1}{\hat{K}_g(i2\pi\nu) + i2\pi\nu} + \frac{1}{\hat{K}_g(-i2\pi\nu) - i2\pi\nu}\right]$$

where $\hat{K}_g(s)$ is the Laplace transform of $K_g(\tau)$

With a Gaussian memory function $K_g(\tau) = A_g e^{-B_g\tau^2}$

Recovers hard-sphere
as B → ∞ ,
Satisfies formal constraints

$$\hat{K}_g(s) = A_g\sqrt{\frac{\pi}{4B_g}}\exp[\frac{s^2}{4B_g}]\ \mathrm{Erfc}[\frac{s}{2\sqrt{B_g}}]$$

We apply the Memory Function description to the solid-like and gas-like components independently

$$\frac{d\Phi_s(t)}{dt} = -\int_0^t A_s e^{-B_s \tau^2} \Phi_s(t-\tau) d\tau$$

$$\frac{d\Phi_g(t)}{dt} = -\int_0^t A_g e^{-B_g \tau^2} \Phi_g(t-\tau) d\tau$$

The self-consistent solution is found by equating moments

$$\Phi(t) = \sum_{n=1}^{\infty} (-1)^n \frac{M_{2n}}{(2n)!} t^{2n} \qquad \text{where } M_{2n} = \langle \omega^{2n} \rangle_F$$

These moments don't exist for the hard-sphere system

$$M_2 = (1 - f_g) M_{2s} + f_g M_{2g},$$
$$M_4 = (1 - f_g) M_{4s} + f_g M_{4g}.$$

and so forth.

M_2 and M_4 are the moment totals, extracted from the full DOS

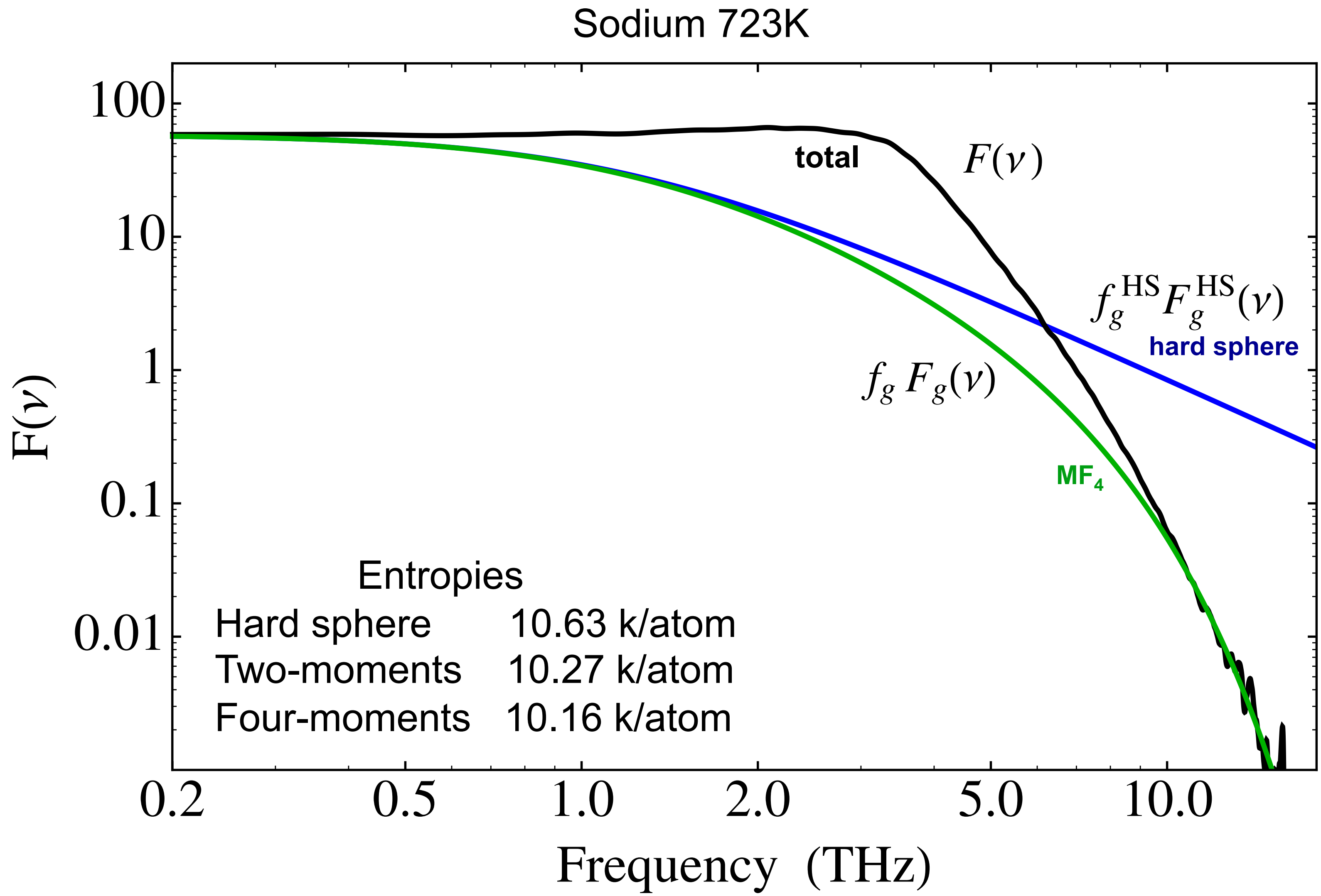
The Memory Function moments are computed through a recursion relation

$$M_{2n} = \sum_{k=1}^{n} (-1)^{k+1} K_0^{(2k-2)} M_{2(n-k)} \qquad K_0^{(n)} = \frac{d^n}{dt^n} K(t)\bigg|_{t=0}$$

For the Gaussian kernel

$$M_2 = A,$$
$$M_4 = A^2 + 2AB.$$

With a solution at the level of four moments, the tail of the gas-like portion blends smoothly with the total density of states

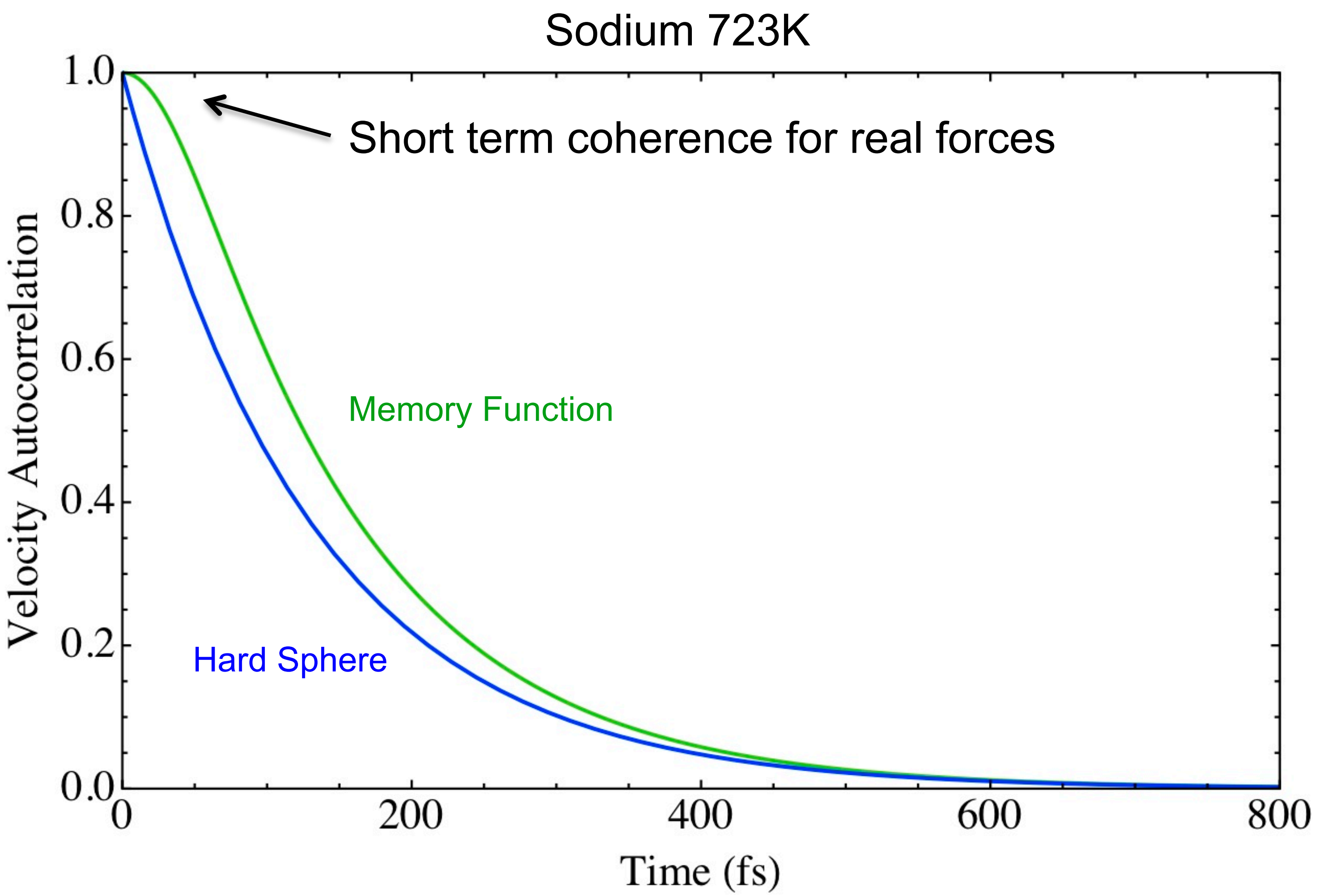


Sodium 723K

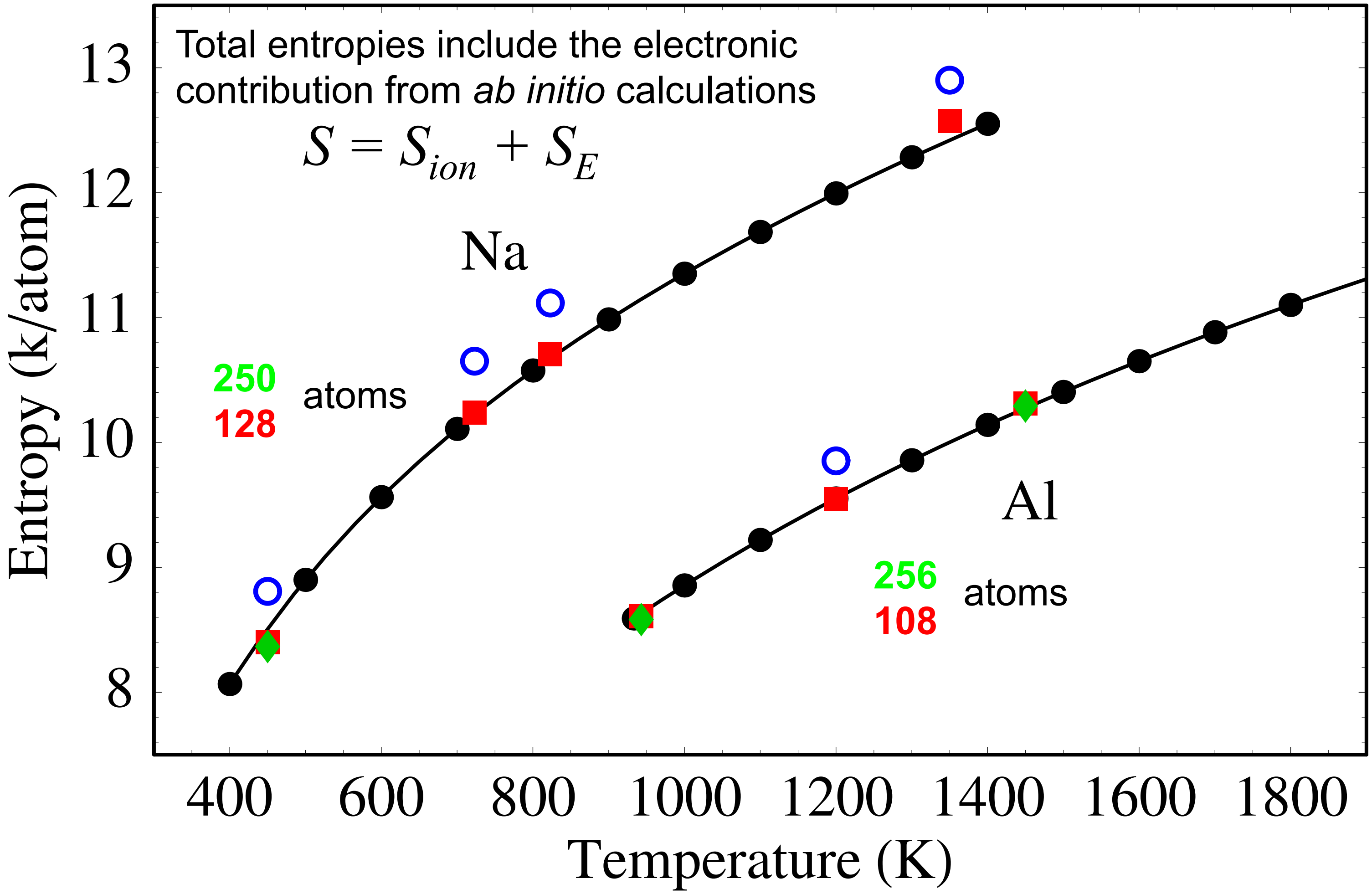
Entropies

Hard sphere	10.63 k/atom
Two-moments	10.27 k/atom
Four-moments	10.16 k/atom

The Memory Function provides a diffusive autocorrelation with a consistently determined coherence time

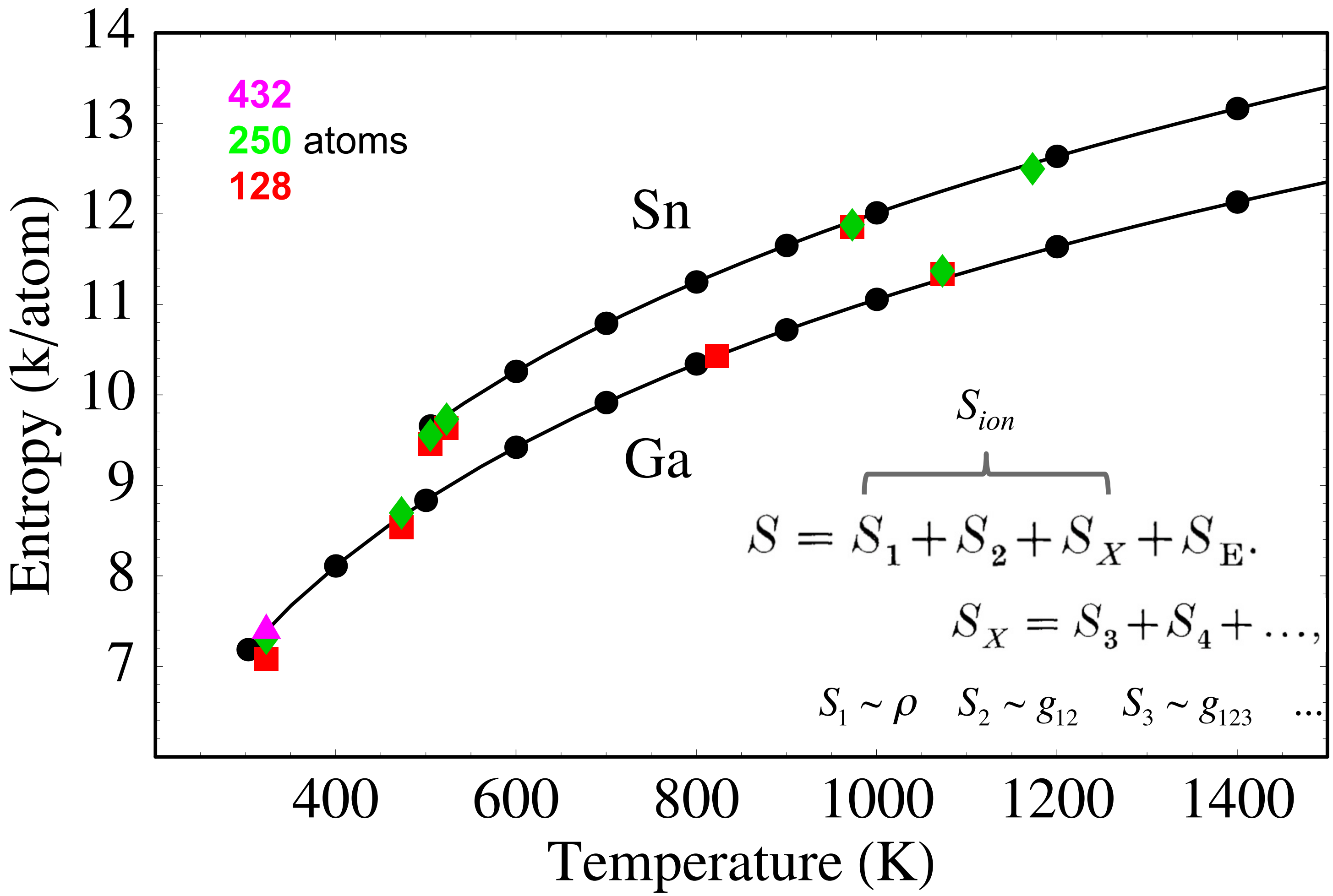


The calculated entropies for sodium agree with data to within ~ 1% with the Memory Function treatment



Symbol widths for calculations represent ~ 1%

Results are equally good for Sn and Ga, which have high correlation entropy, but size effects are apparent



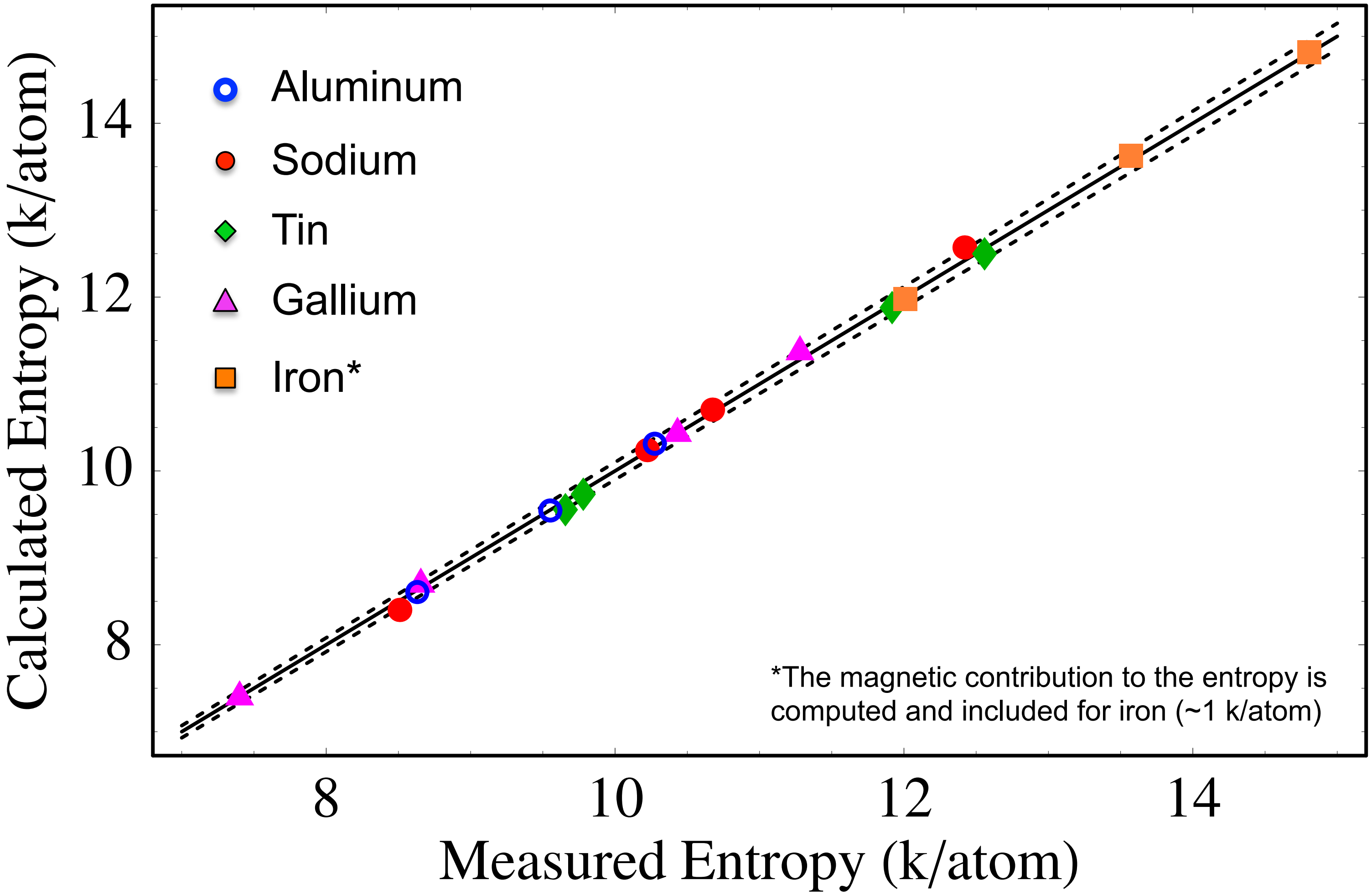
$$S = \underbrace{S_1 + S_2 + S_X}_{S_{ion}} + S_E.$$

$$S_X = S_3 + S_4 + \ldots,$$

$S_1 \sim \rho \quad S_2 \sim g_{12} \quad S_3 \sim g_{123} \quad \ldots$

High correlation entropy appears to contribute to greater size effects

Agreement with data is generally within 1%

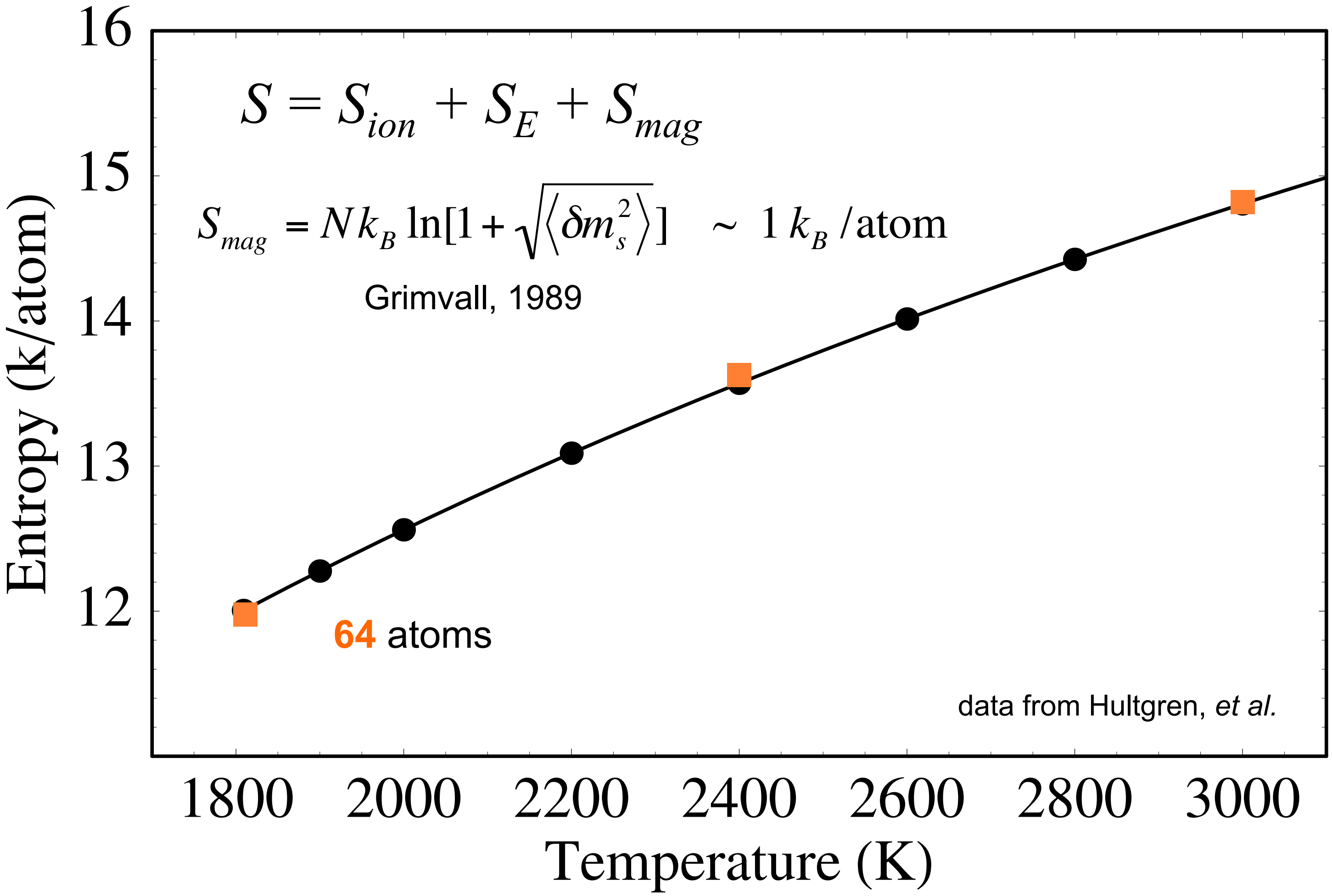


Measured values are Hultgren *et al.* (“selected values” from multiple sources)

Summary

- The two phase (2PT) method of computing liquid entropies systematically overestimates the entropy for liquid metals when modeling the diffusive component with hard spheres
- A quasi-hard sphere autocorrelation component, modeled within the framework of Memory Function theory, eliminates the source of the excess entropy
- The approach is validated against experimental data for several elements with diverse properties
- The calculation of free energies and phase boundaries is greatly simplified with this approach and provides for a direct calculation of melt boundaries
- Shock state entropies and release adiabats are readily calculated

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



$$S = S_{ion} + S_E + S_{mag}$$

$$S_{mag} = N k_B \ln[1 + \sqrt{\langle \delta m_s^2 \rangle}] \quad \sim \; 1\, k_B\,/\text{atom}$$

Grimvall, 1989

data from Hultgren, *et al.*