PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 30:

Quantum effects in statistical mechanics

Reading: Chapter 7 (mostly 7.5)

1. **Statistical mechanics of lattice vibrations**
2. **Other Bose systems**
3. **Bose condensate**

PHYSICS COLLOQUIUM

4 PM

THURSDAY

●

APRIL 15, 2021

“Programming with DNA Outside Living Cells: From Gene Circuits to Self-Assembly”

Cell-free transcription-translation (TXTL) has become a highly versatile experimental environment to construct biochemical systems *in vitro* by executing either natural or synthetic gene circuits. In particular, TXTL enables interrogating biochemical systems quantitatively and in isolation far from the complexity of real living cells. I will present several experiments that my lab has done recently using an all-*E. coli* TXTL system. First, I will present this TXTL system, what it is, what it does. In the second part of my talk, I will show examples of dynamical systems directed by gene circuits executed either in test tubes or in microfluidic chips. In the last part of the talk I will show how we construct synthetic cell systems using TXTL and how synthetic cells are convenient to uncover and quantify fundamental aspects of supramolecular assembly.

Dr. Vincent Noireaux

School of Physics and
Nanotechnology (PAN)
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Minneapolis, MN

21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	#18	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions	#20	03/31/2021
25	Wed: 03/31/2021	App. A & Chap. 7.1	Quantum mechanical effects	#21	04/02/2021
26	Fri: 04/02/2021	Chap. 7.1-7.2	Quantum mechanical effects		
27	Mon: 04/05/2021	Chap. 7.3	Bose and Fermi statistics	#22	04/09/2021
	Wed: 04/07/2021	No class	*Holiday*		
28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 8.1	Interacting particles		
33	Wed: 04/21/2021	Chap. 8.2	Spin magnetism		
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

Your questions –
From Kristen -- 1. Could you highlight the difference between high frequency and low frequency modes?
2. Do we approximate the cube using a whole sphere or simply a quarter of a sphere as shown in figure 7.27?
3. What does the Debye temperature represent physically?

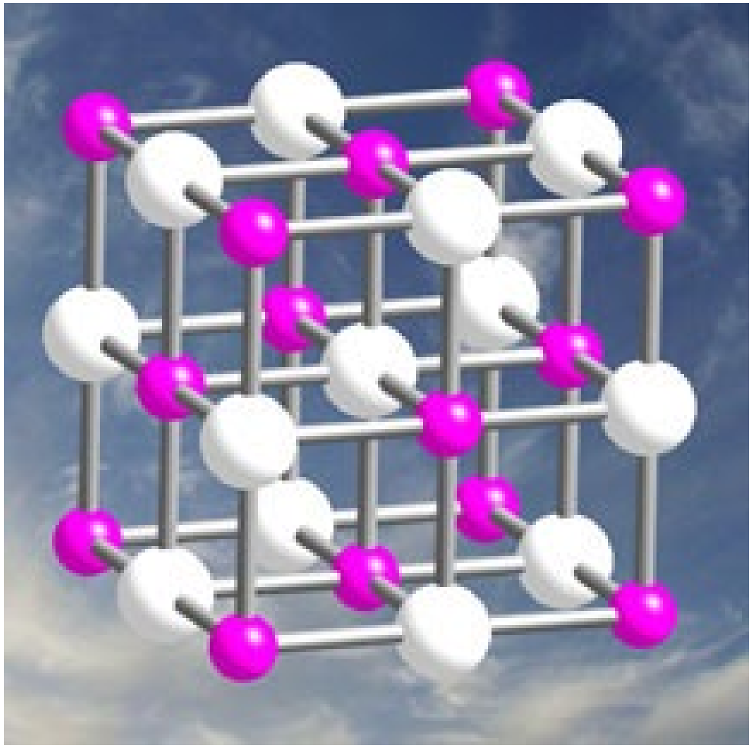
From Noah -- Can you explain the actual meaning of n and n_max? I am having trouble understanding it's physical meaning in crystals and the waves shown in Figure 7.26.

Comment – We will analyze the equations in a somewhat different way by first introducing the notion of density of states for the phonon modes, similar to the treatment of ideal gasses as we did previously.

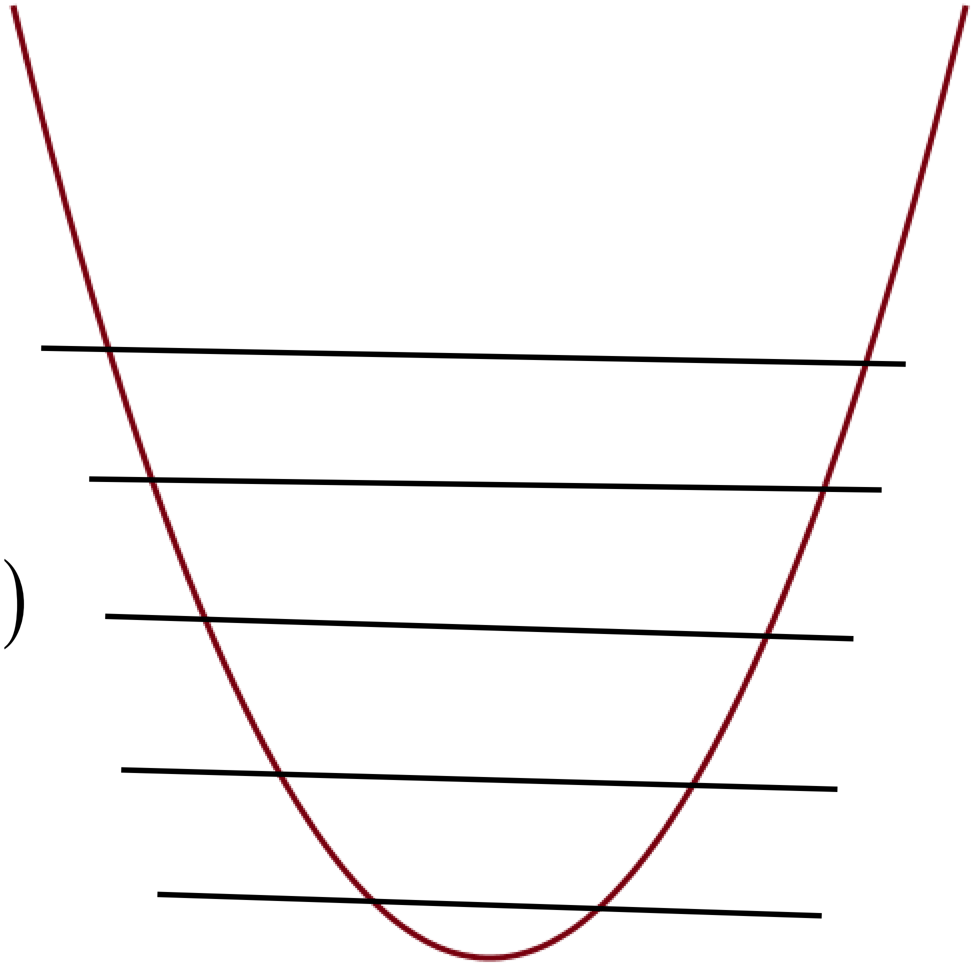
What do vibrations have to do with Bose statistical mechanics?

1. Nothing.
2. Similar mathematics.
3. Physicists never are will to let a beautiful equation go unused.

Image of equilibrium geometry of crystal:



In practice, each of the 3N atoms in the crystal oscillates about its equilibrium position with various characteristic frequencies $\omega^\nu(\mathbf{k})$ depending on wavevector **k** mode number ν.



For each mode $\omega^{\nu}(\mathbf{k})$ there is a harmonic oscillator potential with quantum mechanical eigenvalues $\hbar\omega^{\nu}(\mathbf{k})\left(n+\frac{1}{2}\right)$ for $n = 0,1,2,\ldots.$

In this case, the quantum numbers for each mode n=0,1,2… are not constrained so that the canonical partition function can be evaluated and it is a good approximation to assume that mode ν at each wave vector **k** is independent --

$$Z(T) = \prod_{\nu} \prod_{\mathbf{k}} \left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega^{\nu}(\mathbf{k})(n+\frac{1}{2})} \right)$$

$$= \prod_{\nu} \prod_{\mathbf{k}} \left(\frac{e^{-\beta\hbar\omega^{\nu}(\mathbf{k})/2}}{1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}} \right)$$

$$F(T) = -kT\ln\big(Z(T)\big) = \sum_{\nu\mathbf{k}} \left(\frac{\hbar\omega^{\nu}(\mathbf{k})}{2} + kT\ln\left(1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}\right) \right)$$

$$= \sum_{\nu\mathbf{k}} \left(kT\ln\left(2\sinh\left(\frac{\beta\hbar\omega^{\nu}(\mathbf{k})}{2} \right) \right) \right)$$

Note that even at T=0, vibrations contribute to the Helmholtz free energy. This is called zero point motion.

Thermodynamic functions for vibrations

$$F(T)=\sum_{\nu\mathbf{k}}\left(\frac{\hbar\omega^{\nu}(\mathbf{k})}{2}+kT\ln\left(1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}\right)\right)$$

$$S(T)=-\left(\frac{\partial F}{\partial T}\right)_V=\sum_{\nu\mathbf{k}}\left(-k\ln\left(1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}\right)+\frac{\hbar\omega^{\nu}(\mathbf{k})}{T}\frac{1}{1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}}\right)$$

$$U(T)=F(T)+TS=\sum_{\nu\mathbf{k}}\left(\hbar\omega^{\nu}(\mathbf{k})\left(\frac{1}{2}+\frac{1}{1-e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}}\right)\right)$$

$$C_V(T)=\left(\frac{\partial U}{\partial T}\right)_V=\frac{1}{kT^2}\sum_{\nu\mathbf{k}}\left(\left(\hbar\omega^{\nu}(\mathbf{k})\right)^2\frac{e^{\beta\hbar\omega^{\nu}(\mathbf{k})}}{\left(e^{\beta\hbar\omega^{\nu}(\mathbf{k})}-1\right)^2}\right)$$

Note that at high T such that $\beta\hbar\omega^{\nu}(\mathbf{k})<<1$ for all modes,

$$C_V(T\rightarrow\infty)\approx k\sum_{\nu\mathbf{k}}(1)=3Nk$$

How can we evaluate these quantities? Again, it is convenient to calculate the density of states for the vibrational modes. For this various units can be used for the vibrational frequencies such as the following --

In practice, it is convenient to express frequencies in wavenumbers:

$$\tilde{\omega} = \frac{\omega}{2\pi c}\ (\mathrm{cm}^{-1}) \quad \text{with} \quad F_{vib}(T) = \int_0^\infty d\tilde{\omega}\, f_{vib}(\tilde{\omega}, T)$$

where the weighted phonon DOS factor is

$$f_{vib}(\tilde{\omega}, T) \equiv k_B T \ln\left(2\sinh\left(\frac{hc\tilde{\omega}}{2k_B T}\right)\right) g(\tilde{\omega})$$

Here $g(\tilde{\omega}) = \frac{V}{(2\pi)^3}\sum_{\nu}\int d^3k\,\delta\left(\tilde{\omega} - \tilde{\omega}^{\nu}(\mathbf{k})\right)$ with $\int_0^\infty d\tilde{\omega}\, g(\tilde{\omega}) = 3N$

Plot of lattice vibration modes for diamond plotted for various wavevectors

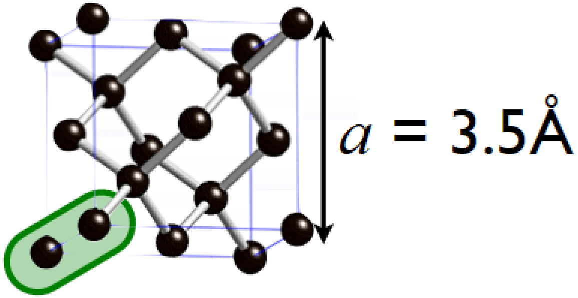
https://th.fhi-berlin.mpg.de/th/Meetings/DFT-workshop-Berlin2009/Talks/OnlinePublication/0630-4T_20090630-1_FH_-_phonon_tutorial_talk_web.pdf

Felix Hanke & Martin Fuchs
June 30, 2009

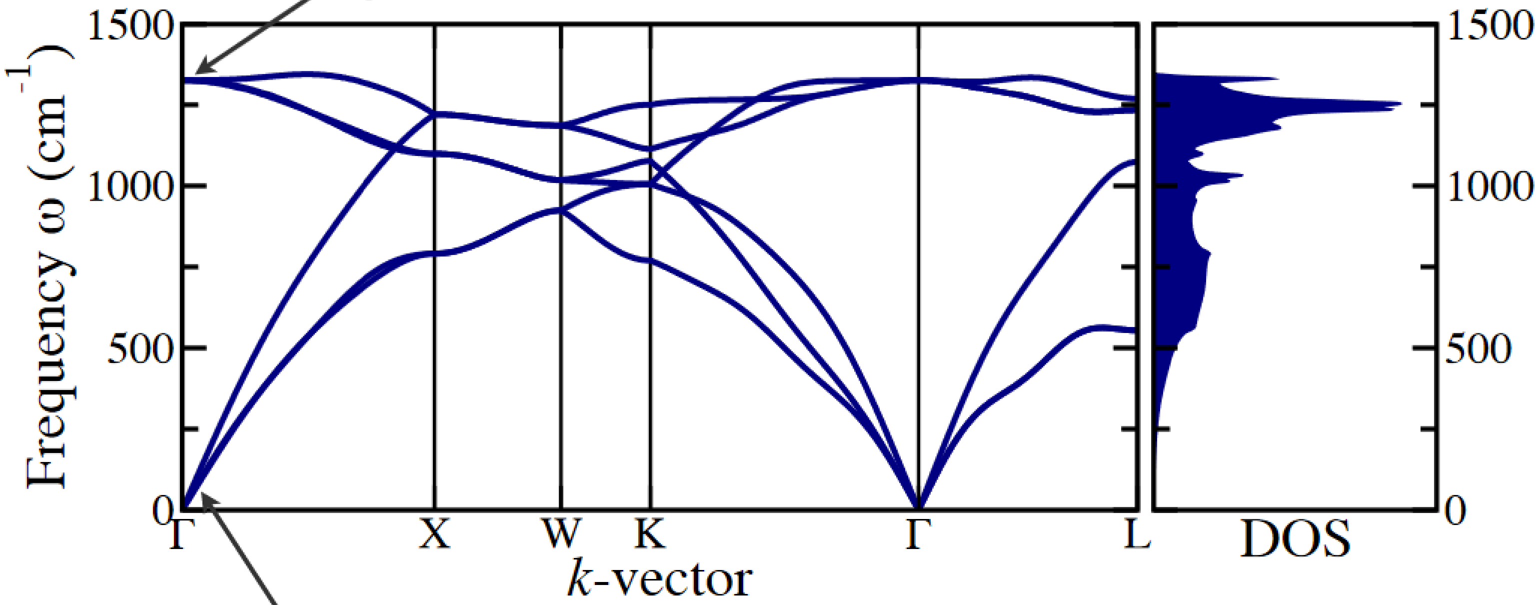
Phonon dispersion relation

Diamond

fcc conventional cell
2 atoms per primitive cell
= 6 phonon branches

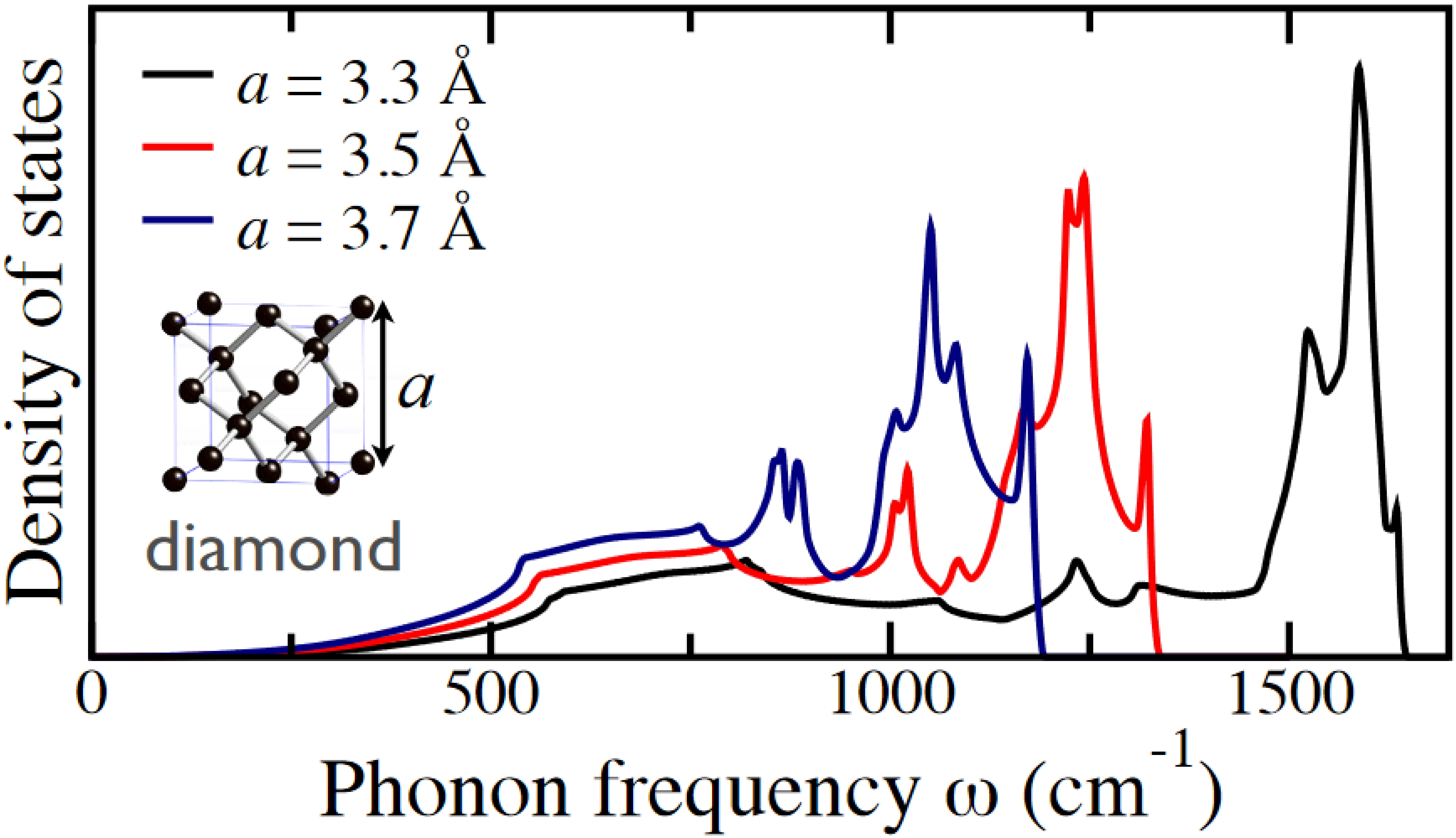


optical branches



acoustic branches

g(ε)   plots from previously cited presentation showing how the density of states is very sensitive to volume (lattice constant)

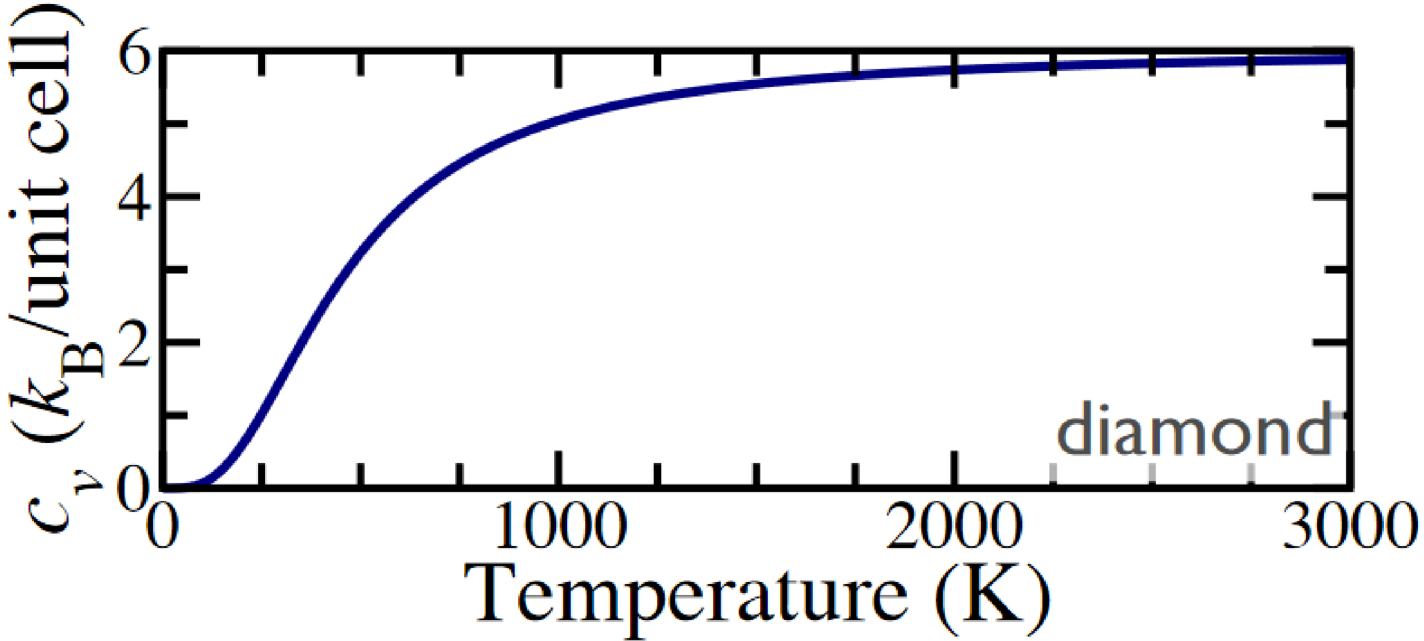


Heat capacity: c_V

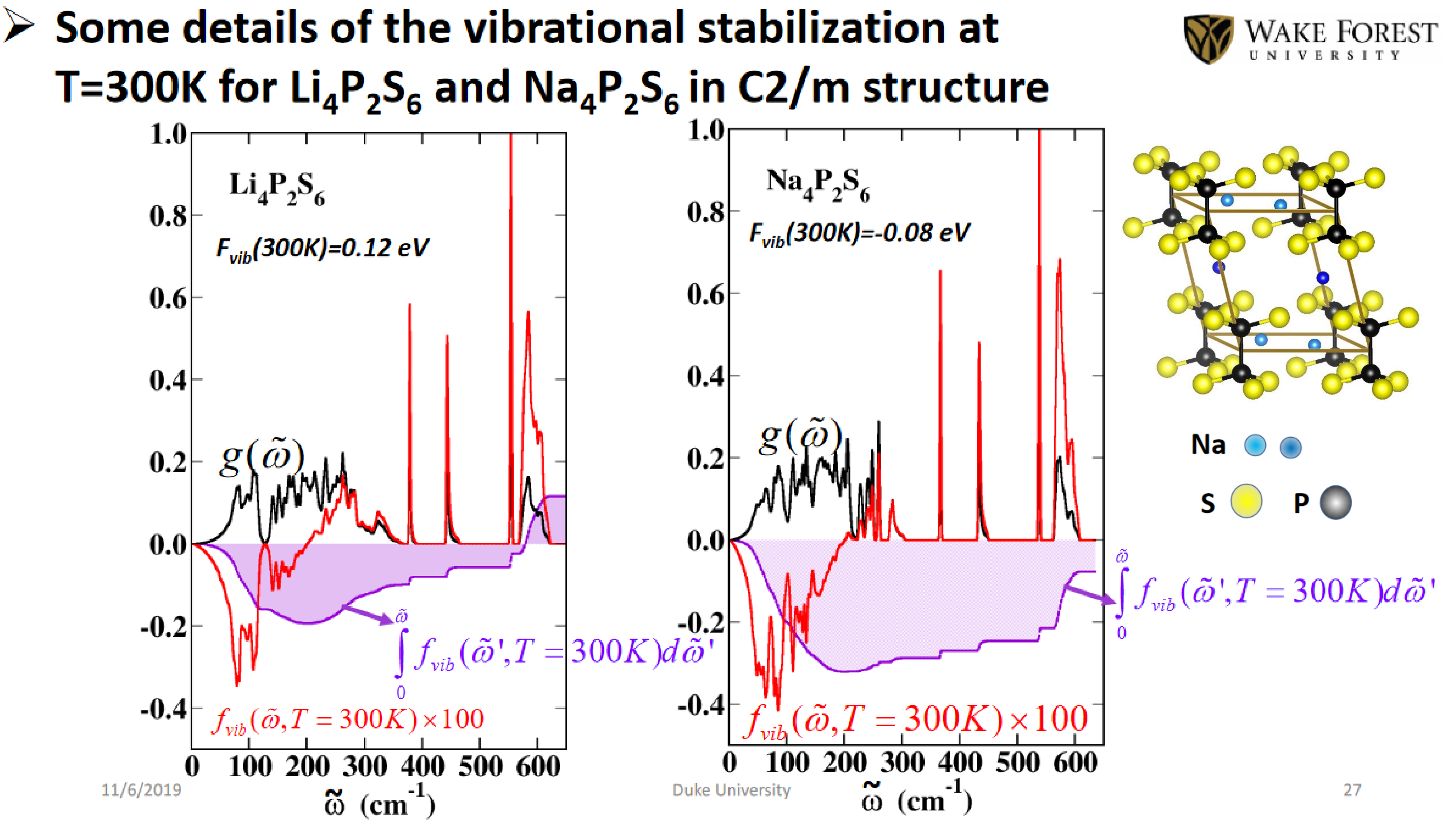
Computed from free energy

From Hanke & Fuckes (continued)

$$
\begin{aligned}
c_v(T) &= T\left.\frac{\mathrm{d}S}{\mathrm{d}T}\right|_V = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_V \\
&= \int \mathrm{d}\omega\; g(\omega)\frac{(\hbar\omega)^2}{k_\mathrm{B}T^2}\frac{\exp(\hbar\omega/k_\mathrm{B}T)}{(\exp(\hbar\omega/k_\mathrm{B}T)-1)^2}
\end{aligned}
$$



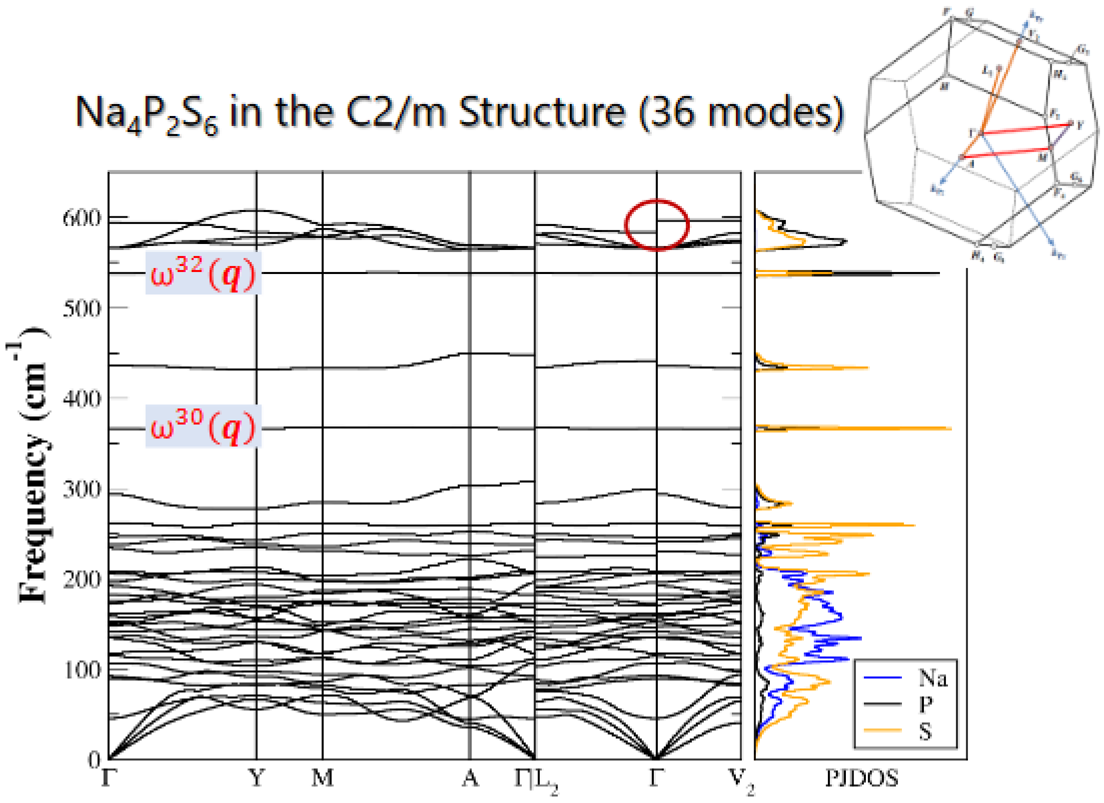
Example from a recent paper by graduate student Yan Li



- **Some details of the vibrational stabilization at T=300K for $Li_4P_2S_6$ and $Na_4P_2S_6$ in C2/m structure**

Representation of the phonon modes

$Na_4P_2S_6$ in the C2/m Structure (36 modes)



Na^+ 0~300 cm^{-1}

$(P_2S_6)^{4-}$ 300~600 cm^{-1}

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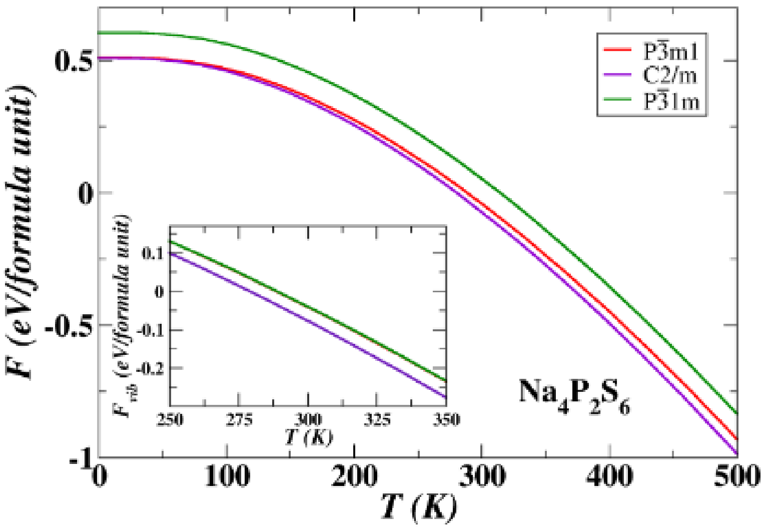
[1] Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)

[2] Li et al., *J. Phys. Condens. Matter,* **32,** 055402 (2020)

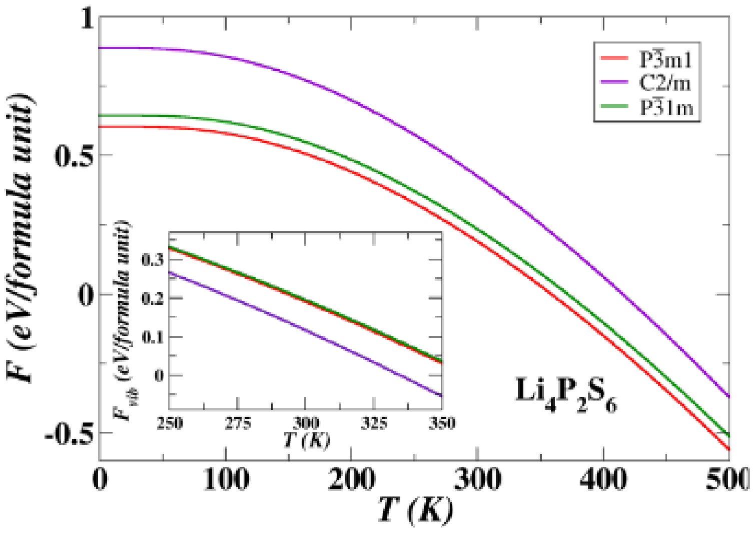
Helmholtz free energy: $F = U_{SL} + F_{vib}$



U_{SL}: $P\bar{3}m1 = C2/m < P\bar{3}1m$

F_{vib}: $C2/m < P\bar{3}m1 = P\bar{3}1m$

→ **F_{lowest}: C2/m (expt.[1,2])**



U_{SL}: $P\bar{3}m1 < P\bar{3}1m < C2/m$

F_{vib}: $C2/m < P\bar{3}m1 = P\bar{3}1m$

→ **F_{lowest}: $P\bar{3}m1$ (expt.[3])**

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[1] Kuhn et al., *Z. Anorg. Allg. Chem.* **640**, 689-692 (2014)

[2] Hood et al., *J. Solid State Ionics* **284**, 61 (2016)

[3] Neuberger et al., *Dalton Trans.* **47**, 11691-11695 (2018)

In this study, the estimate of the phonon contributions to the Helmholtz free energy helped explain why the two similar materials take different structural forms at room temperature.

Back to the general equations

Calculation of the heat capacity:

$$C_V(T) = \frac{1}{kT^2} \sum_{\nu \mathbf{k}} \left(\left(\hbar\omega^{\nu}(\mathbf{k})\right)^2 \frac{e^{\beta\hbar\omega^{\nu}(\mathbf{k})}}{\left(e^{\beta\hbar\omega^{\nu}(\mathbf{k})} - 1\right)^2} \right)$$

Introducing density of states:

$$g(\epsilon) = \frac{V}{(2\pi)^3} \sum_{\nu} \int d^3k \delta\left(\epsilon - \hbar\tilde{\omega}^{\nu}(\mathbf{k})\right) \quad \text{with} \quad \int_0^{\infty} d\epsilon \; g(\epsilon) = 3N$$

$$C_V(T) = \frac{1}{kT^2} \int_0^{\infty} d\epsilon \; g(\epsilon) \frac{\epsilon^2 e^{\beta\epsilon}}{\left(e^{\beta\epsilon} - 1\right)^2}$$

Debye model to approximate *g*(ε)

Based on the notion that at low frequency (ε) the vibrations behave like sound waves through the material with a characteristic speed *c.* (Note that this is the speed of sound not light!!!)   In more detail sound waves in different directions of the material can have different speeds, but we will characterize the average by *c.*

Density of states for Debye model

$$g_D(\epsilon) = \begin{cases} \dfrac{3V\epsilon^2}{2\pi^2\hbar^3c^3} & \text{for } \epsilon < kT_D \\ 0 & \text{for } \epsilon > kT_D \end{cases}$$

$$\text{where } \int_0^{kT_D} g_D(\epsilon)d\epsilon = 3N \qquad\qquad kT_D = 2\pi\hbar c\left(\frac{3N}{4\pi V}\right)^{1/3}$$

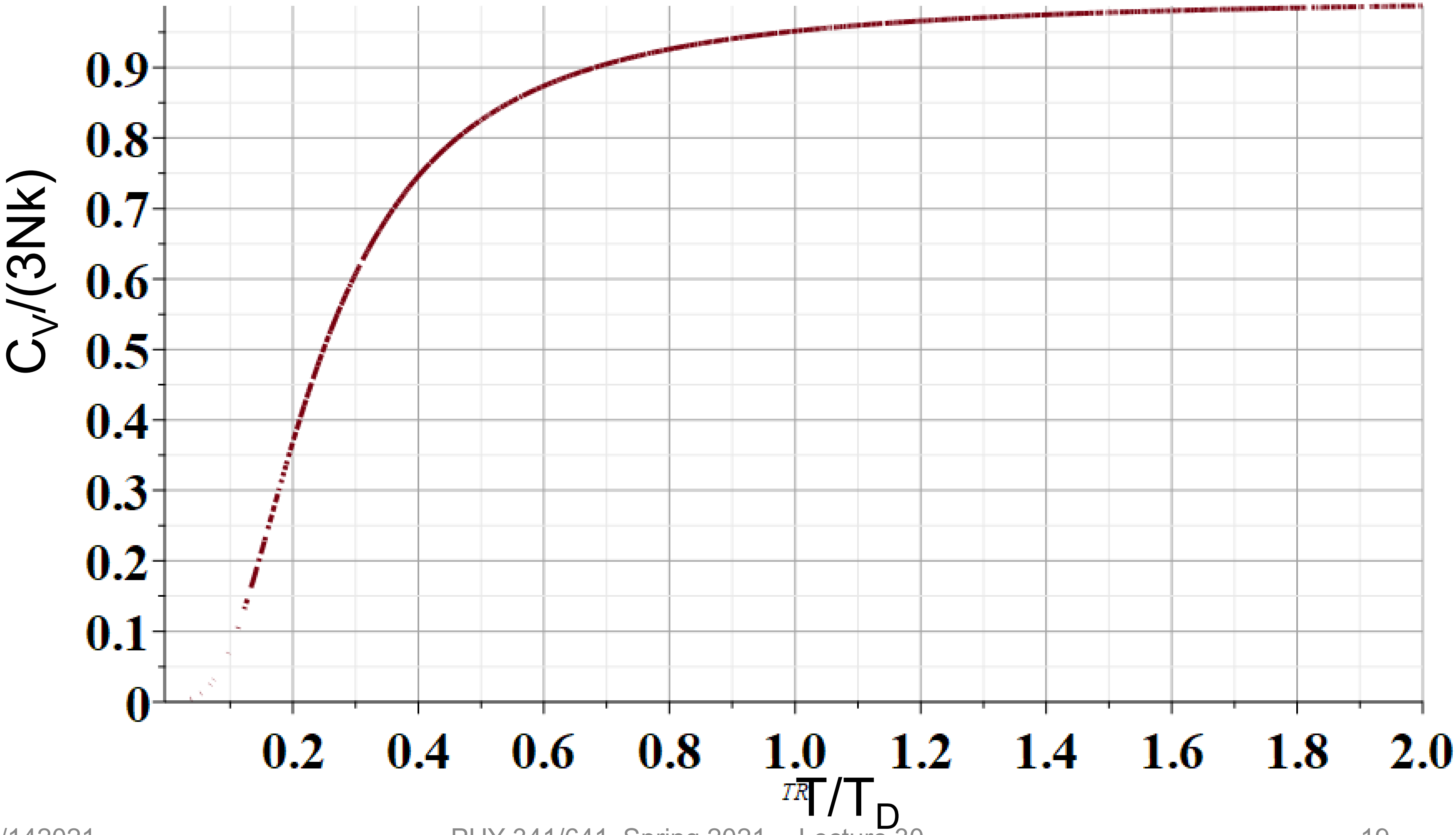
Evaluation of heat capacity in the Debye model

$$C_V(T) = \frac{1}{kT^2}\int_0^\infty d\epsilon\; g(\epsilon)\frac{\epsilon^2 e^{\beta\epsilon}}{\left(e^{\beta\epsilon}-1\right)^2} \approx \frac{1}{kT^2}\frac{3V}{2\pi^2\hbar^3c^3}\int_0^{kT_D} d\epsilon\;\; \frac{\epsilon^4 e^{\beta\epsilon}}{\left(e^{\beta\epsilon}-1\right)^2}$$

$$= \; k^4T^3\frac{3V}{2\pi^2\hbar^3c^3}\int_0^{T_D/T} dx\;\; \frac{x^4e^x}{\left(e^x-1\right)^2} \qquad \text{where } kT_D = 2\pi\hbar c\left(\frac{3N}{4\pi V}\right)^{1/3}$$

$$= 9Nk\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T} dx\;\; \frac{x^4e^x}{\left(e^x-1\right)^2}$$

$$C_V(T)=9Nk\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}dx\ \frac{x^4e^x}{\left(e^x-1\right)^2}$$



Some typical values of T_D

Material	**T_D (K)**
Na (metal)	150
C (diamond)	1860
Fe (metal)	420