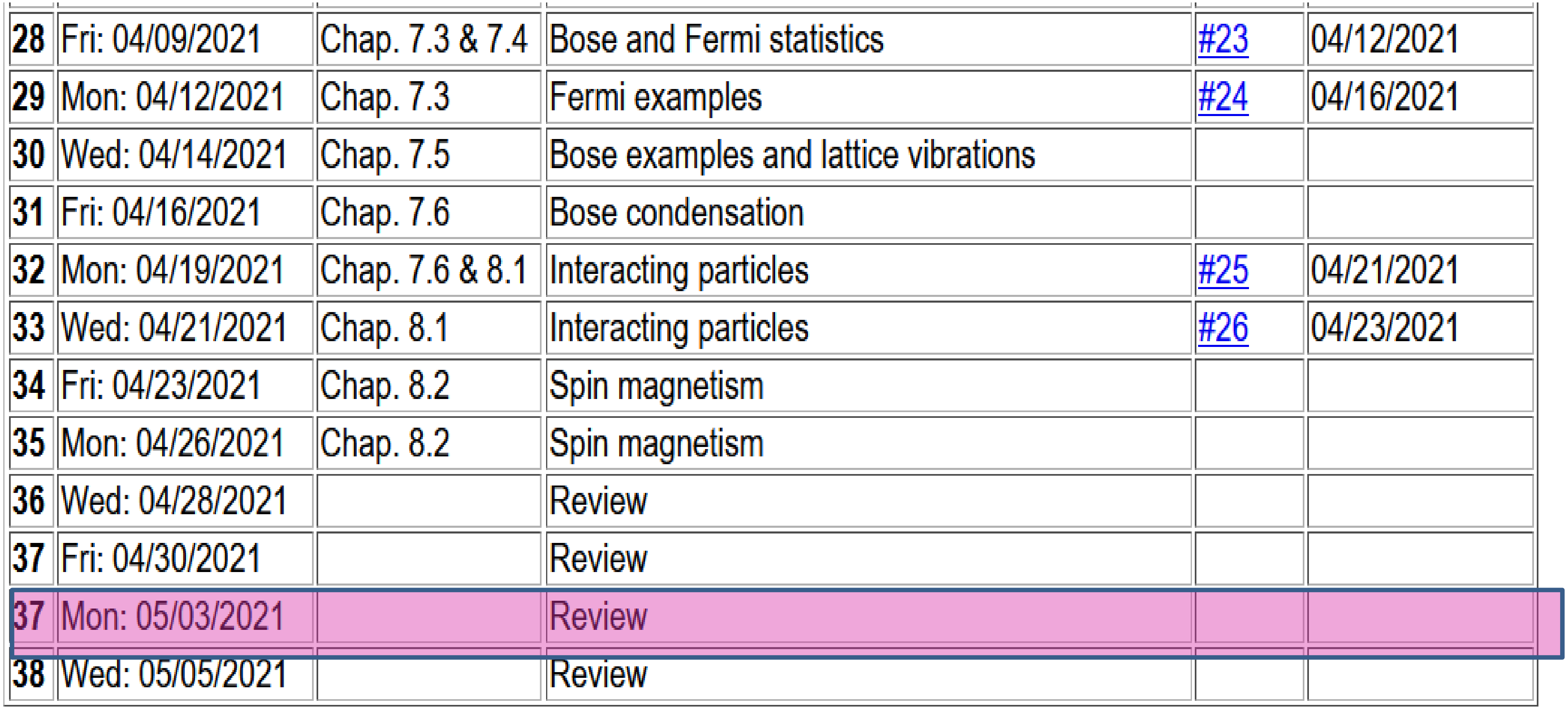
PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 38:

Review Part 3

1. **Ideal gas containing a mixture of particles**
2. **Effects of particle interactions**
3. **Phase equilibria**
4. **Chemical equilibria**



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. 7.6 & 8.1	Interacting particles	#25	04/21/2021
33	Wed: 04/21/2021	Chap. 8.1	Interacting particles	#26	04/23/2021
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		

Important dates: Final exams available < May 6; due May 14
Outstanding work due May 14

Generalizing the thermodynamic functions for a single component system --

Internal energy	$U = U(S,V,N)$	$dU = TdS - PdV + \mu dN$
Entropy	$S = S(U,V,N)$	$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H = H(S,P,N) = U + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz energy	$F = F(T,V,N) = U - ST$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G = G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$

It is useful to consider systems containing several components $N \rightarrow N_1, N_2, ...$ where N_i denotes particles of type "i". For the moment, we are assuming that no reactions (chemical, nuclear, etc.) occur.

Generalizing thermodynamic functions to multi-component systems --

It is useful to consider systems containing several components $N \rightarrow N_1, N_2, ...$ where N_i denotes particles of type "i". For the moment, we are assuming that no reactions (chemical, nuclear, etc.) occur.

Entropy: $S(U,V,N_1,N_2,...)$ $\quad dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i$ where $T\left(\frac{\partial S}{\partial N_i}\right)_{U,V,\{N_j j\neq i\}} = \mu_i$

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,\{N_j j\neq i\}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,\{N_j j\neq i\}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,\{N_j j\neq i\}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,\{N_j j\neq i\}}$$

Internal energy $\quad U = U(S,V,\{N_i\}) \quad dU = TdS - PdV + \sum_i \mu_i dN_i$

Enthalpy $\quad H = H(S,P,\{N_i\}) = U + PV \quad dH = TdS + VdP + \sum_i \mu_i dN_i$

Helmholtz energy $\quad F = F(T,V,\{N_i\}) = U - ST \quad dF = -SdT - PdV + \sum_i \mu_i dN_i$

Gibbs free energy $\quad G = G(T,P,\{N_i\}) = F + PV \quad dG = -SdT + VdP + \sum_i \mu_i dN_i$

Thermodynamics of mixing -- first consider a two-component (binary) system $N_A=N(1-x)$ $N_B=xN$

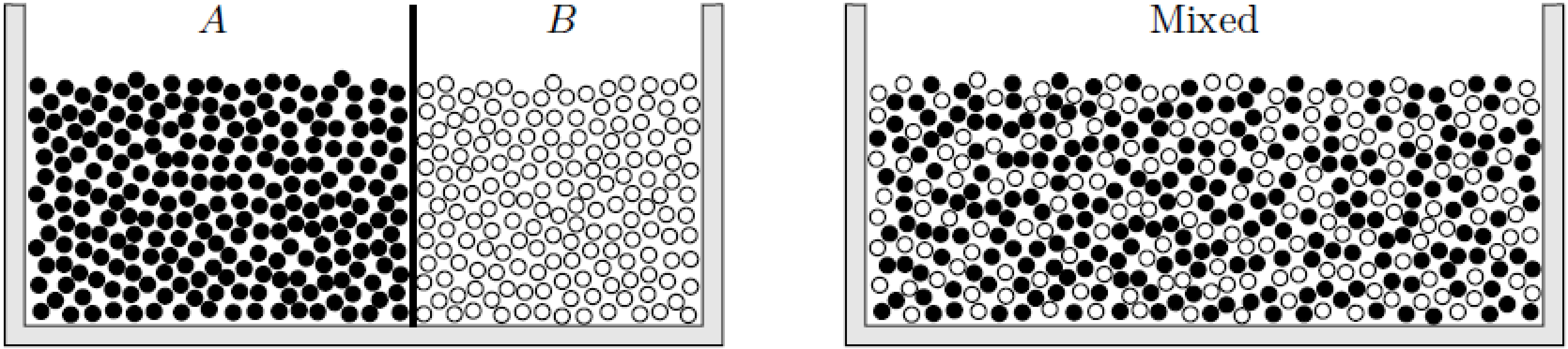


Figure 5.24. A collection of two types of molecules, before and after mixing. Copyright ©2000, Addison-Wesley.

Separated system

$$G(T,P,N,x)=(1-x)G_A(T,P,(1-x)N)+xG_B(T,P,xN)$$

Mixed system depends on details of system even if no chemical reactions occur.

Possible mixing behaviors.

Consider the case of the monoatomic ideal gas for which we derived the Gibbs free energy expression:

$$G(T,P,N) = -NkT\left(\ln\left(\frac{kT}{P}\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\right)\right) = -NkT\ln\left(\frac{T^{5/2}}{P}\right) + G_0$$

P independent constant

For binary example -- system $N_A=N(1-x)$ $N_B=xN$

For the case of separated gases, both at pressure P:

$$G_{separated} = -NkT\ln\left(\frac{T^{5/2}}{P}\right) + (1-x)G_{0A} + xG_{0B}$$

Notion of partial pressure when the gases are mixed -- $P_A + P_B = P$

$P_A = (1-x)P \qquad\qquad P_B = xP$

$$G_{mixed} = -(1-x)NkT\ln\left(\frac{T^{5/2}}{(1-x)P}\right) - xNkT\ln\left(\frac{T^{5/2}}{xP}\right) + (1-x)G_{0A} + xG_{0B}$$

$$G_{mixed} - G_{separated} = NkT\left(\left(1-x\right)\ln(1-x) + x\ln x\right)$$

Also note that $S_{mixed} - S_{separated} = -\left(\frac{\partial\left(G_{mixed} - G_{separated}\right)}{\partial T}\right)_{P,N,x}$

$$= -Nk\left(\left(1-x\right)\ln(1-x) + x\ln x\right)$$

Ideal mixing of binary system --

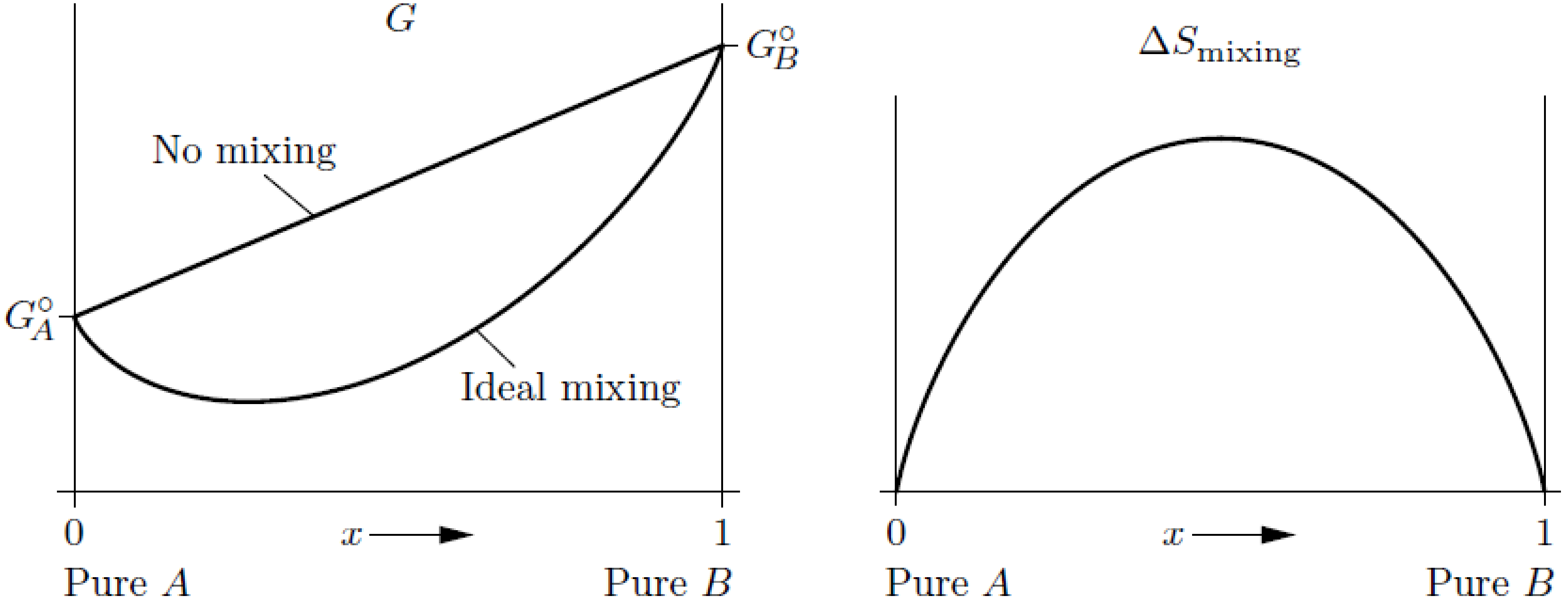
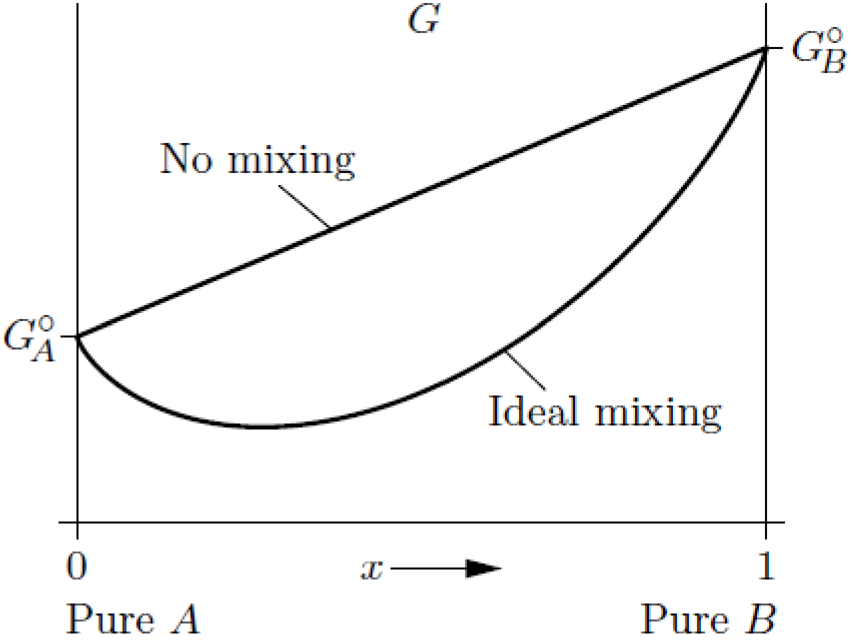


Figure 5.25. Before mixing, the free energy of a collection of A and B molecules is a linear function of $x = N_B/(N_A + N_B)$. After mixing it is a more complicated function; shown here is the case of an "ideal" mixture, whose entropy of mixing is shown at right. Although it isn't obvious on this scale, the graphs of both ΔS_{mixing} and G (after mixing) have vertical slopes at the endpoints. Copyright ©2000, Addison-Wesley.



Given this plots, which configuration is more favorable?

a. A and B separate
b. A and B ideally mixed

Question –

What might the analysis of the mixing differ for the Helmholtz free energy?

What physics is the ideal gas model missing?

$$\mathcal{H}_{ideal} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i}$$

$$\mathcal{H}_{real} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i} + \Phi\left(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N\right)$$

- At low density, pairwise potential effects can be estimated in terms of the virial coefficient
- More generally, the potential effects can be treated with idealized models or numerically

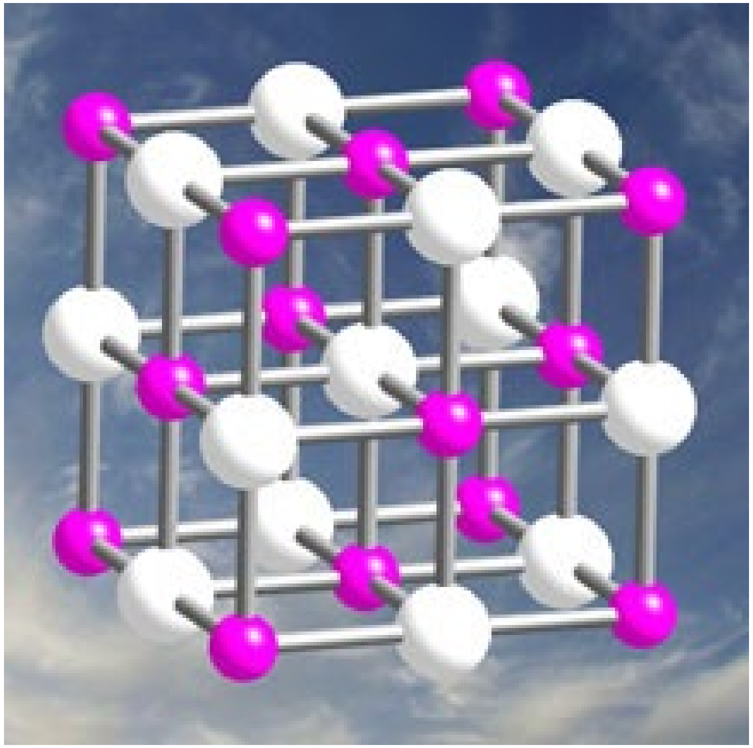
Properties of matter due to particle interactions

1. Different phases of matter
   a. Gas
      - **Have discussed ideal gas and dilute gas approximations**
   b. Liquid
      - **Difficult for quantitative treatment**
   c. Solid (including various crystal forms)
      - **Reasonable analysis near equilibrium possible**
2. Reactions between particles
   - **Will discuss equilibrium reactions next time**

Thermo(static) analysis follow from the notion that at equilibrium, the thermodynamic potential function take its minimum value.

Treatment of the thermodynamics of lattice vibrations

Image of equilibrium geometry of crystal:



$$\mathcal{H}_{real} = \sum_{i=1}^{N} \frac{\left|\mathbf{p}_i\right|^2}{2m_i} + \Phi\left(\mathbf{r}_1, \mathbf{r}_2 \ldots. \mathbf{r}_N\right)$$

At equilibrium, $\left\{\mathbf{r}_1, \mathbf{r}_2 \ldots. \mathbf{r}_N\right\} \to \left\{\mathbf{r}_1^0, \mathbf{r}_2^0 \ldots. \mathbf{r}_N^0\right\}$

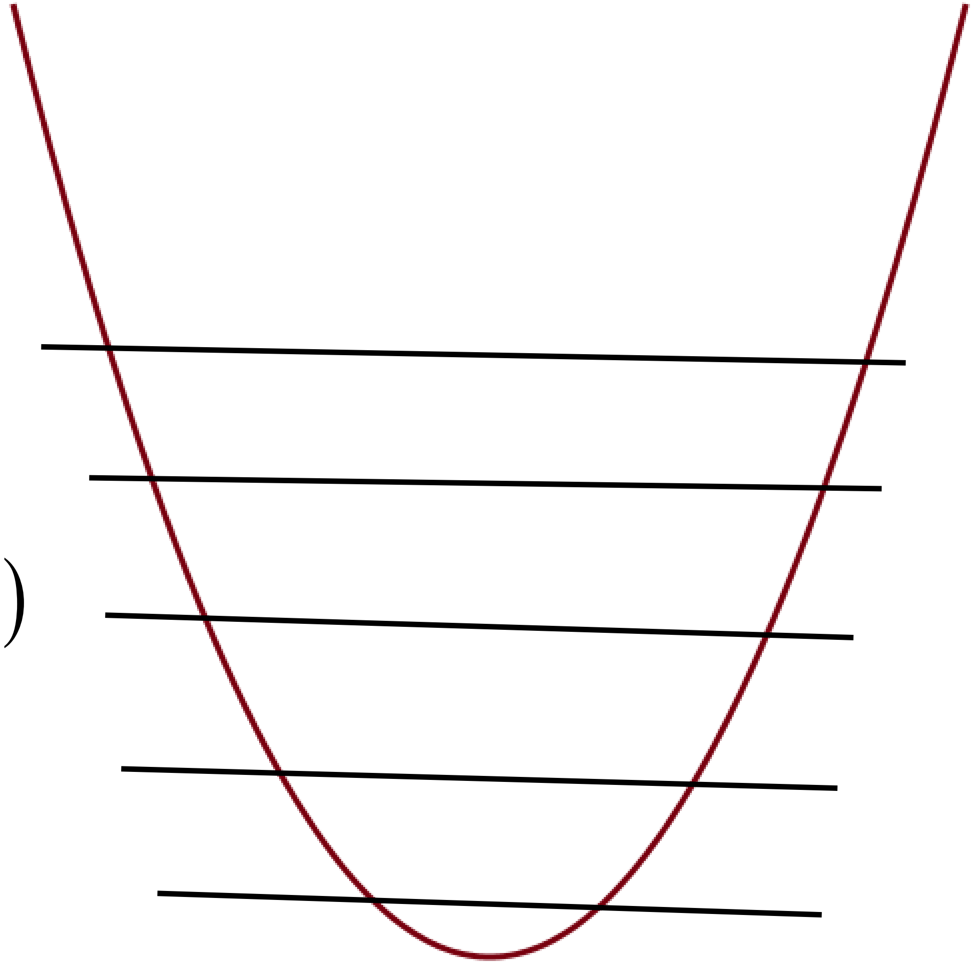
Near equilibrium, $\mathcal{H}_{real} \to \sum_{i=1}^{N} \frac{\left|\mathbf{p}_i\right|^2}{2m_i} + \Phi\left(\mathbf{r}_1^0, \mathbf{r}_2^0 \ldots. \mathbf{r}_N^0\right) + \frac{1}{2}\sum_{ij}\left(\mathbf{r}_i - \mathbf{r}_i^0\right) \cdot \frac{\partial^2 \Phi}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \cdot \left(\mathbf{r}_j - \mathbf{r}_j^0\right)$

Near equilibrium, $\mathcal{H}_{real} \rightarrow \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i} + \Phi\left(\mathbf{r}_1^0, \mathbf{r}_2^0 .... \mathbf{r}_N^0\right) + \frac{1}{2}\sum_{ij}\left(\mathbf{r}_i - \mathbf{r}_i^0\right) \cdot \frac{\partial^2 \Phi}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \cdot \left(\mathbf{r}_j - \mathbf{r}_j^0\right)$

Note that thanks to the Born-Oppenheimer approximation, the classical treatment of the interaction potential can be accomplished reasonably rigorously. However, the treatment of the atomic vibrations themselves should be treated quantum mechanically

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 $n = 0, 1, 2, \ldots.$



it is a good approximation to assume that mode ν at each wave vector **k** is independent. The quantum numbers for each mode n=0,1,2… are not constrained so that the canonical partition function involves a geometric summation

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

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

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

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

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

Thermodynamic functions for vibrations

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

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

$$U_{vib}(T) = F_{vib}(T) + TS_{vib} = \sum_{\nu\mathbf{k}} \left(\hbar\omega^{\nu}(\mathbf{k}) \left(\frac{1}{2} + \frac{1}{1 - e^{-\beta\hbar\omega^{\nu}(\mathbf{k})}} \right) \right)$$

$$C_{V\,vib}(T) = \left(\frac{\partial U_{vib}}{\partial T}\right)_V = \frac{1}{kT^2} \sum_{\nu\mathbf{k}} \left(\left(\hbar\omega^{\nu}(\mathbf{k})\right)^2 \frac{e^{\beta\hbar\omega^{\nu}(\mathbf{k})}}{\left(e^{\beta\hbar\omega^{\nu}(\mathbf{k})} - 1\right)^2} \right)$$

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

$$C_{V\,vib}(T \to \infty) \approx k \sum_{\nu\mathbf{k}} (1) = 3Nk$$

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:

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

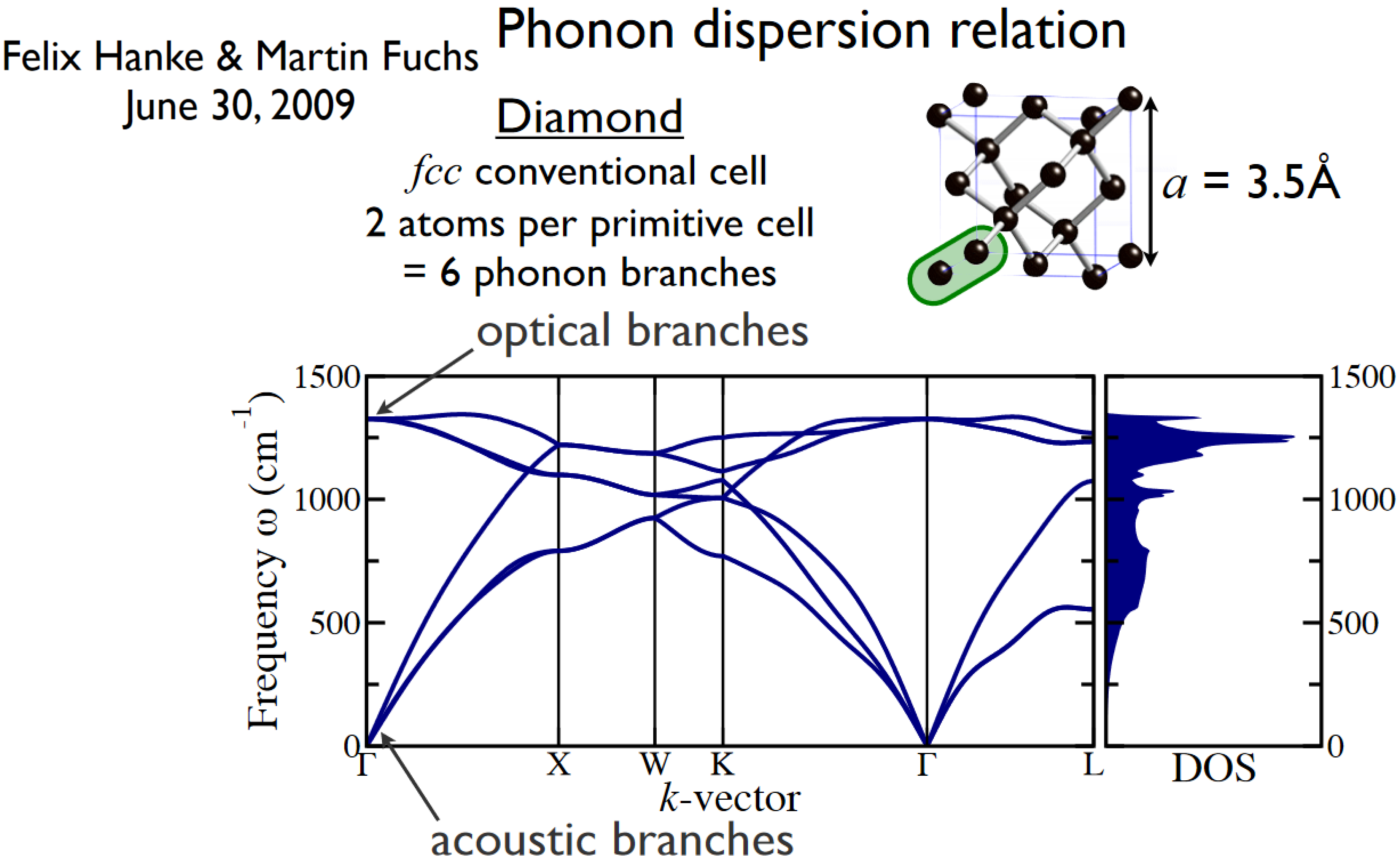
where the weighted phonon DOS factor is

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

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



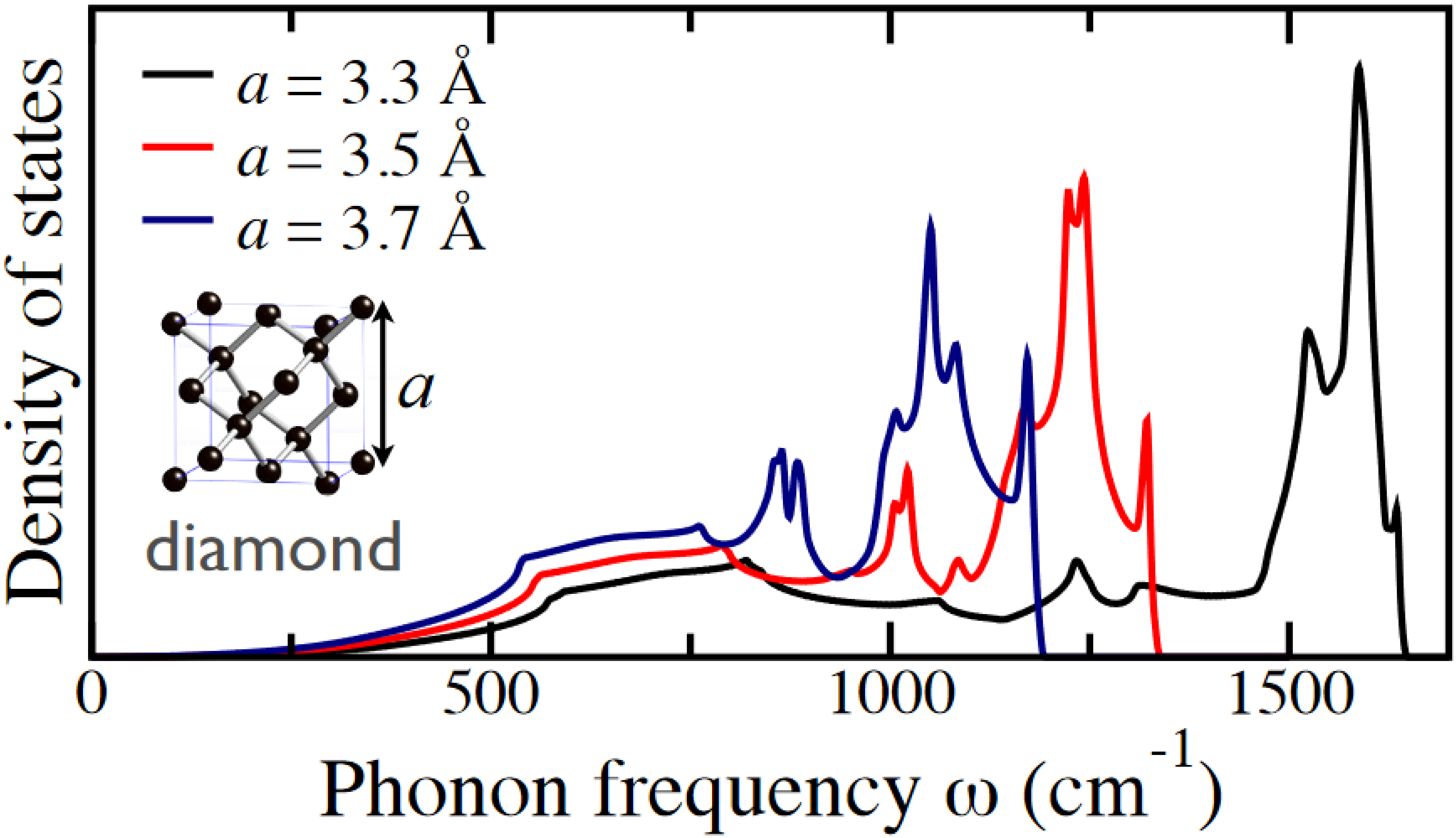
Felix Hanke & Martin Fuchs
June 30, 2009

Phonon dispersion relation

Diamond

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

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

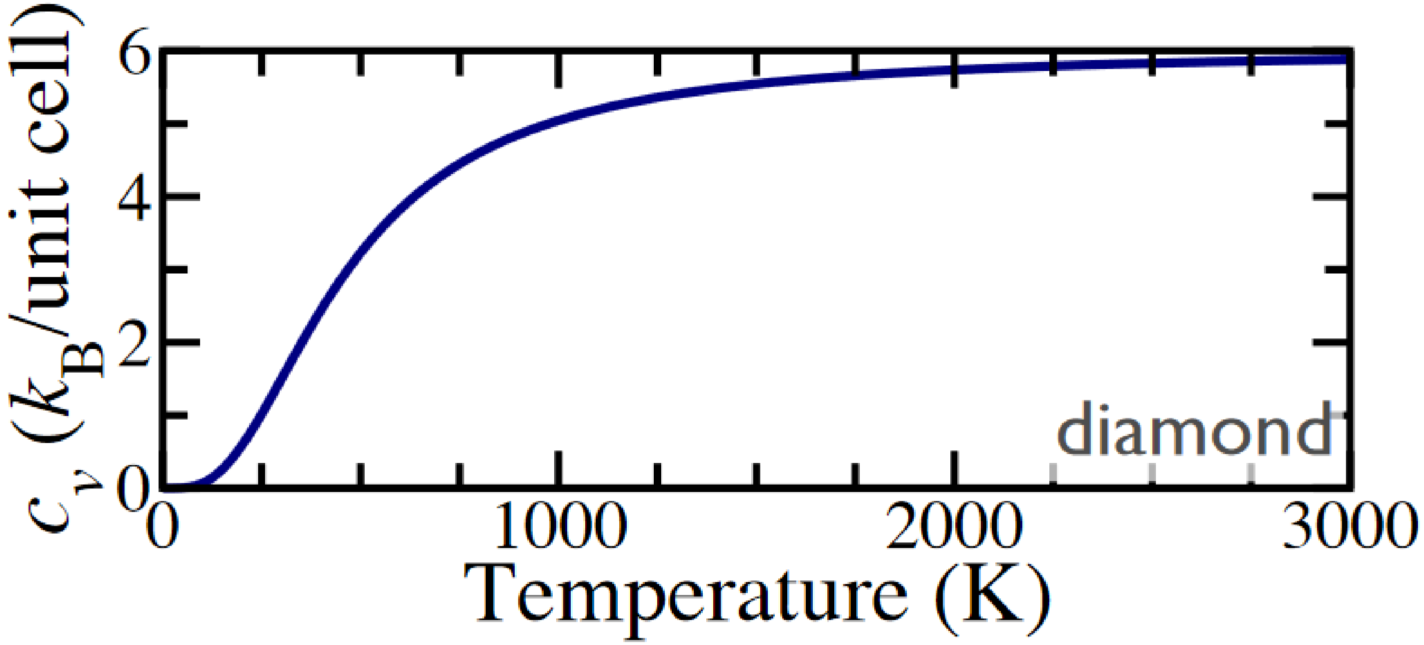


Heat capacity: c_V

Computed from free energy

From Hanke & Fuckes (continued)

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



Simple approximation to density of vibrational states --

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

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

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

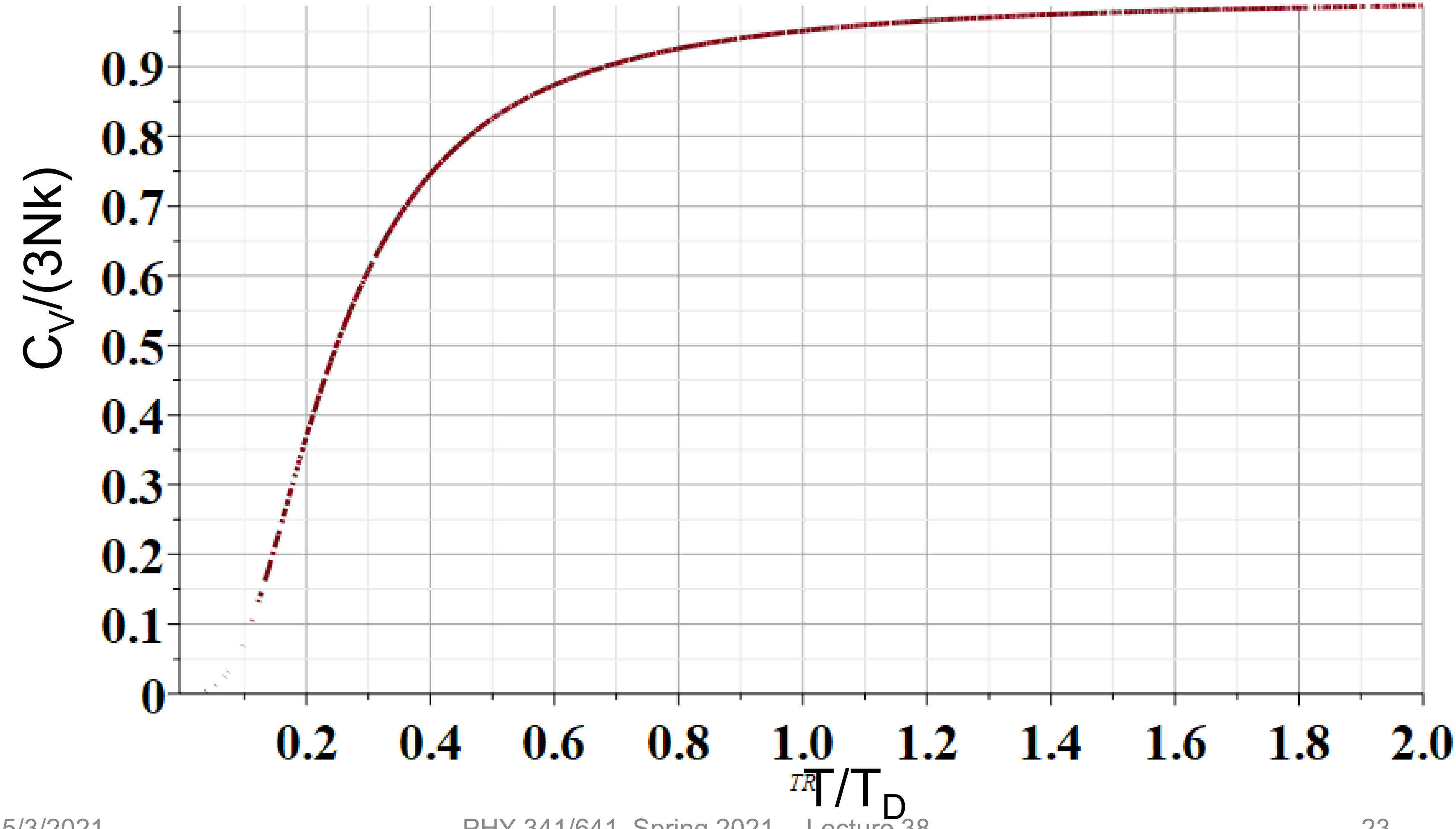
Evaluation of heat capacity in the Debye model

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

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

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

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



Some typical values of T_D

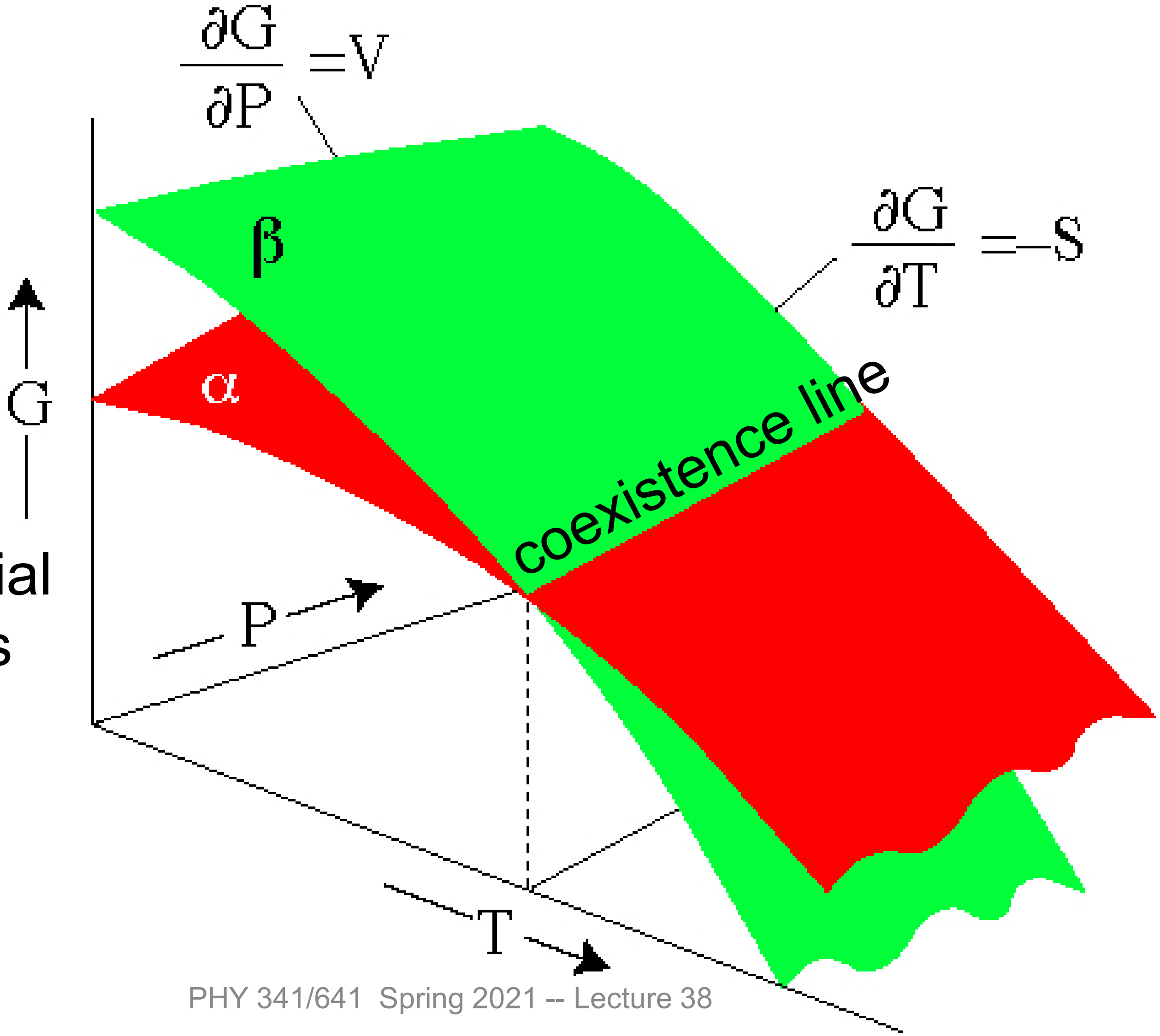
Material	**T_D (K)**
Na (metal)	150
C (diamond)	1860
Fe (metal)	420

While detailed analysis of interacting systems may not be always possible, the general rules of thermodynamics (thermostatics) still apply.

Some general principles of phase transitions --

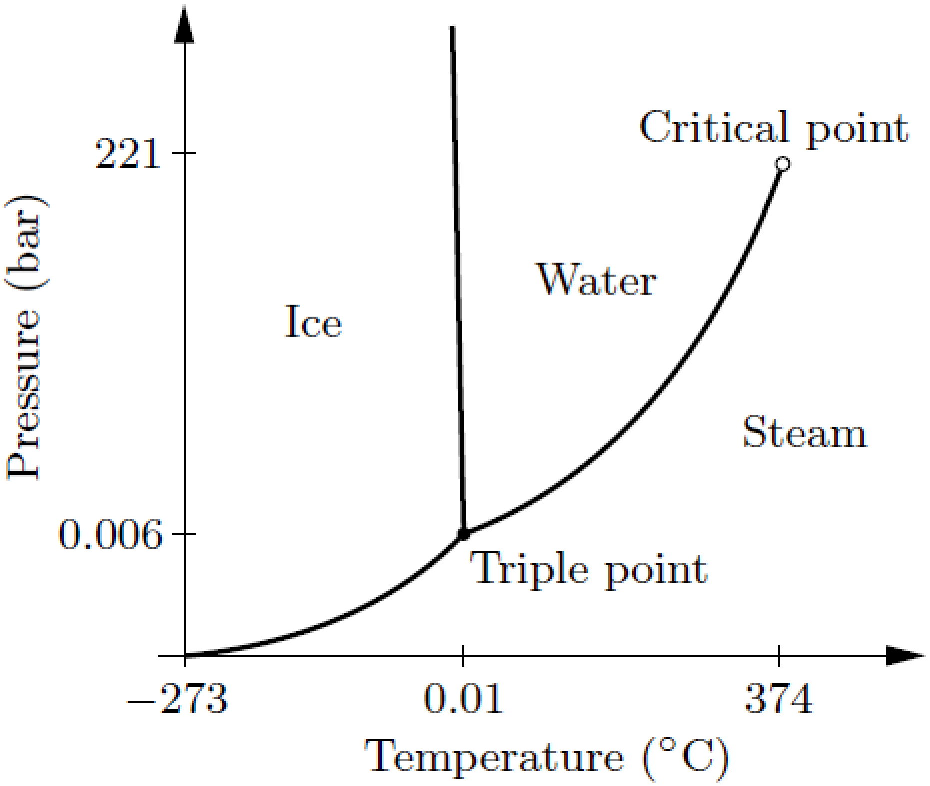
Behavior of Gibbs free energy for a material that changes phase

http://hacker.faculty.geol.ucsb.edu/geo124T/lecture.html



Example material that has phases α and β --

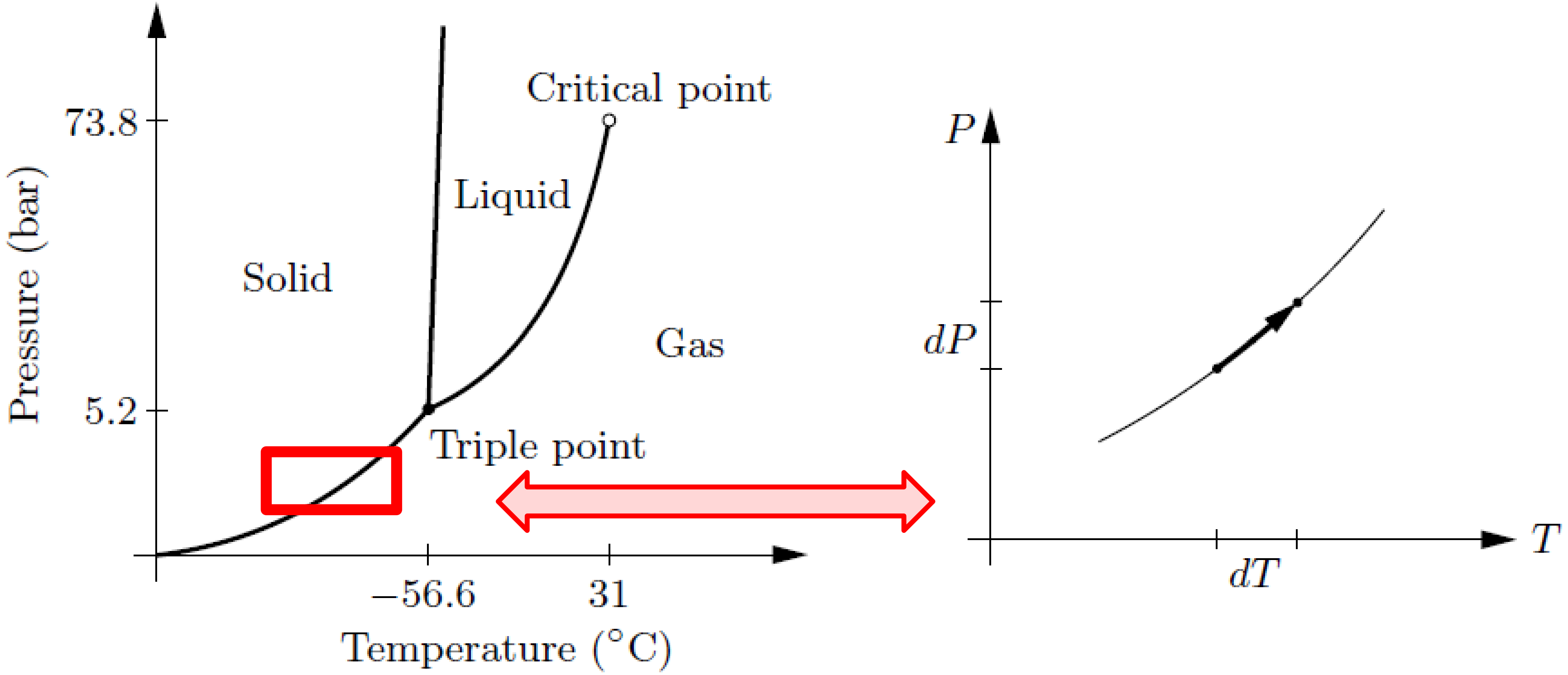
Coexistence lines as a function of T and P for phases of water



T (°C)	P_v (bar)	L (kJ/mol)
−40	0.00013	51.16
−20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994). Copyright ©2000, Addison-Wesley.

Analysis of coexistence curve – the Clausius-Clapeyron equation



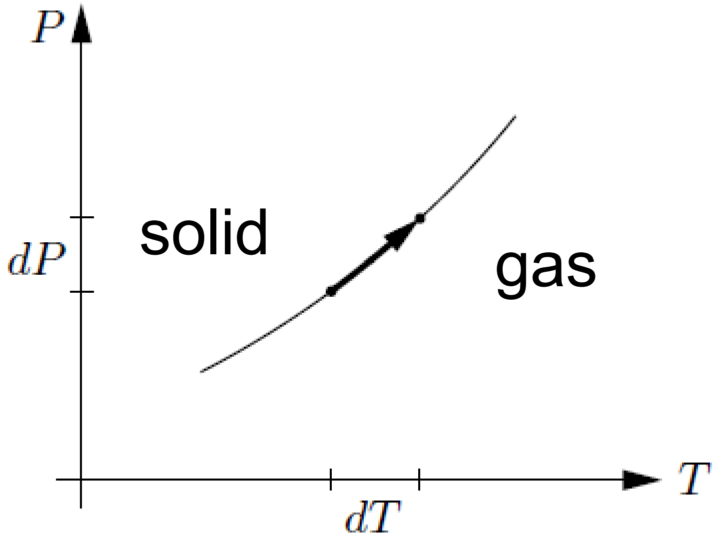
At the phase boundary: $G_{solid} = G_{gas}$

Along the coexistence curve (at fixed number of particles):

$$dG_{solid} = -S_{solid}\,dT + V_{solid}\,dP = dG_{gas} = -S_{gas}\,dT + V_{gas}\,dP$$

Slope of phase boundary line: $\dfrac{dP}{dT} = \dfrac{S_{gas} - S_{solid}}{V_{gas} - V_{solid}}$

Analysis of coexistence curve – the Clausius-Clapeyron equation



Slope of phase boundary line:

$$\frac{dP}{dT} = \frac{S_{gas} - S_{solid}}{V_{gas} - V_{solid}}$$

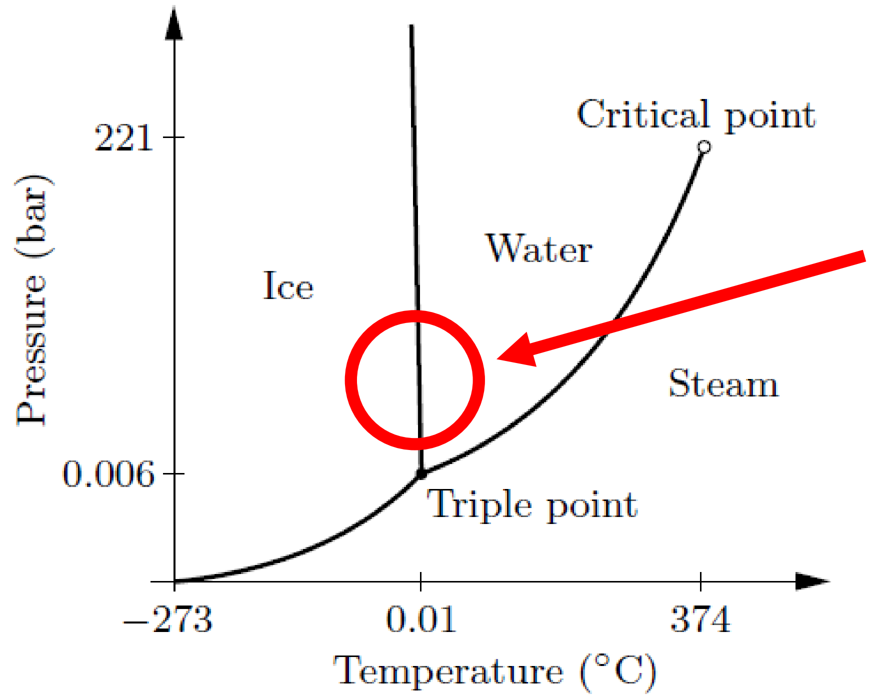
Define latent heat: $L \equiv T\left(S_{gas} - S_{solid}\right)$

$$\frac{dP}{dT} = \frac{L}{T\left(V_{gas} - V_{solid}\right)}$$

Clausius-Clapeyron equation

Example of Clausius-Clapeyron equation -- for water ice and liquid at T=273 K and P= 1 atm=1.01325 x 10^5 Pa

For 1 kg of water:
L=333000 J
$V_{solid}=1.091 \times 10^{-3}\ m^3$ $V_{liquid}=1.0 \times 10^{-3}\ m^3$



$$\frac{dP}{dT} = -1.34\times 10^{7}\ Pa/K$$

Unusual property of ice

What temperature does ice under P> 1 atm melt?