液体のエントロピーの 第一原理計算

First-principles calculation of entropy for liquids

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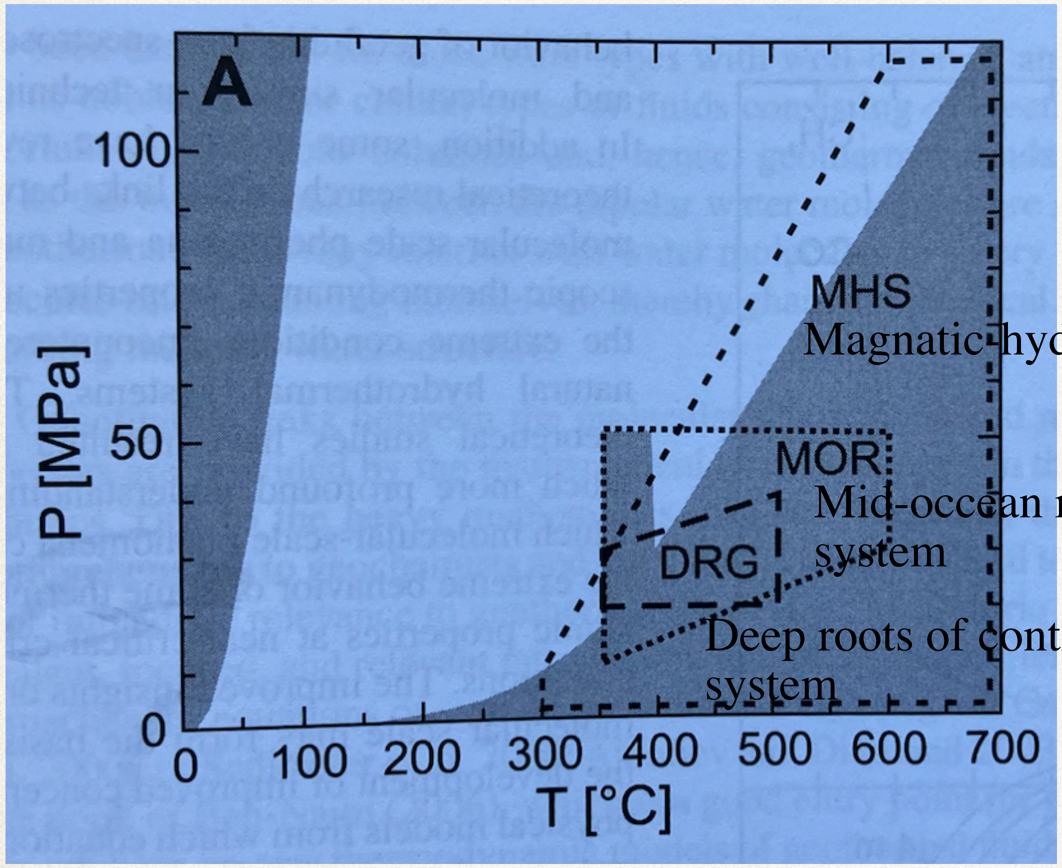
Lack of thermodynamic data for liquids

Range of applicability of the HKF (Helgeson -Kirkham-Flowers) equation of state



Magnatic hydrothermal system

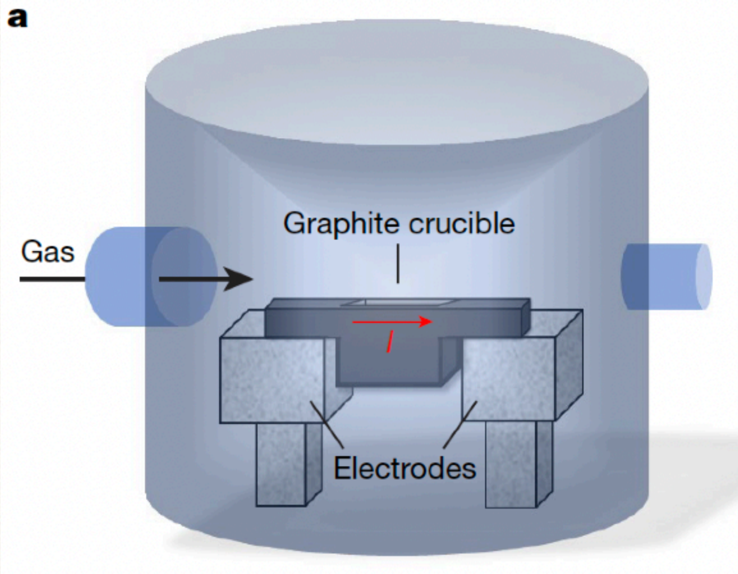
Mid-occean ridge hydrothermal system

Deep roots of continental geothermal system

T. Driesner, in *Thermodynamics of Geothermal Fluids*, A. Stefansso, *et al.* eds. (Miner. Soc. Am., 2013)

Growth of diamond in liquid metal at 1 atm pressure

Y. Gong *et al.*, Nature **629**, 348 (2024)



Gas source: $CH_4 + H_2$

Liquid: Ga + Fe + Ni + Si

× ○ ○ ? C dissolves

$$F = U - TS$$ Entropy

Statistical-Mechanics Approach

N-particle correlation function $g_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)$

$$\boxed{S = S_1 - k_\mathrm{B}\frac{\rho^N}{N!}\int g_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)\ln\left[g_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]d\mathbf{r}_1\ldots d\mathbf{r}_N}$$

Expansion with respect to density

$$S = S_1 + S_2 + S_3 + \ldots$$

$$S_1 = \frac{3}{2} - \ln\rho\Lambda^3$$

$$S_2 = -\frac{1}{2}\rho^2\int g_2(\mathbf{r}_1,\mathbf{r}_2)\ln\left[g_2(\mathbf{r}_1,\mathbf{r}_2)\right]d\mathbf{r}_1 d\mathbf{r}_2$$

$$S_3 = -\frac{1}{3!}\rho^3\int g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\ln\left[\delta g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\right]d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

$$\Lambda = \frac{h}{(2\pi m K_\mathrm{B}T)^{1/2}}$$

de Broglie thermal wavelength

$$\delta g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \frac{g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g_2(\mathbf{r}_1,\mathbf{r}_2)g_2(\mathbf{r}_2,\mathbf{r}_3)g_2(\mathbf{r}_3,\mathbf{r}_1)}$$

1) D. C. Wallace, Intl. J. Quant. Chem. **54**, 425 (1994).
2) A. Baranyai and D. J. Evans, Phys. Rev. A **40**, 3817 (1989).
5) I. Yokoyama and S. Tsuchiya, Materials Transactions **41**, 67 (2002).
6) I. Yokoyama, Materials Transactions **43**, 1421 (2002).
3) M. Gao and M. Widom, J. Phys. Chem. B **122**, 3550 (2018).
4) M. Widom and M. Gao, Entropy **21**, 131 (2019).

Thermodynamic Approach

$$\boxed{S(T) = \int_0^T \frac{C(T')}{T'} dT'}$$

$$C_x = \left(\frac{\partial U}{\partial T}\right)_X$$

$$U = \overline{E_{\mathrm{tot}}(t)}$$

DFT + MD simulation

1. The total-energy approach is consistent with the thermodynamic definition of entropy.

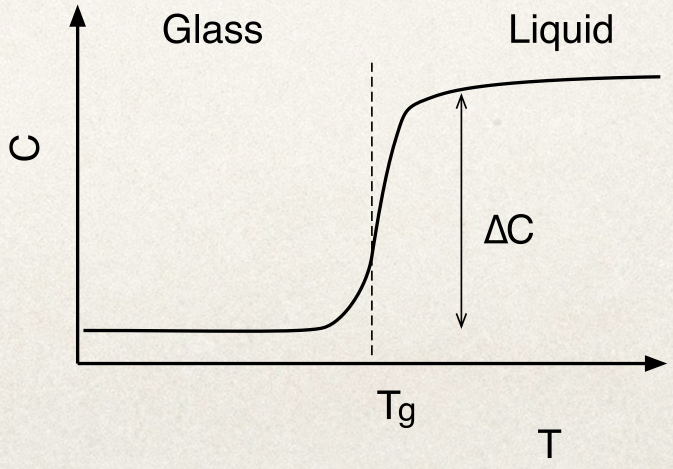
Only the total entropy has a sense.

2. The accuracy entirely relies on the accuracy of specific heat.

Specific heat of liquids

Specific heat jump at the glass transition

K. Shirai, et al., J. Phys.: CM **34**, 375902 (2022)
K. Shirai, et al., J. Phys.: CM **35**, 505401 (2023)



First-principles calculation of specific heat

Specific heat $C_x = \left(\frac{\partial U}{\partial T}\right)_X$

Microscopic energy

$$E_{\mathrm{tot}}(t) = E_{\mathrm{GS}}(\{\mathbf{R}_j(t)\}) + \frac{1}{2}\sum_j M_j v_j(t)^2$$

⬇ in thermodynamic equilibrium

Internal energy

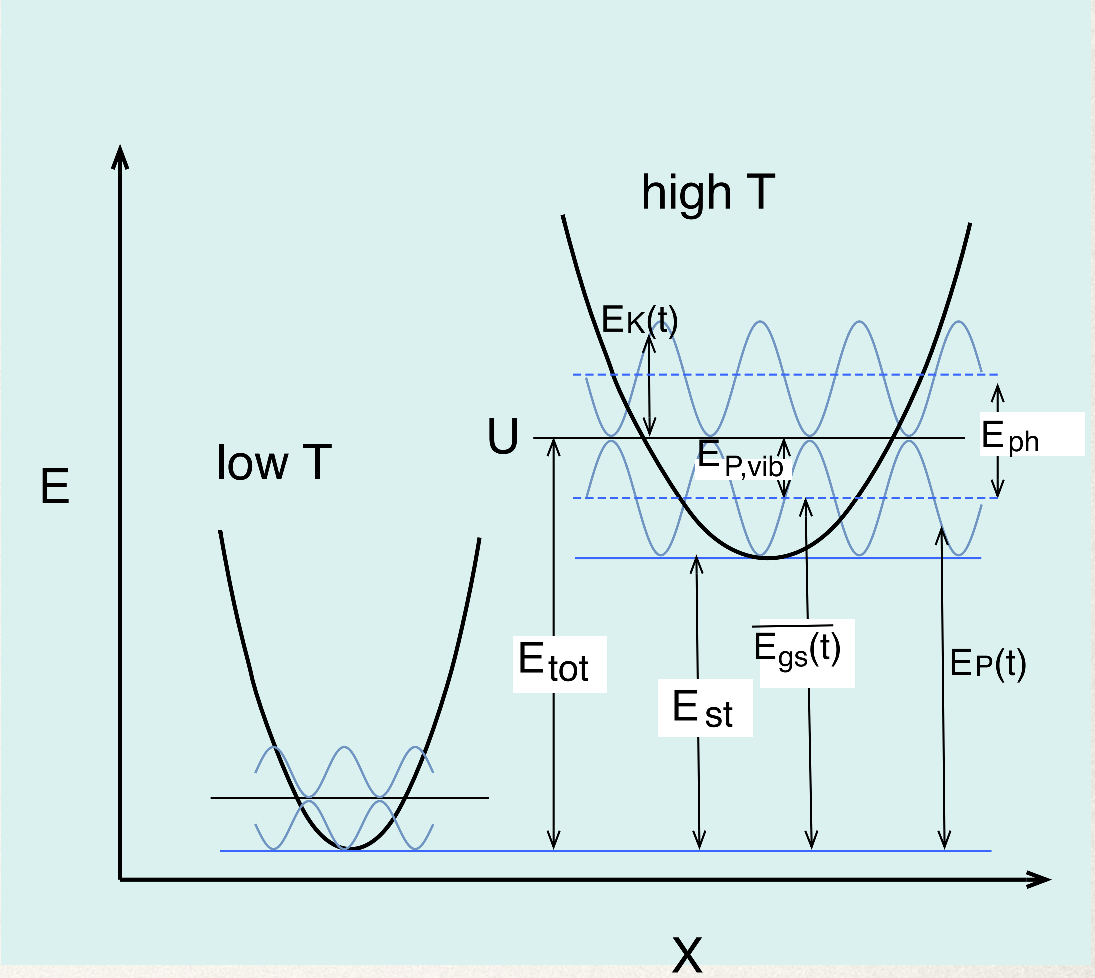
$$U = \overline{E_{\mathrm{tot}}(t)} = \overline{E_{\mathrm{GS}}(\{\mathbf{R}_j(t)\})} + \overset{\frac{3}{2}k_{\mathrm{B}}T}{\boxed{\frac{1}{2}\sum_j \overline{M_j v_j(t)^2}}}$$

For solids, Harmonic approx.

$$\mathbf{R}_j(t) = \bar{\mathbf{R}}_j + \mathbf{u}_j(t)$$

$$\underbrace{E_{\mathrm{st}}(\{\bar{\mathbf{R}}_j\})}_{\text{structural part (configurational)}} + \underbrace{E_{\mathrm{ph}}(T)}_{\text{phonon}} + \underbrace{E_{\mathrm{te}}(V)}_{\text{thermal expansion}}$$

$$\boxed{C_{\mathrm{p}} = C_{\mathrm{st}} + C_{\mathrm{ph}} + C_{\mathrm{te}}}$$



in adiabatic MD

Phonon contribution to specific heat

For solids

$$E_{\text{ph}} = \sum_k \left(\bar{n}_k + \frac{1}{2} \right) \hbar \omega_k$$

$$C_{\text{ph}}(T) = k_{\text{B}} \int \left(\frac{\hbar\omega}{k_{\text{B}}T} \right)^2 \frac{e^{\hbar\omega/k_{\text{B}}T}}{(e^{\hbar\omega/k_{\text{B}}T} - 1)^2} g(\omega) d\omega$$

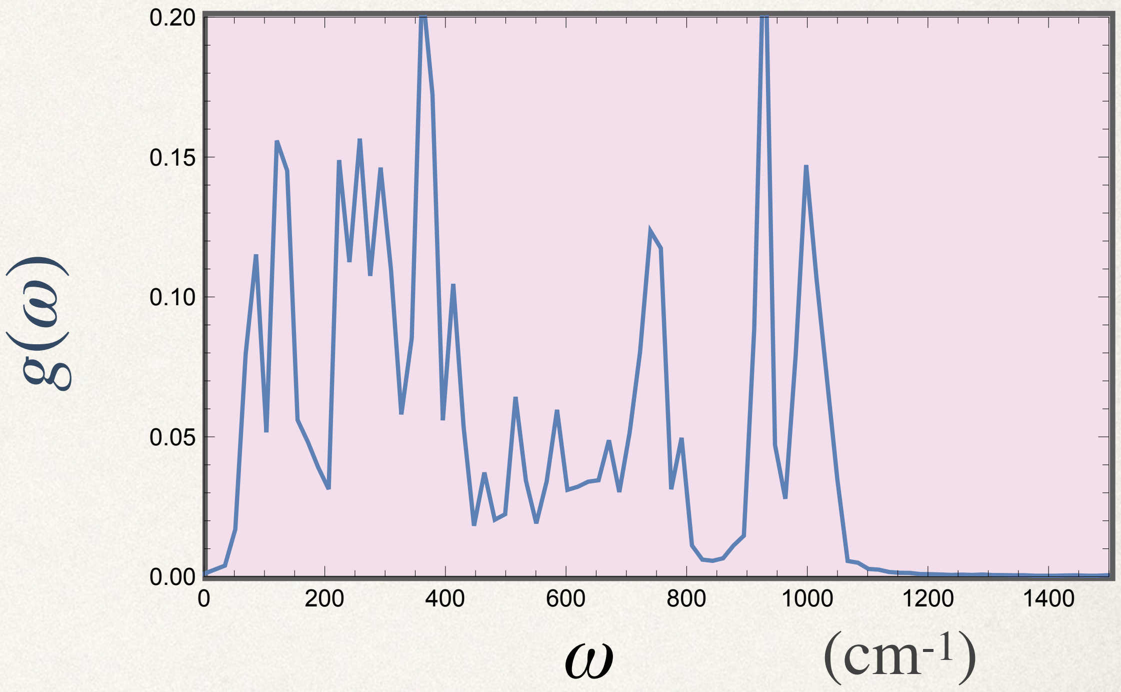
$$C_p = C_{\text{st}} + C_{\text{ph}} + C_{\text{te}}$$

structural part

phonon

thermal expansion

Phonon DOS of SiO₂



$$g(\omega) = \frac{1}{3N\frac{3}{2}k_{\text{B}}T} \sum_j^{3N} \frac{1}{2} M_j f^*_{v_j}(\omega) f_{v_j}(\omega)$$

For liquids

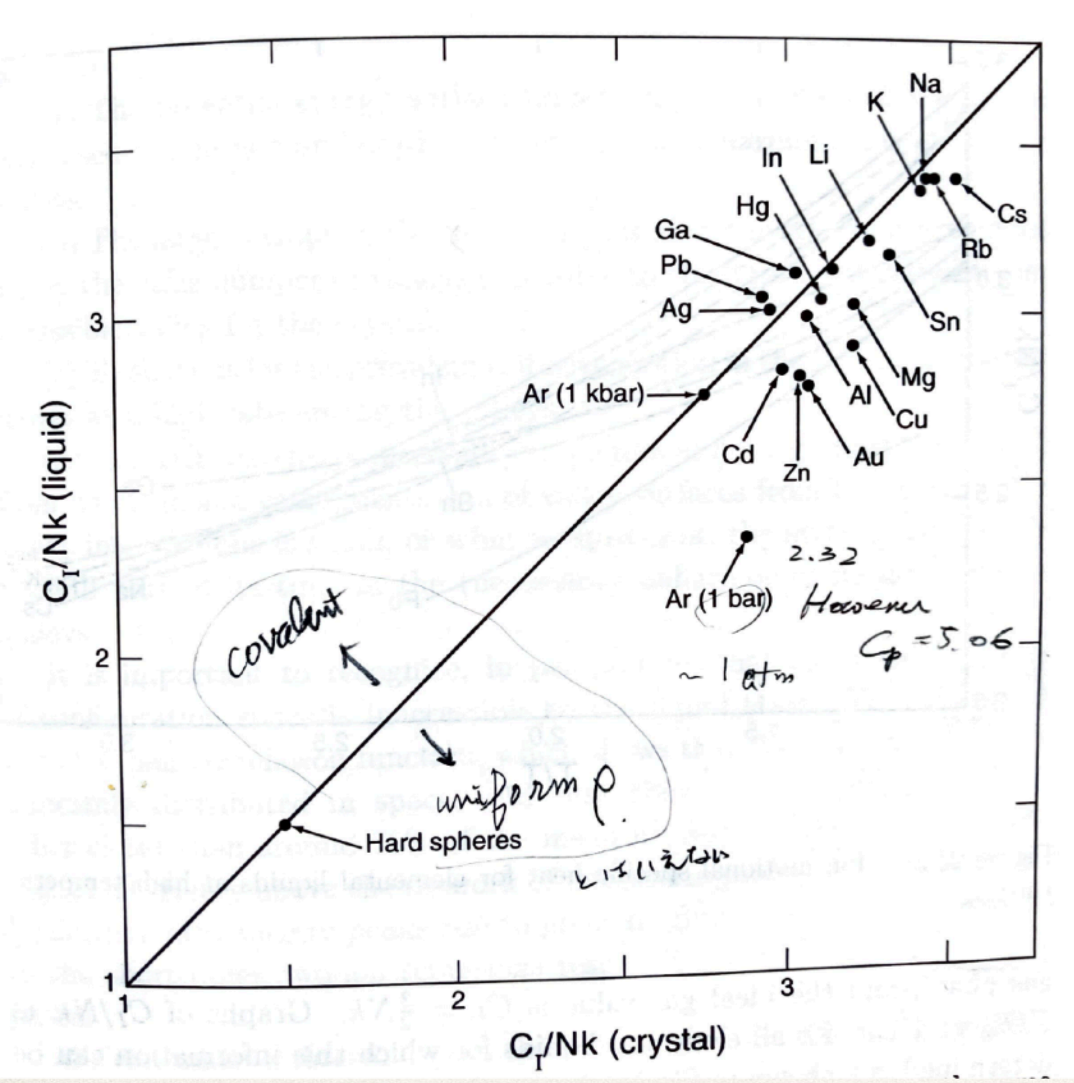
Is the phonon-picture realistic for liquids? → No!

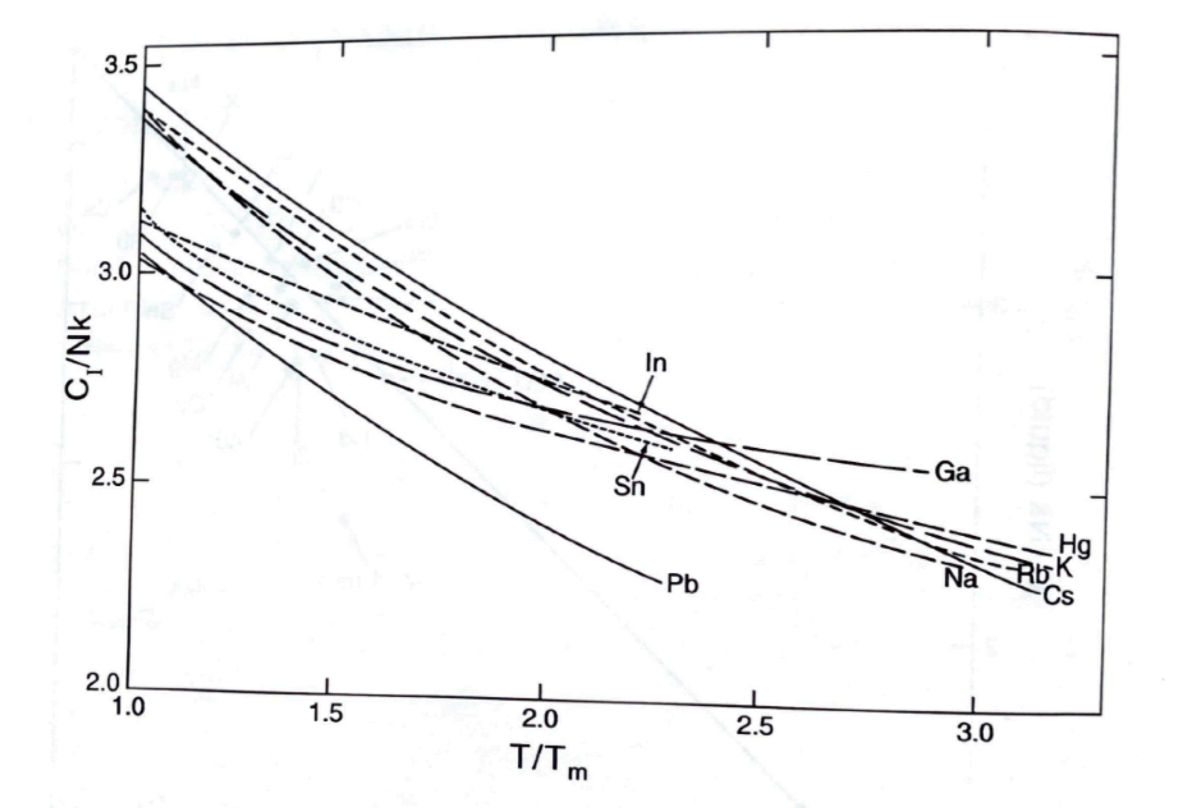
$$U = \overline{E_{\text{tot}}(t)}$$

Effect of energy dissipation

→ Need of adiabatic MD simulation

Phonon model for C_V of liquids





D. C.Wallace, *Statistical Physics of Crystals and Liquids: A guide to highly accurate equations of state* (World Scientific, Singapore, 2002).

Phonon model

K. Trachenko and V. V. Brazhkin, Phys. Rev. B **83**, 014201 (2011).

D. Bolmatov, V. V. Brazhkin, and K. Trachenko, Sci. Rep. **2**, 421 (2012).

K. Trachenko and V. V. Brazhkin, Rep. Prog. Phys. **79**, 016502 (2016).

J. E. Proctor, Phys. Fluids **32**, 107105 (2020).

M. Baggioli and A. Zaccone, Phys. Rev. E **104**, 014103 (2021).

$$C_V = R\left[3 - \left(\frac{\omega_c}{\omega_D}\right)^3\right]$$

by Trachenko

Adiabatic Relaxation Method

What is the definition of temperature? ↔ What is the definition of equilibrium?

GB statement of the second law

> "For a fixed U and fixed constraints ξ_j, the isolate system has one and only one stable equilibrium state."

E. P. Gyftopoulos and G. P. Beretta, *Thermodynamics - Foundations and Applications* (Dover, 2005), p. 62.

$$E(\{\mathbf{R}_j(0)\}) \xrightarrow[\text{relaxation}]{U=\overline{E(t)}} U = U(T, \{\bar{\mathbf{R}}_j\})$$

$$\frac{3}{2}k_\mathrm{B}T = \left\langle \frac{1}{2}Mv_j^2 \right\rangle$$

⬇

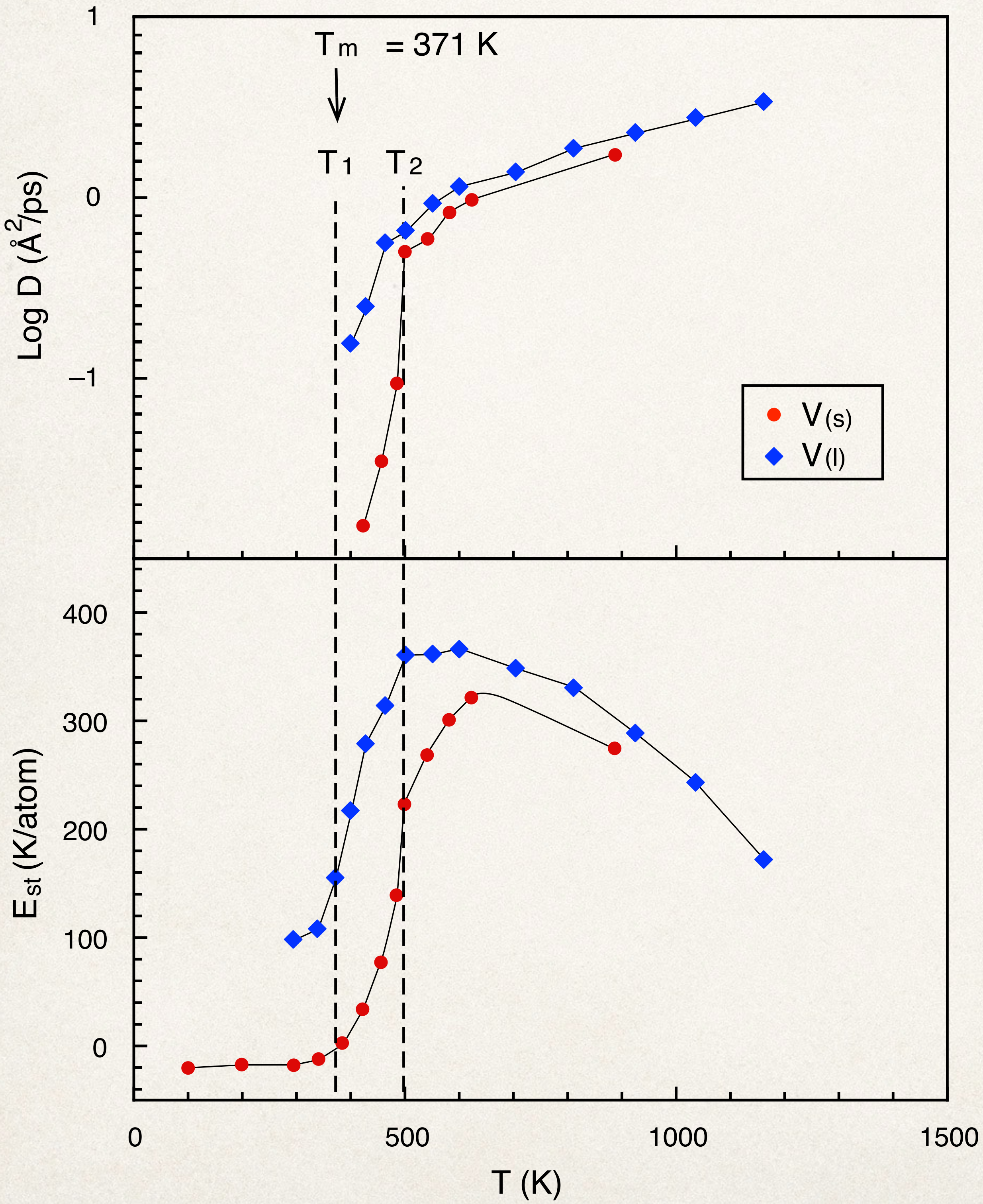
Adiabatic (spontaneous) relaxation process is recommended.

NEV ensemble

not *NTP* ensemble

K.S, J. Phys. Commun. **4**, 085015 (2020)
J. Phys. Commun. **5**, 015004 (2021)
Foundations, **5**, 9 (2025).

Sodium



Simulation by Phase/0

$N = 128$

GGA+NC potential

$E_{\mathrm{cut}} = 18$ Ry　　2^3 k mesh

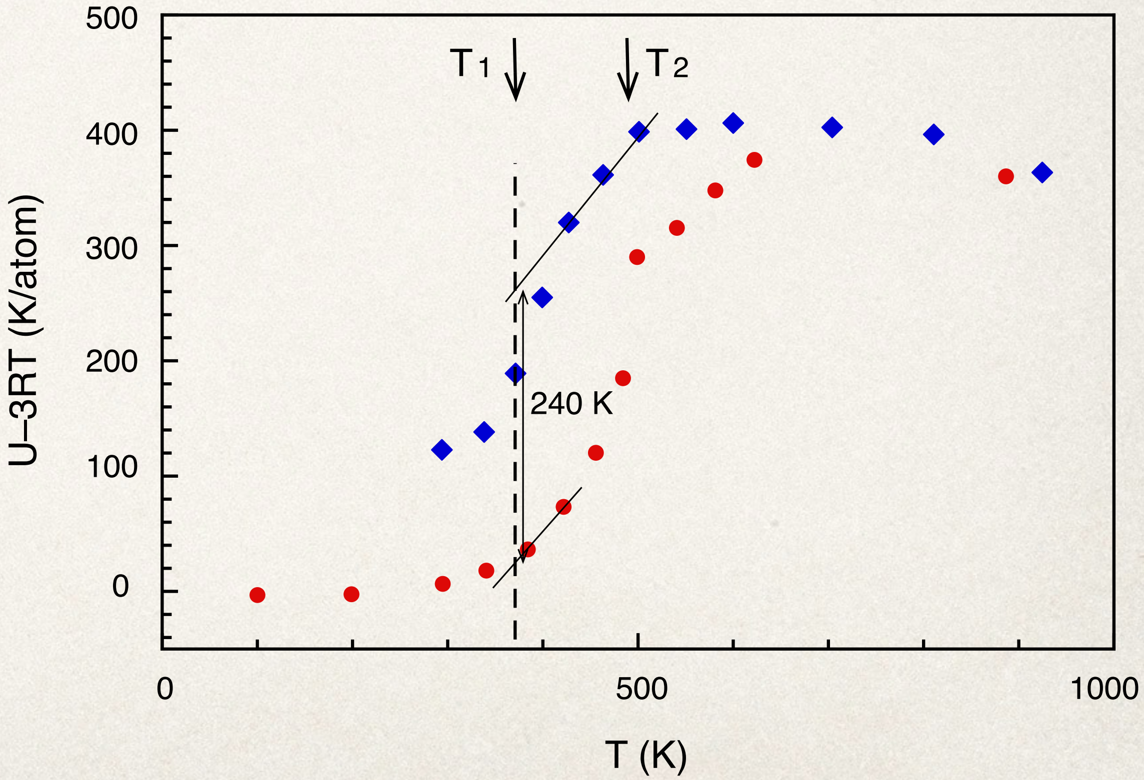
$\Delta t = 1.2$ fs　　$t_{sm} = 2.4 - 4.8$ ps

Exp.

$T_{\mathrm{m}} = 371$ K

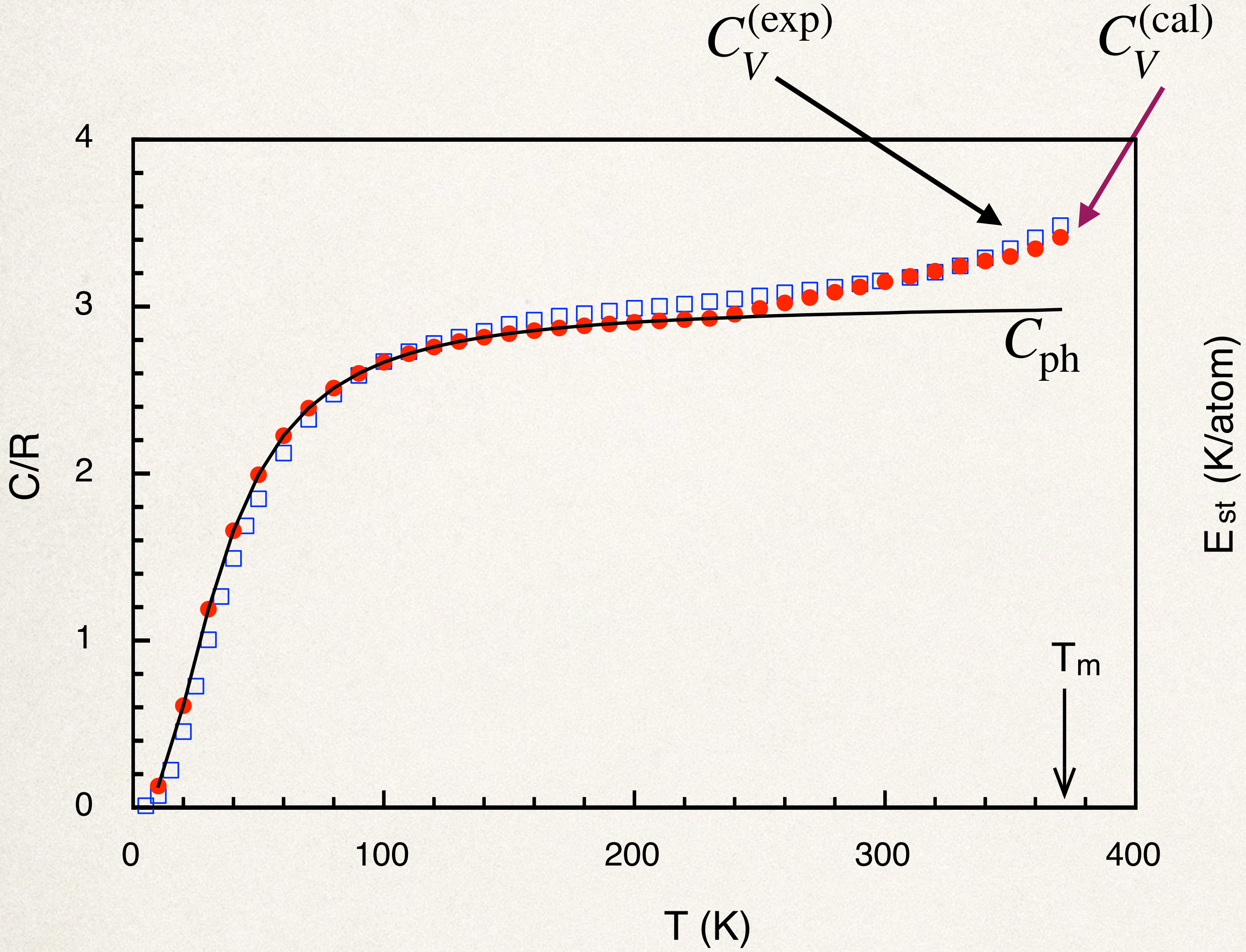
$H_{\mathrm{m}} = 26$ meV

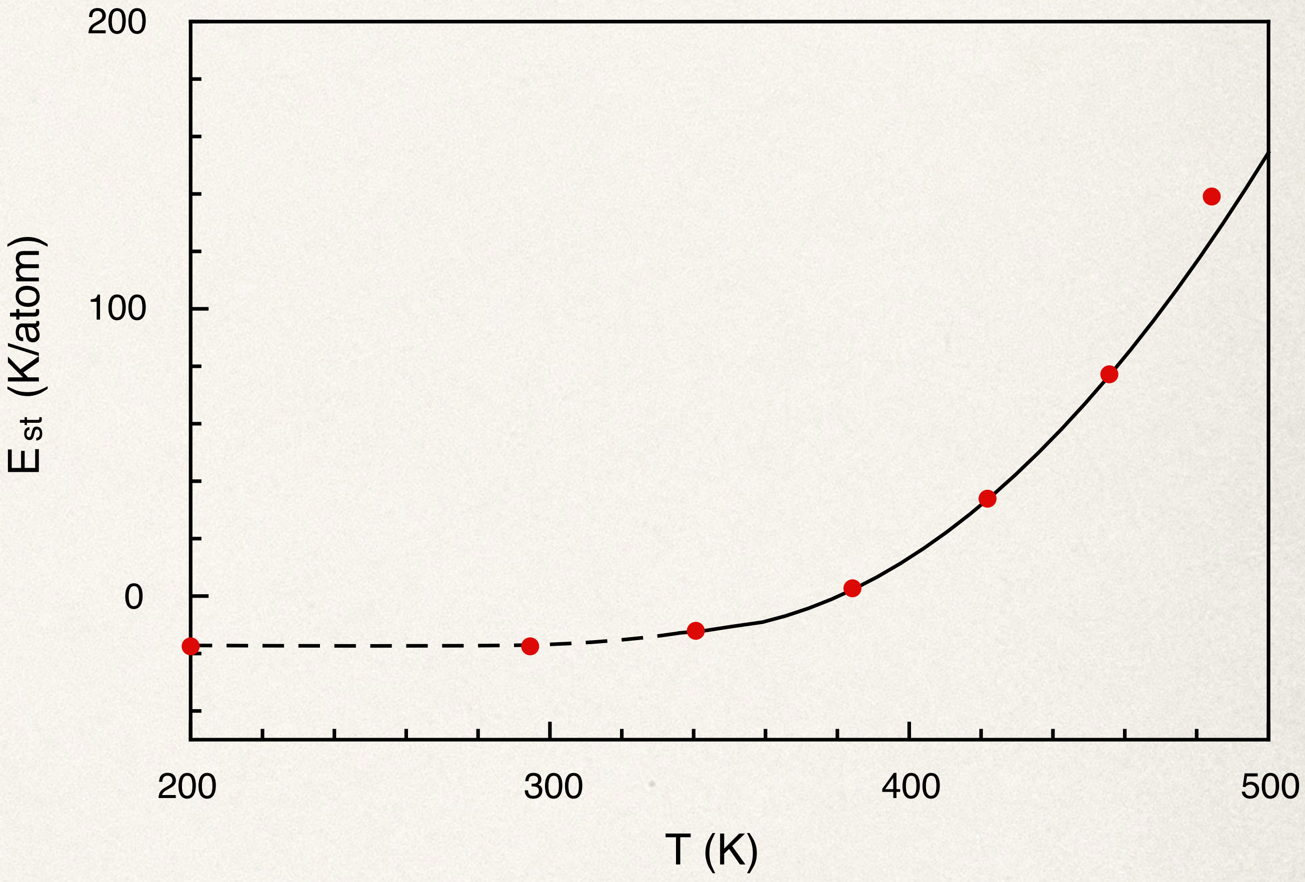
CRC Handbook of Chemistry and Physics, (CRC, 2011)



K. Shirai *et al*., J. Phys.: Condens. Matter **37**, 135901 (2025)

Specific heat of solid

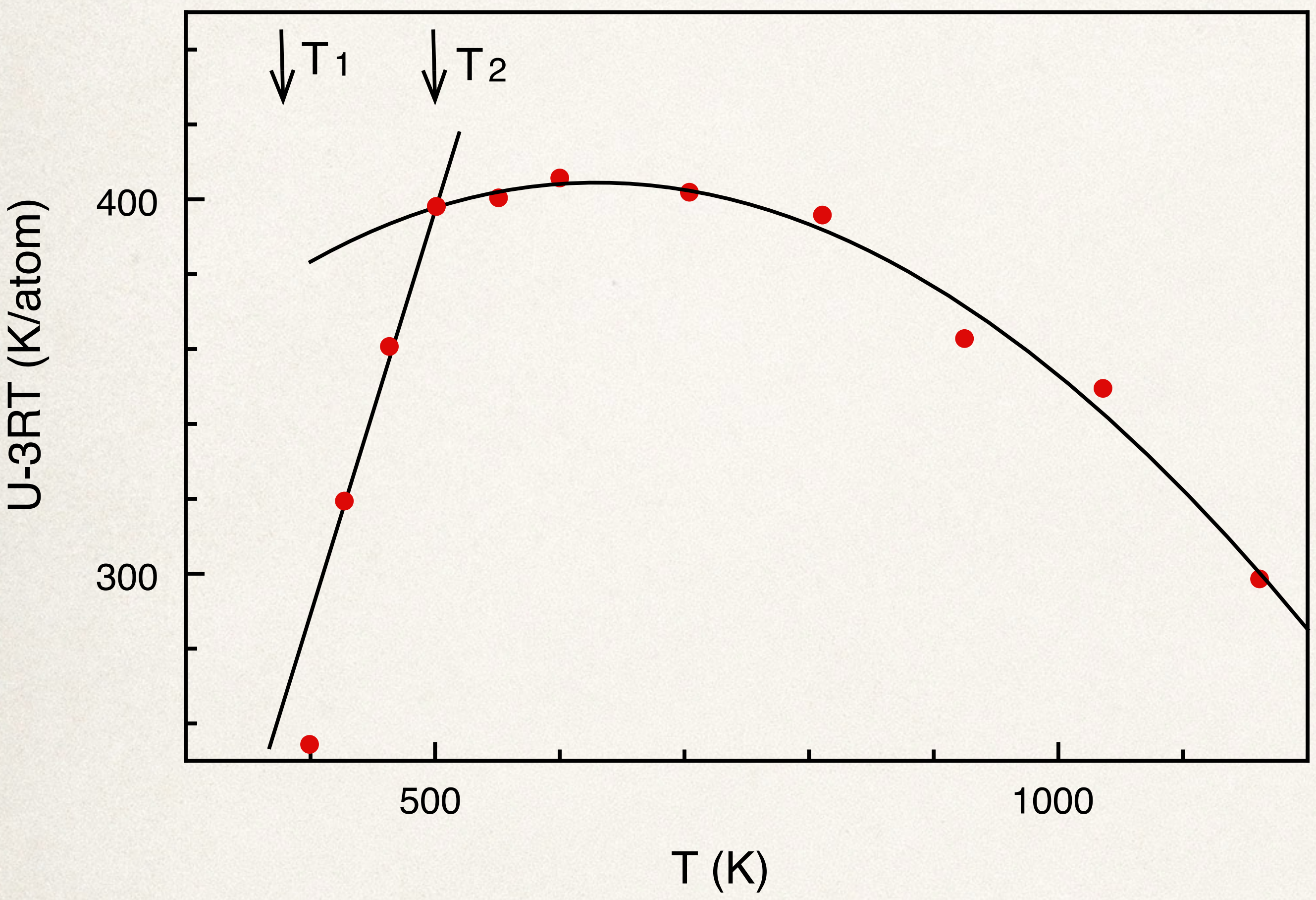


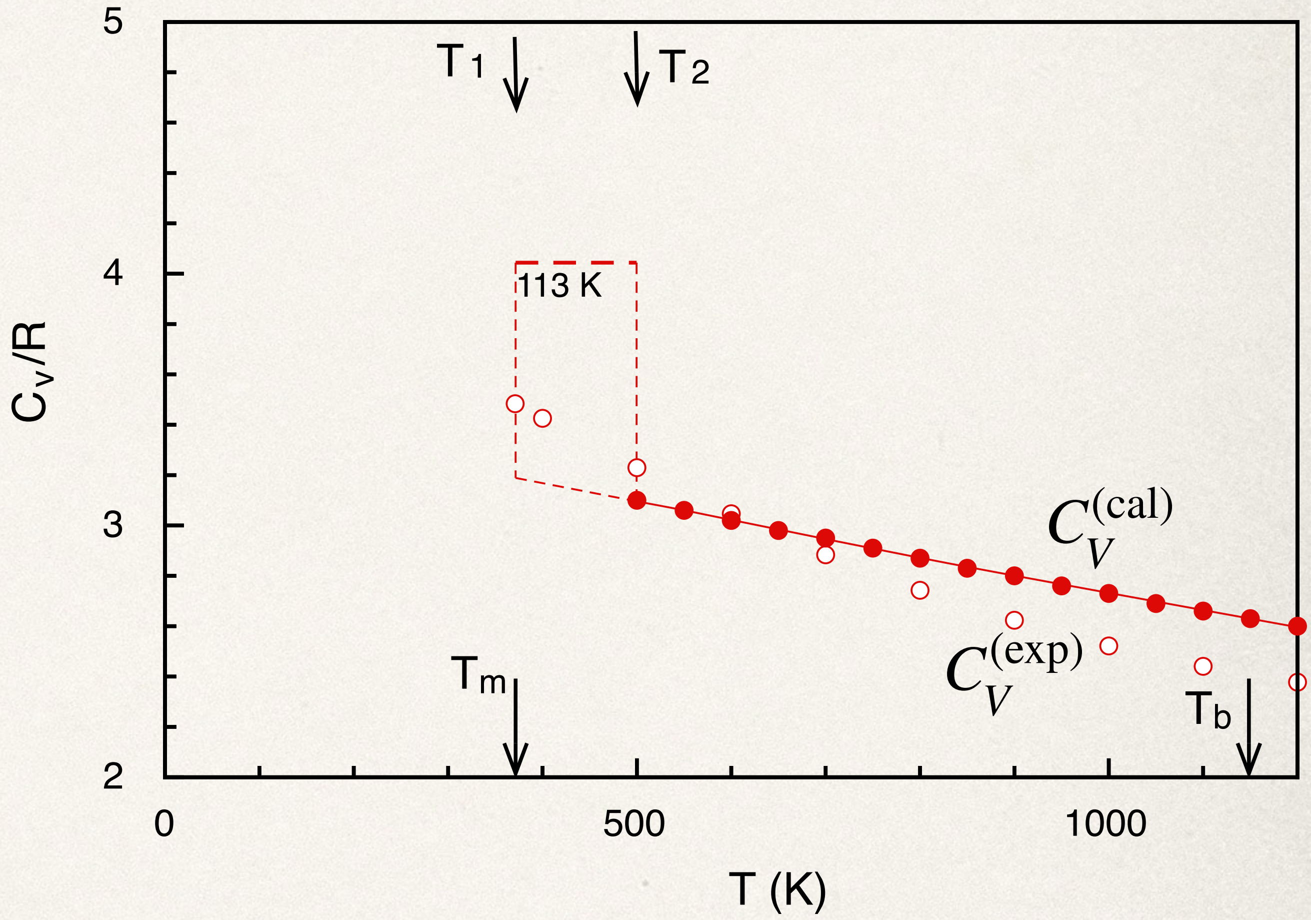


$$C_V = C_{\mathrm{ph}} + C_{\mathrm{st}}$$

Expt.) C. B. Alcock, M. W. Chase, and V. P. Itkin, J. Phys. Chem. Ref. Data **23**, 385 (1994).

Specific heat of liquid





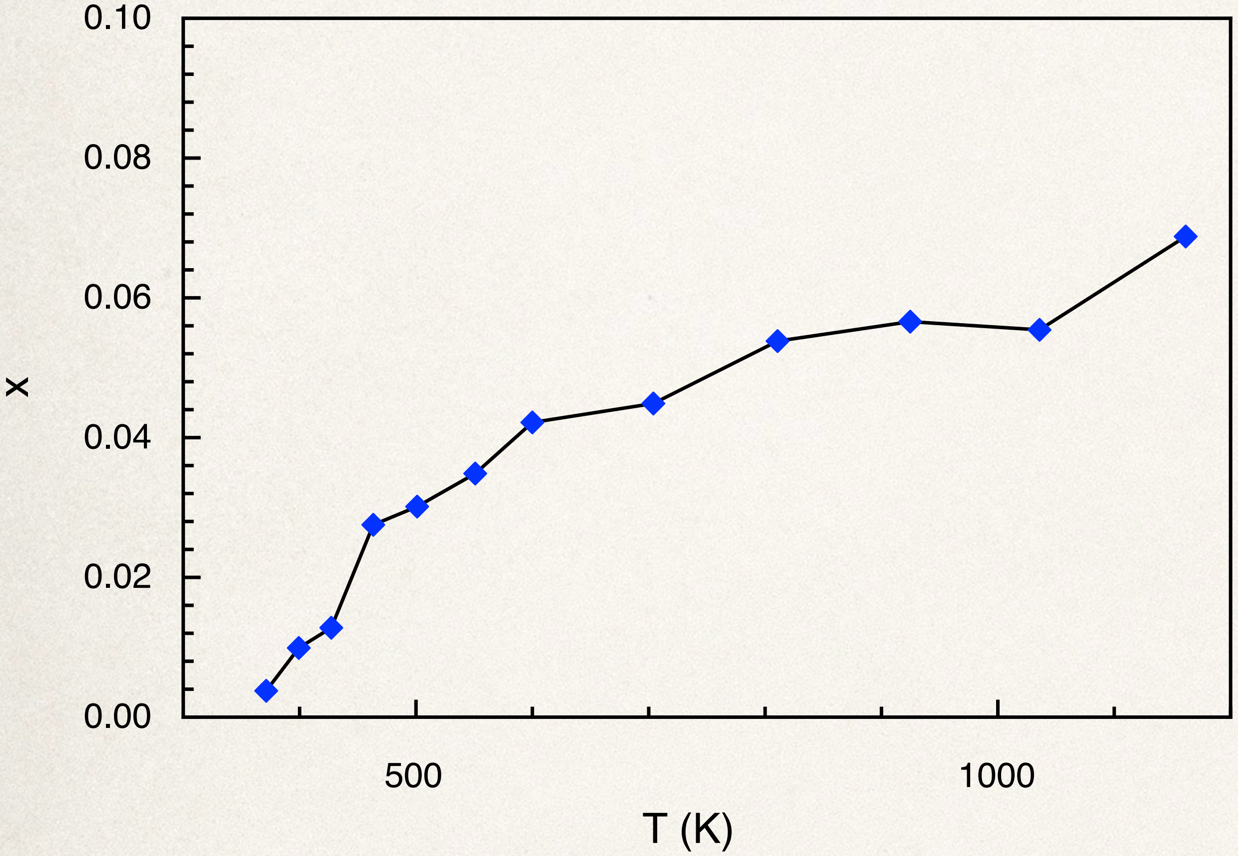
fitted by

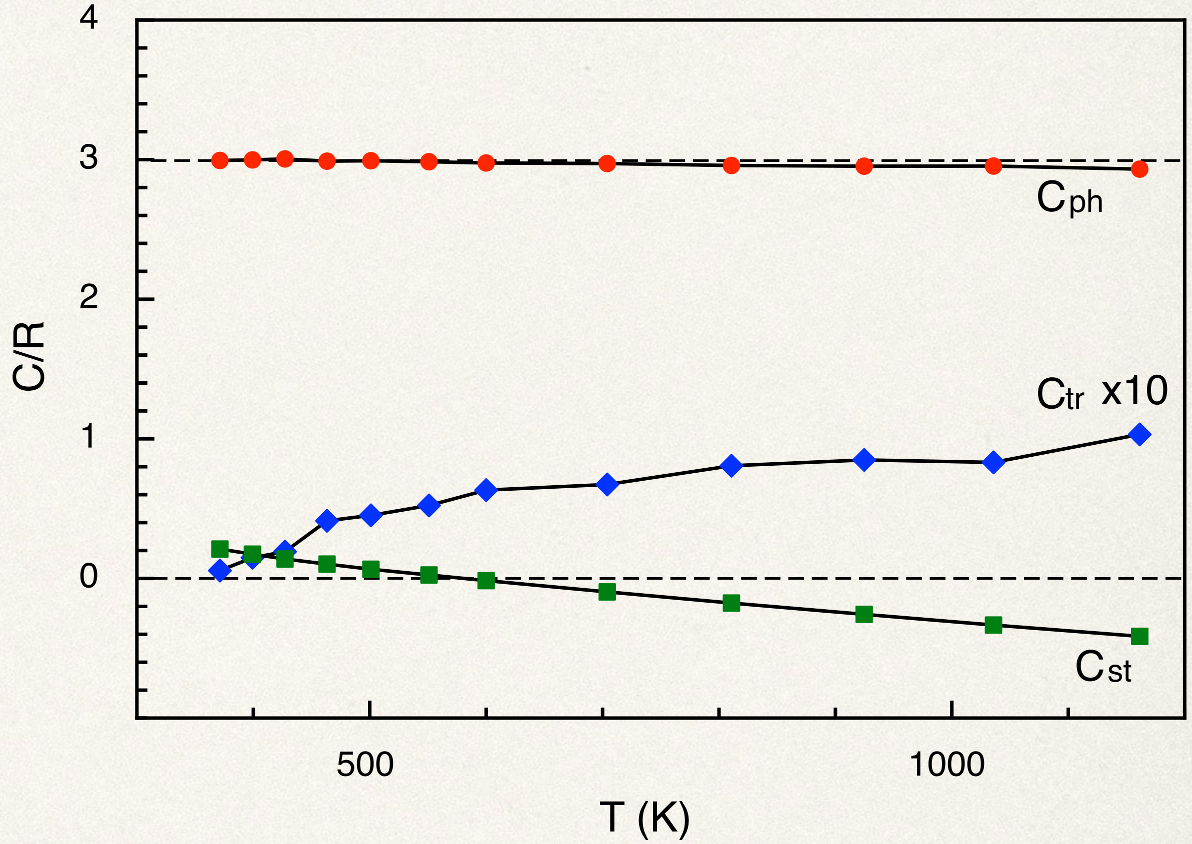
$$U(T) = a_0 + a_1 T + a_2 T^2$$

Exp) J. K. Fink and L. Leibowitz, *Thermodynamic and Transport Properties of Sodium Liquid and Vapor*, Argonne National Laboratory Report, 1995, ANL-RE-95/2.

Temperature dependence on C_V

Zero-frequency components of phonons





$$g(\omega) = \frac{1}{3N\frac{3}{2}k_{\mathrm{B}}T}\sum_{j}^{3N}\frac{1}{2}M_j f^*_{v_j}(\omega) f_{v_j}(\omega)$$

$$\int g(\omega)d\omega = 1$$

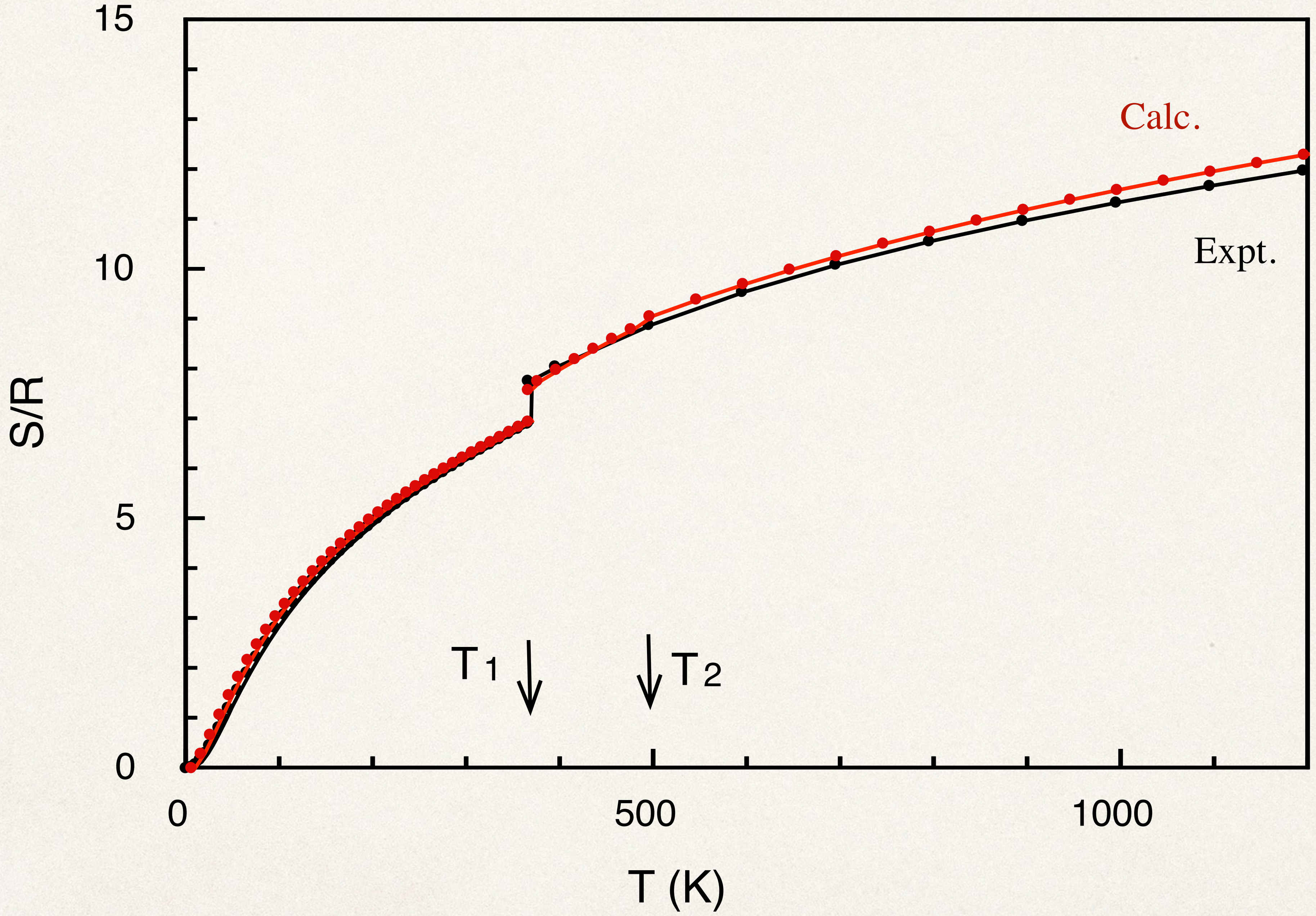
$$\int_{\omega>0} g(\omega)d\omega = 1 - x$$

$$C_V = C_{\mathrm{st}} + C_{\mathrm{tr}} + C_{\mathrm{ph}}$$

$$U = E_{\mathrm{st}} + \underset{\frac{3}{2}x}{\underline{E_{\mathrm{tr}}}} + \underset{\frac{6}{2}(1-x)}{\underline{E_{\mathrm{ph}}}}$$

in unit $k_{\mathrm{B}}T$

Entropy



Expt.)
C. B. Alcock, M. W. Chase, and V. P. Itkin, J. Phys. Chem. Ref. Data **23**, 385 (1994).

Summary

It has been demonstrated that entropy of a liquid can be obtained by the adiabatic relaxation method.

The calculation of the specific heat of the liquid Na reproduced the observed decrease in C_v as T increases.

→ The effect of energy dissipation but not the phonon effect.

The BE statistics should not be applied to excitations in liquids.

K. Shirai, H. Momida, K. Sato, and S. Hyun, *First-principles calculation of the entropy of liquids with a case study on sodium*, arXiv:2411.10930