PHY 341/641 Thermodynamics and Statistical Mechanics

MWF: Online at 12 PM & FTF at 2 PM

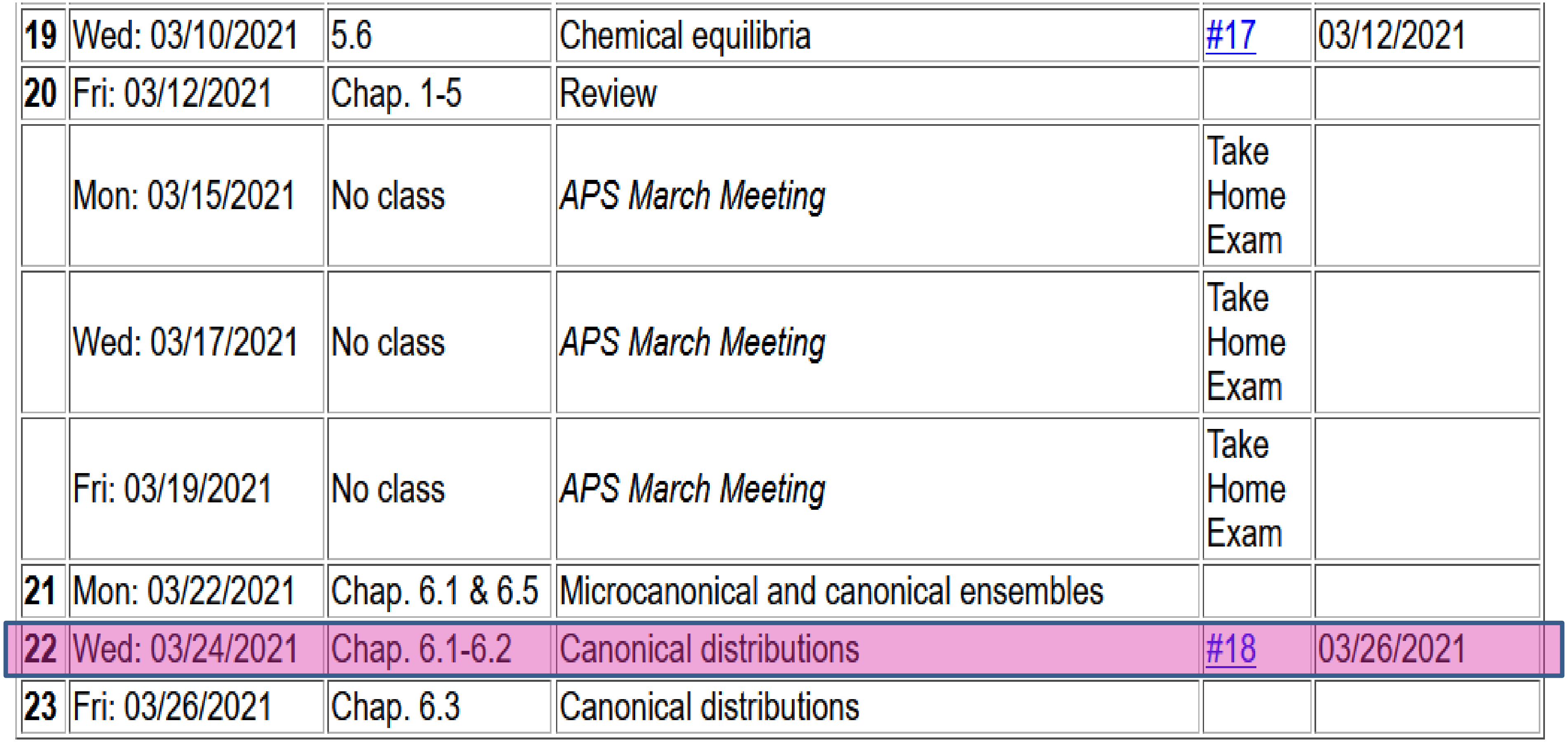
Record!!!

Discussion for Lecture 22:

Introduction to statistical mechanics – Analysis of physical properties for canonical ensembles

Reading: Chapter 6.1-6.2

1. Simple examples
2. Experimental evidence
3. More complicated examples



19	Wed: 03/10/2021	5.6	Chemical equilibria	#17	03/12/2021
20	Fri: 03/12/2021	Chap. 1-5	Review		
	Mon: 03/15/2021	No class	*APS March Meeting*	Take Home Exam	
	Wed: 03/17/2021	No class	*APS March Meeting*	Take Home Exam	
	Fri: 03/19/2021	No class	*APS March Meeting*	Take Home Exam	
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. 6.3	Canonical distributions		

PHY 341/641 -- Assignment #18

March 24, 2021

Continue reading Chapter 6 in **Schroeder** .

Consider a single particle which can be in one of 3 states having energies $U_1=0$, $U_2=\Delta$, and $U_3=2\Delta$ according to a canonical distribution.

1. Write an expression for the partition function of this system.
2. Write an expression for the heat capacity at constant volume for this system.
3. Using convenient units, make a plot of the heat capacity of this system.

PHYSICS COLLOQUIUM

THURSDAY
•
MARCH 25, 2021

4 PM online

"You Have Your Physics Results. Now What"

In a talk that I am hoping will quickly morph into a free-flowing Q and A session, I will discuss the roles of journals in general and PRL in particular in disseminating physics results through a cascading sequence involving journal editors, referees, conference chairs, journalists, department chairs, deans, funding agencies, and others. While some of the essential tools of physics dissemination are in essence unchanged, the arrival of social media, search engines, and electronic repositories have us in a state of flux.

Samindranath Mitra, PhD
Editor
Physical Review Letters
American Physical Society

Your questions – (some from Monday)

From Michael -- Could you further elaborate on how we are able to determine that hydrogen atoms are much more abundant in the sun's atmosphere than any other types of atoms? What does the partition function in regards to rotational energy actually mean?

From Noah -- When talking about degenerate states for a particle in a system is this the same thing as talking about the macrostates of the system or is it different because we are only concerned with a single particle?
Section 6.5 is all about finding a quantity that increases in a system with constant temperature. Are there analogous quantities for all of the physical parameters like constant pressure and constant volume?

From Kristen -- 1. When computing the average values for the energy, for example, the probabilities that we are using, is that the number of atoms in that state which just happens to represent the probability of it being in that state? Could you define the probability that we learned about in class today in this context? 2. Why do we divide by Z in the average value equation? 3. Could you explain a bit more about what the equipartition theorem actually tells us?

From Parker -- Should we think of the partition function for energy as the weighted average for a discrete set of energy levels?

Important results concerning the notion of the canonical system

Partition function:

$$Z(T) \equiv \sum_{s'} e^{-U_{s'}/kT} = \sum_{s'} e^{-\beta U_{s'}} \quad \text{where } \beta = \frac{1}{kT}$$

More generally, the system also depends on volume and number of particles -- $Z(T, V, N)$

Relationship of partition function to Helmholtz free energy:

$$U - TS = F = -kT \ln Z$$

Evaluating averages for a canonical distribution:

Probability for state s: $\mathscr{P}_s = \dfrac{e^{-U_s/kT}}{Z} = \dfrac{e^{-\beta U_s}}{Z}$ $\qquad \beta \equiv \dfrac{1}{kT}$

Average energy for canonical ensemble:

$$\langle U_s \rangle = \frac{1}{Z}\sum_{s'} U_{s'} e^{-U_{s'}/k_B T} = -\frac{\partial \ln Z}{\partial \beta}$$

Heat capacity for canonical ensemble:

$$C_V = \frac{\partial \langle U_s \rangle}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial \langle U_s \rangle}{\partial \beta}$$

$$= \frac{1}{k_B T^2}\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{1}{k_B T^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2\right)$$

$$= \frac{1}{kT^2}\left(\langle U_s{}^2 \rangle - \langle U_s \rangle^2\right)$$

Other quantities that can be calculated based on the Helmholtz free energy

$$F(T,V,N) = -kT\ln Z\left(T,V,N\right)$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \left(\frac{-\partial\left(kT\ln Z\right)}{\partial T}\right)_{V,N} = -k\ln Z - kT\left(\frac{\partial\left(\ln Z\right)}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P = -kT\left(\frac{\partial\left(\ln Z\right)}{\partial V}\right)_{T,N}$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu = -kT\left(\frac{\partial\left(\ln Z\right)}{\partial N}\right)_{T,V}$$

Some examples assuming a discrete set of energies for U_s

These discrete states typically come from quantum systems. At the moment, we will only use the discrete nature of these states and leave the more detailed aspects of quantum statistical mechanics for later (Chapter 7).

Simple example of a single particle system –

Suppose you have a single particle which is well described by a canonical distribution among two discrete internal energies $U_1=0$ and $U_2=\Delta$

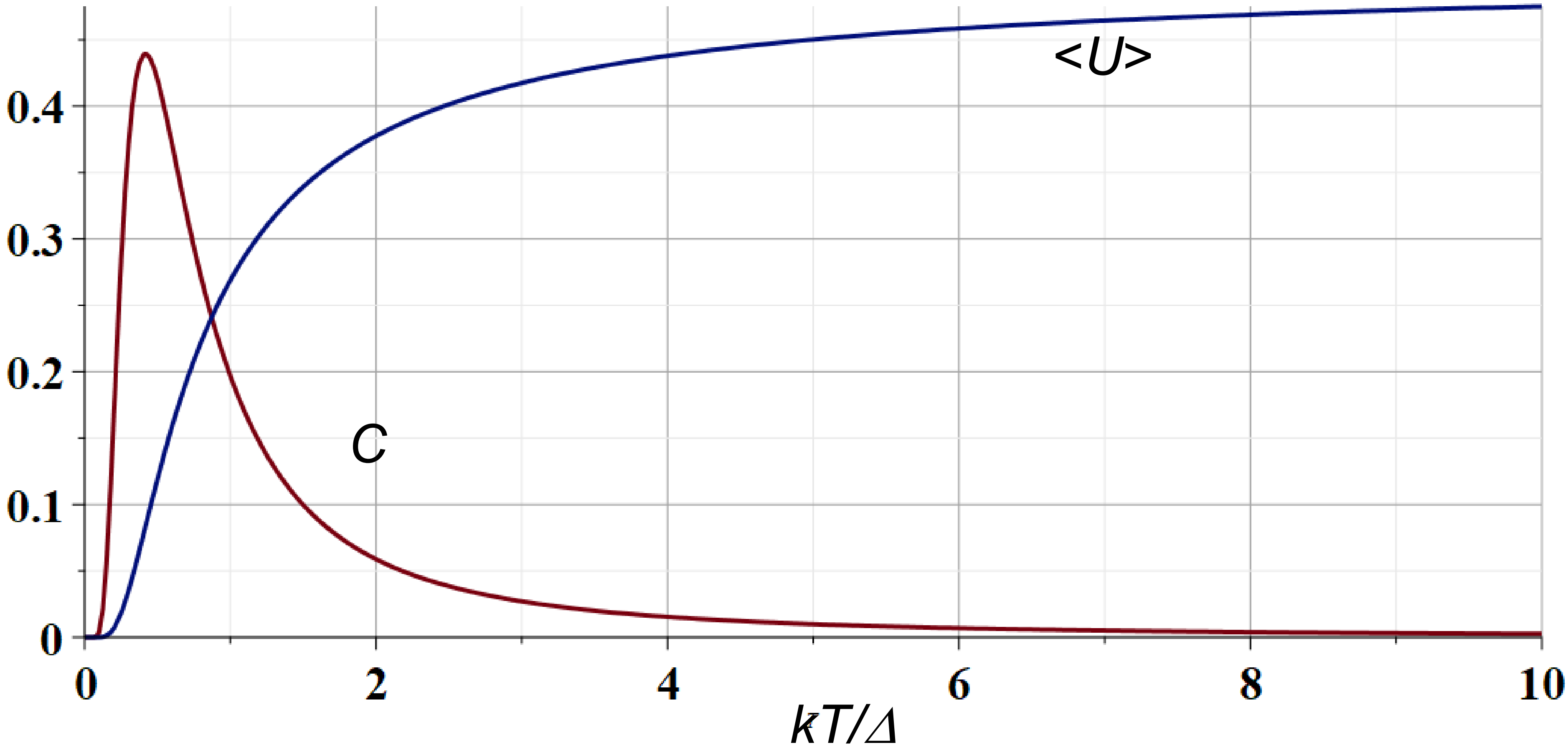
$$Z(T) \equiv \sum_{s'} e^{-U_{s'}/kT} = 1 + e^{-\Delta/kT}$$

$$\langle U_s \rangle = \frac{1}{Z}\sum_{s'} U_{s'} e^{-U_{s'}/k_B T} = \frac{1}{Z}\left(\Delta e^{-\Delta/kT}\right)$$

$$\left\langle \left(U_s\right)^2 \right\rangle = \frac{1}{Z}\sum_{s'} U_{s'}^2 e^{-U_{s'}/k_B T} = \frac{1}{Z}\left(\Delta^2 e^{-\Delta/kT}\right)$$

$$C_V = \frac{1}{kT^2}\left(\left\langle U_s{}^2\right\rangle - \left\langle U_s\right\rangle^2\right) = \frac{1}{kT^2}\left(\frac{\Delta^2 e^{-\Delta/kT}}{Z} - \frac{\Delta^2 e^{-2\Delta/kT}}{Z^2}\right)$$

Single particle which is well described by a canonical distribution among two discrete internal energies $U_1=0$ and $U_2=\Delta$

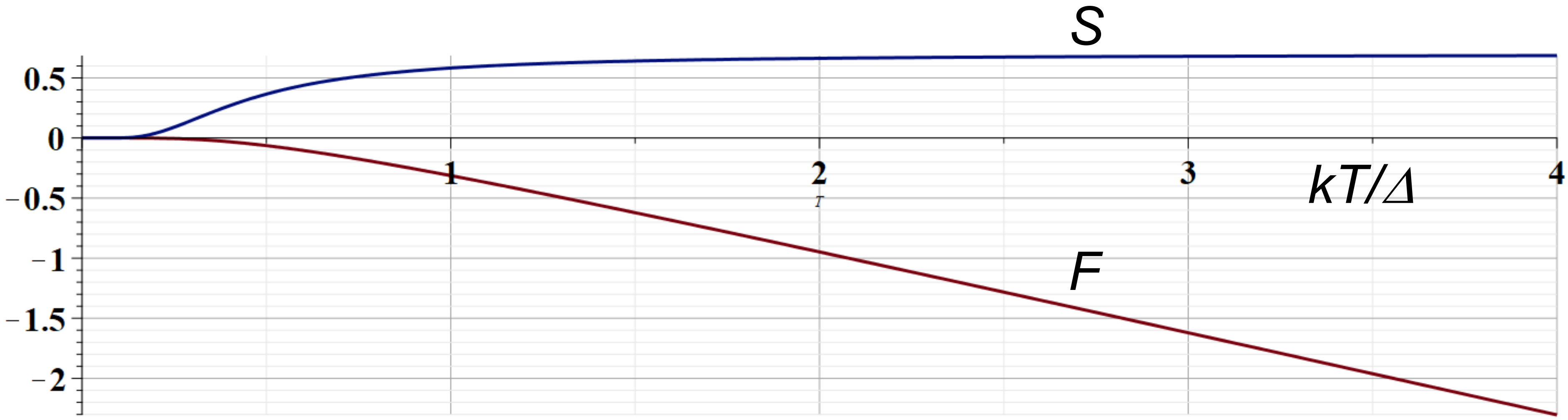


More results for our simple model from the Helmholtz free energy

$$F(T) = -kT\ln Z(T) = -kT\ln\left(1+e^{-\Delta/kT}\right)$$

$$S(T) = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \left(\frac{\partial\left(kT\ln Z\right)}{\partial T}\right)_{V,N} = k\ln Z + kT\left(\frac{\partial\left(\ln Z\right)}{\partial T}\right)_{V,N}$$

$$= k\ln\left(1+e^{-\Delta/kT}\right) + \frac{\Delta}{T}\frac{e^{-\Delta/kT}}{1+e^{-\Delta/kT}}$$



Question – what happens if the zero of energy shifts? Suppose you have a single particle which is well described by a canonical distribution among two discrete internal energies $U_1=a$ and $U_2=a+\Delta$

A. Nothing changes
B. All results change

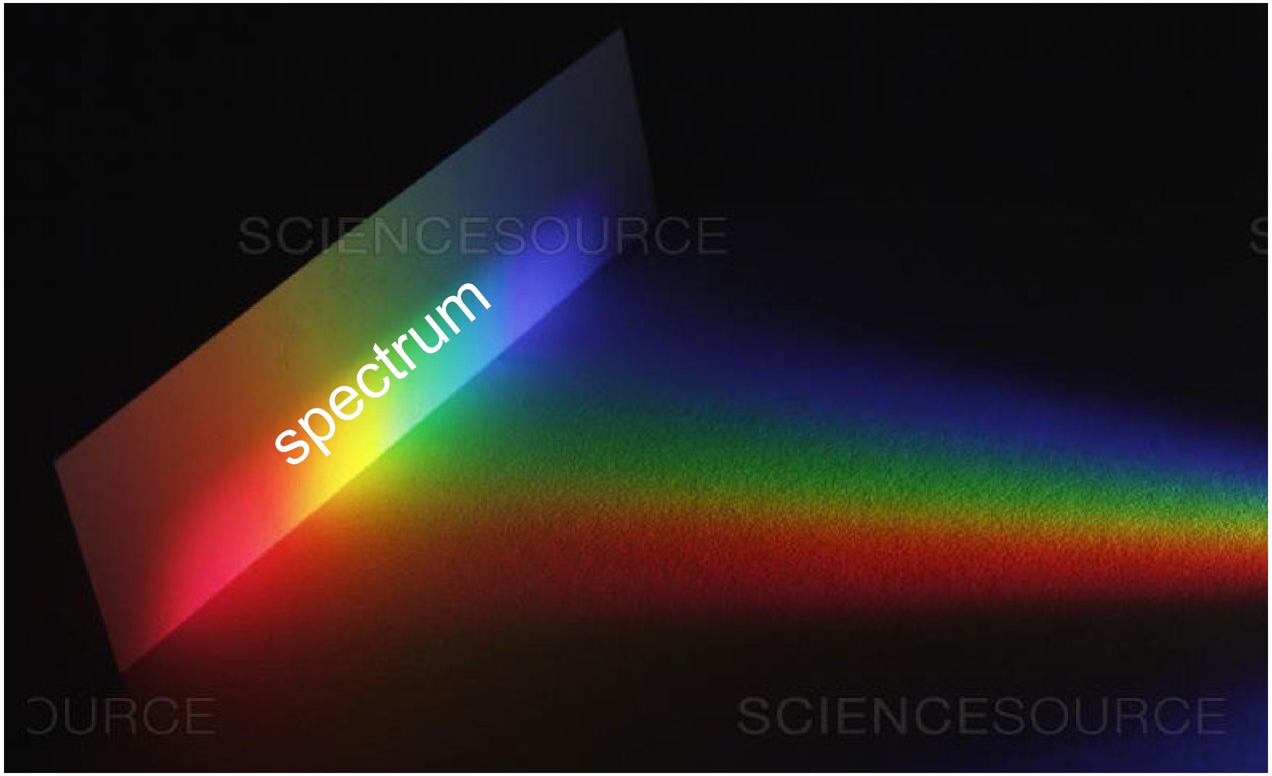
$$Z'(T) \equiv \sum_{s'} e^{-U'_{s'}/kT} = e^{-a/kT} + e^{-(a+\Delta)/kT} = e^{-a/kT}\left(1+e^{-\Delta/kT}\right)$$

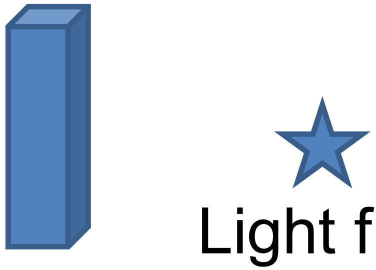
$$\left\langle U'_s \right\rangle = \frac{1}{Z'}\sum_{s'} U'_{s'}\, e^{-U'_{s'}/k_BT} = a + \frac{1}{Z}\left(\Delta e^{-\Delta/kT}\right) = a + \left\langle U_s \right\rangle$$

$\Rightarrow$ Internal energy shifts by a

$\Rightarrow F' = F + a$

Experimental evidence of canonical distribution (your book refers to the terms as Boltzmann factors)



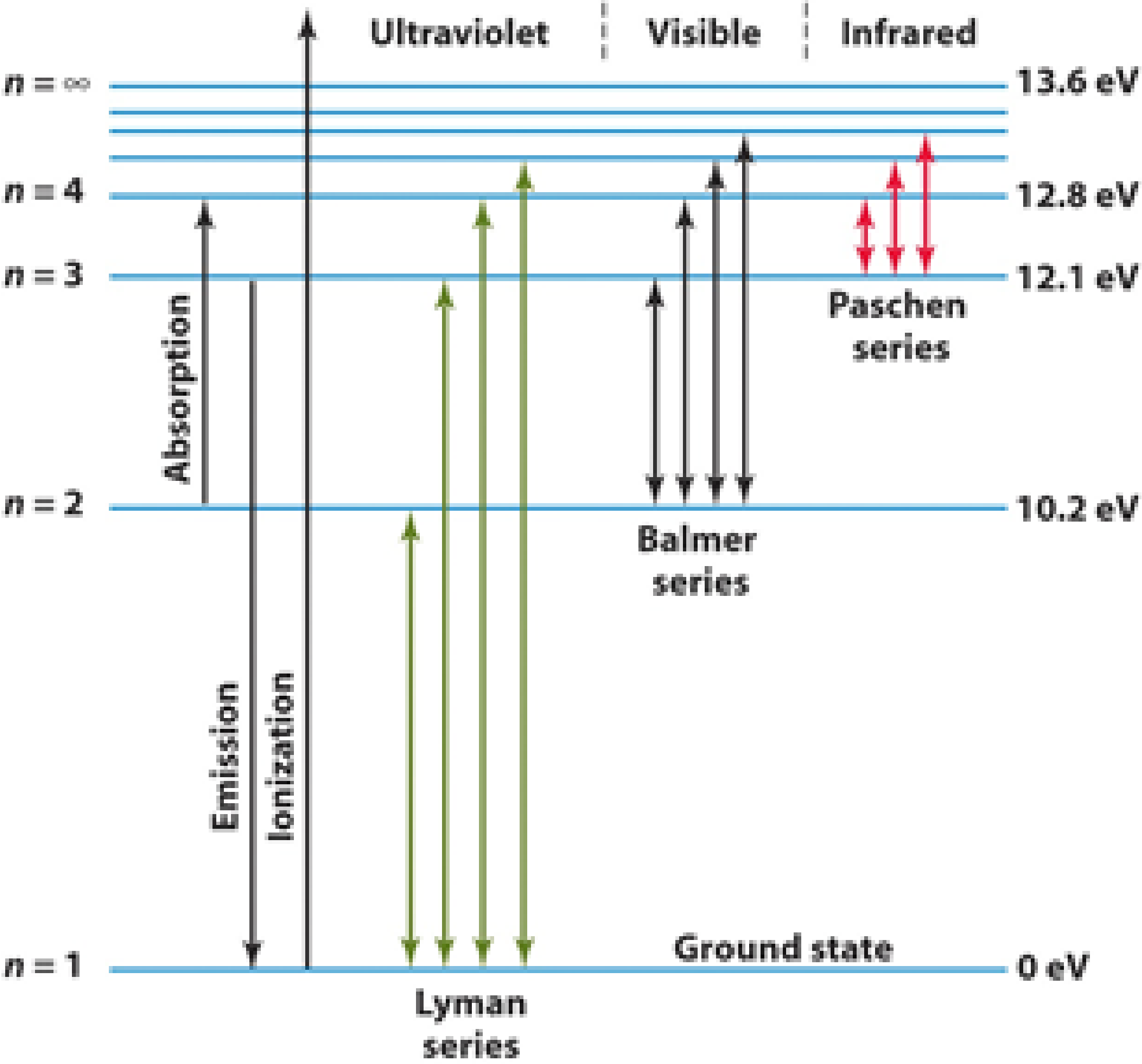


Diffractometer

Light from star

Spectral analysis of star light can be used to identify characteristic atomic transitions. Assuming the Boltzmann distribution, we can deduce the star temperature.

Hydrogen energy levels and transitions



Focusing H spectrum --

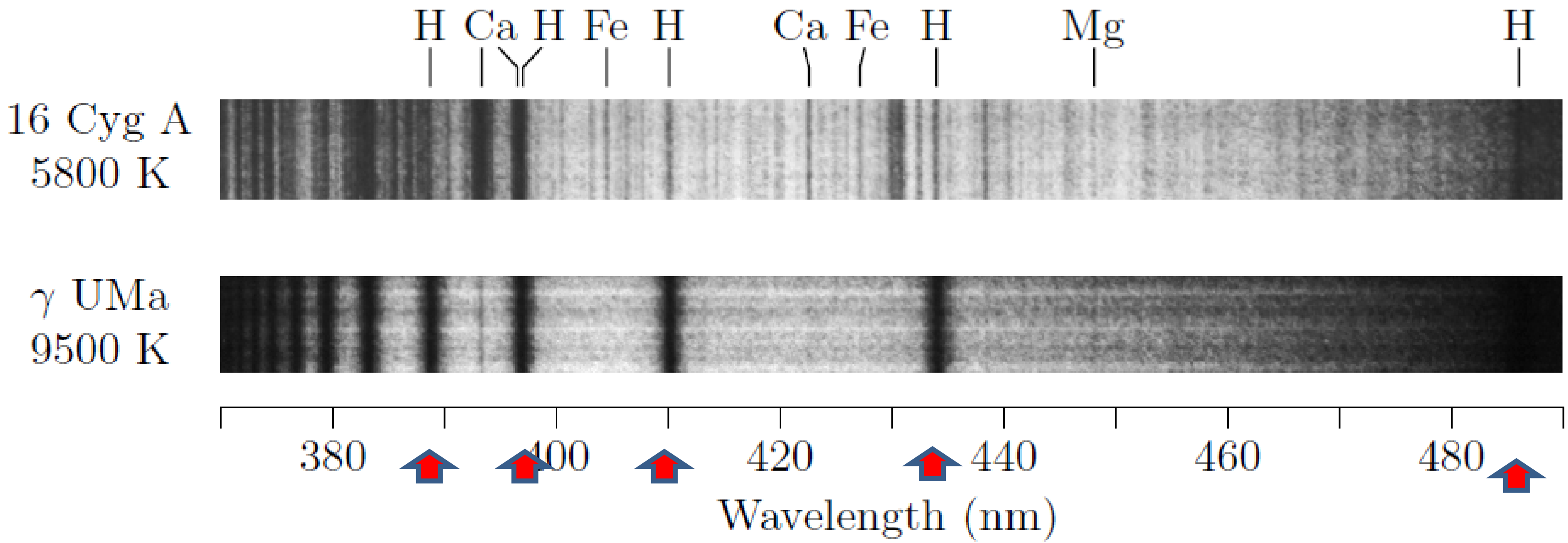


Figure 6.4. Photographs of the spectra of two stars. The upper spectrum is of a sunlike star (in the constellation Cygnus) with a surface temperature of about 5800 K; notice that the hydrogen absorption lines are clearly visible among a number of lines from other elements. The lower spectrum is of a hotter star (in Ursa Major, the Big Dipper), with a surface temperature of 9500 K. At this temperature a much larger fraction of the hydrogen atoms are in their first excited states, so the hydrogen lines are much more prominent than any others. Reproduced with permission from Helmut A. Abt et al., *An Atlas of Low-Dispersion Grating Stellar Spectra* (Kitt Peak National Observatory, Tucson, AZ, 1968). Copyright ©2000, Addison-Wesley.

Hydrogen spectral lines in the Balmer series

$$\lambda_n = \frac{\lambda_{Rydberg}}{\frac{1}{2^2} - \frac{1}{n^2}} \qquad \lambda_{Rydberg} = 91.12670504 \text{ nm}$$

$$\lambda_8 = 388.8 \quad \lambda_7 = 396.9 \quad \lambda_6 = 410.1 \quad \lambda_5 = 433.9 \quad \lambda_4 = 486.0$$

The probability of seeing these Balmer series lines is based on the probability of H being in the *n*=2 state which is proportional to $\mathrm{e}^{-118370/T}$ where T is given in Kelvin.

For *T*=5800 K $\quad \mathrm{e}^{-118370/T} = 1\times 10^{-9}$

For *T*=9500 K $\quad \mathrm{e}^{-118370/T} = 4\times 10^{-6}$

Note that these lines are absorbed from the star’s total spectrum.

Another example – rotations of a diatomic molecule

Quantum mechanics tells us that the rotational energy levels of rotating diatomic molecule has discrete states specified by intergers $j = 0, 1, 2, 3 \ldots$

$E(j) = j(j+1)\epsilon$ each with degeneracy $2j+1$

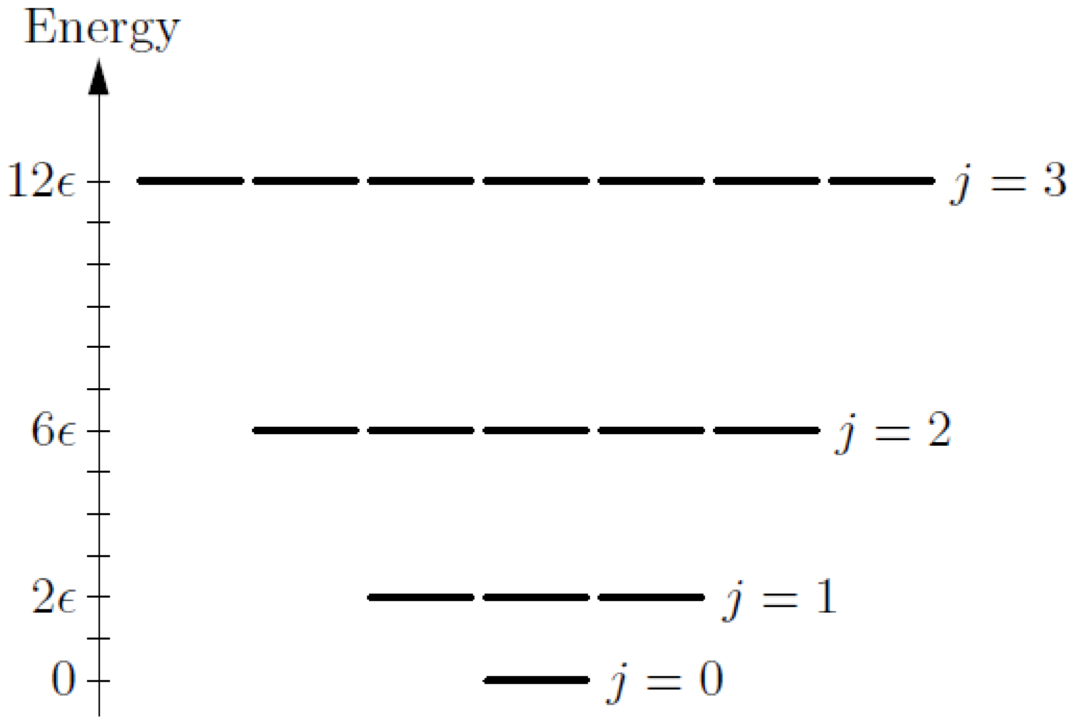


Figure 6.6. Energy level diagram for the rotational states of a diatomic molecule. Copyright ©2000, Addison-Wesley.

For each diatomic molecule within a canonic ensemble, the partition function is given by

$$Z_{rot} = \sum^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}$$

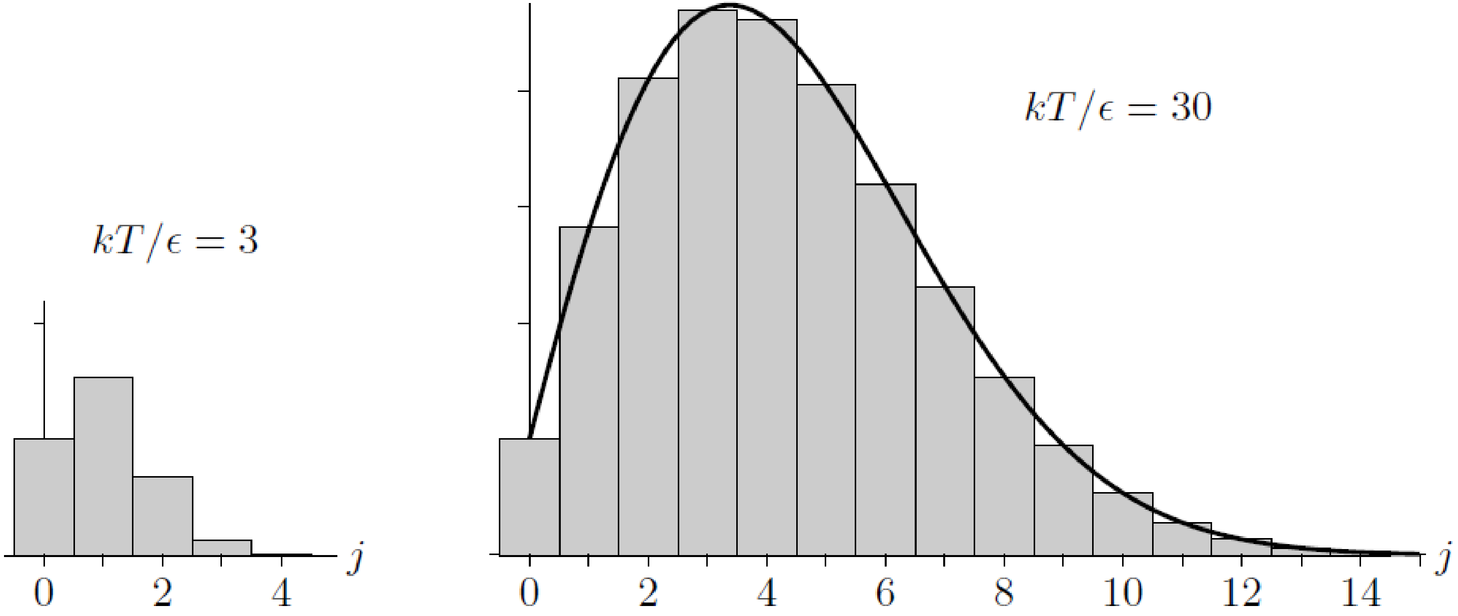
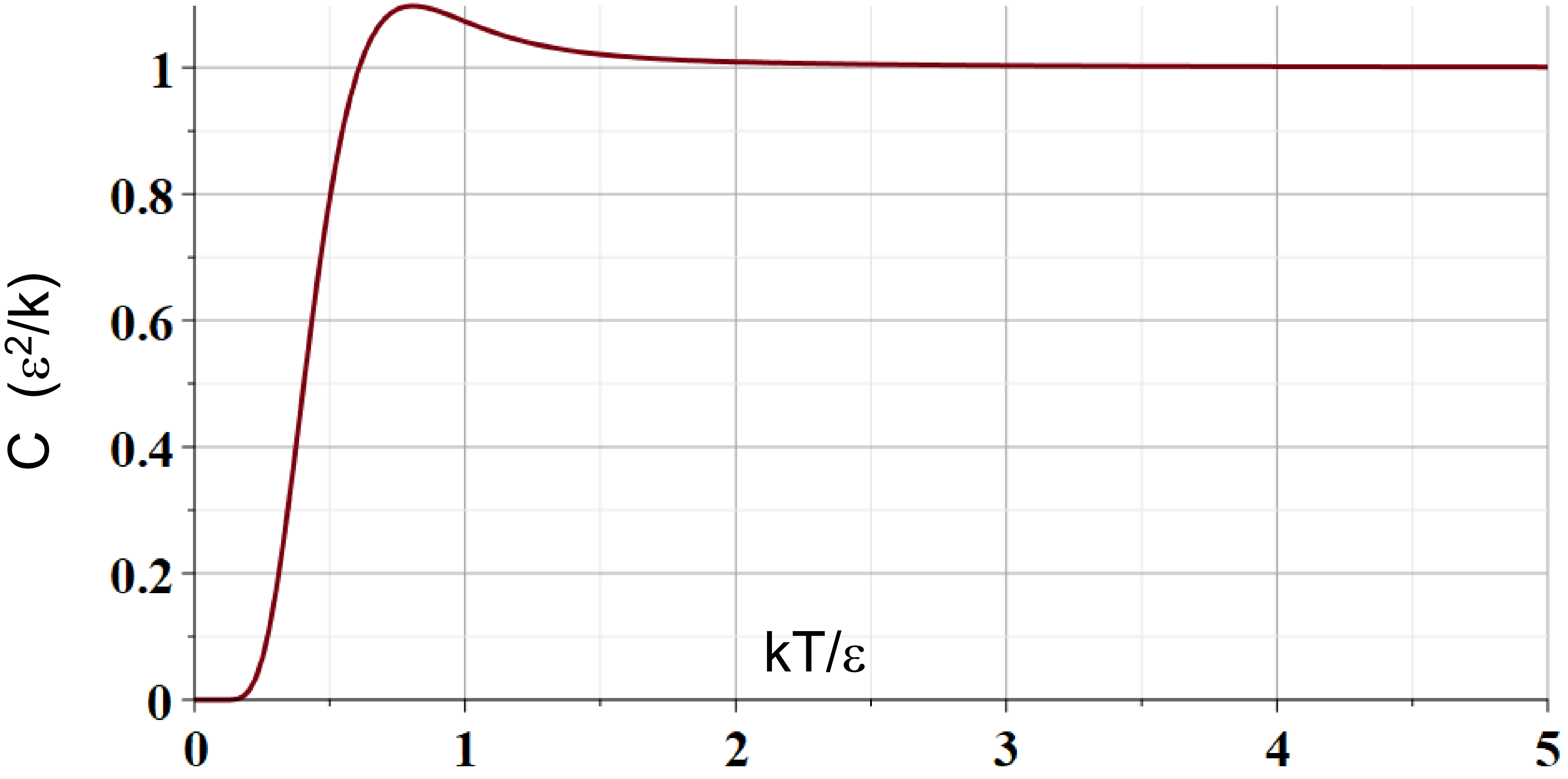


Figure 6.7. Bar-graph representations of the partition sum 6.30, for two different temperatures. At high temperatures the sum can be approximated as the area under a smooth curve. Copyright ©2000, Addison-Wesley.

From the partition function: $Z_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT}$

we can calculate various thermodynamic parameters --

$$C_v = \frac{1}{kT^2}\left(\langle U^2 \rangle - \langle U \rangle^2\right)$$



So far, we have considered single particles in a canonical ensemble, what happens when we have N non-interacting particles?

A. $Z_N = N Z_1$
B. $Z_N = (Z_1)^N$
C. Something else?