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

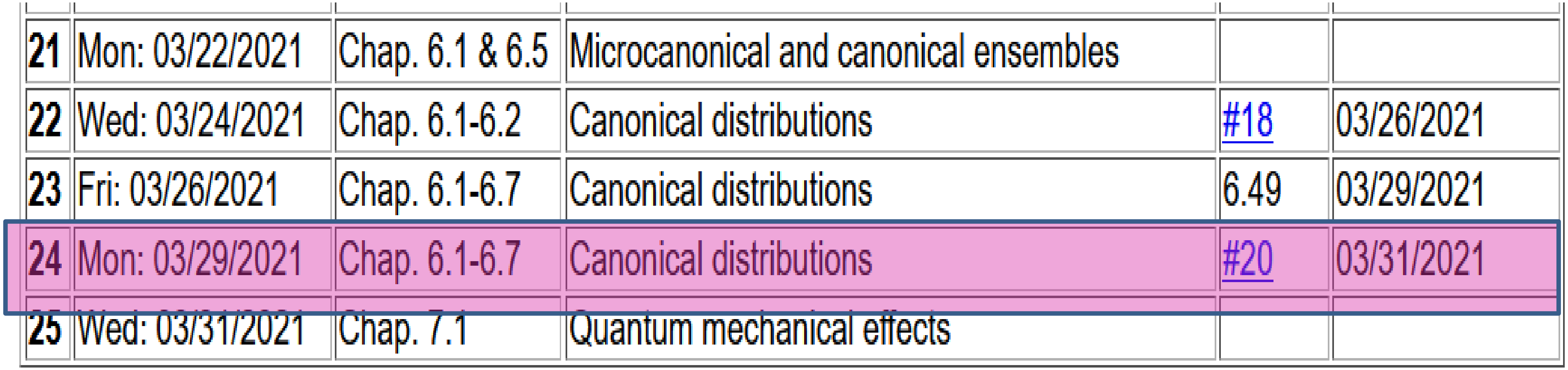
Record!!!

Discussion for Lecture 24:

Introduction to statistical mechanics – Canonical ensembles and their thermodynamic properties

Reading: Chapter 6.1-6.7

1. **Maxwell-Boltzmann velocity distribution**
2. **More examples of (semi) classical canonical distributtions**



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	Chap. 7.1	Quantum mechanical effects		

PHY 341/641 -- Assignment #20

March 29, 2021

Complete reading Chapter 6 in **Schroeder** .

Consider a system of Avogadro's number of Ne atoms (atomic mass 14.007) in a container of volume 1 m^3 in equilibrium with a heat bath at temperature T=300 K.

1. Find the most probable speed of a Ne atom.
2. Find the fraction of Ne atoms which have a speed equal or larger than the most probable speed.

Your questions –

From Michael -- How are we able to tell if a molecule has a degenerate ground state or not? Does this information have to be given to us?

From Kristen -- 1. What exactly does the Ztotal of a system tell us about the system in physical or conceptual terms? 2. I understand that each molecule configuration has a different translational partition function, and that this depends on the momentum, is the momentum the only thing that makes each function different or are there other factors? 3. How does the quantum volume differ from the regular volume we discussed in class?

From Rich -- How does the summation formula for Zrot change with identical atoms?

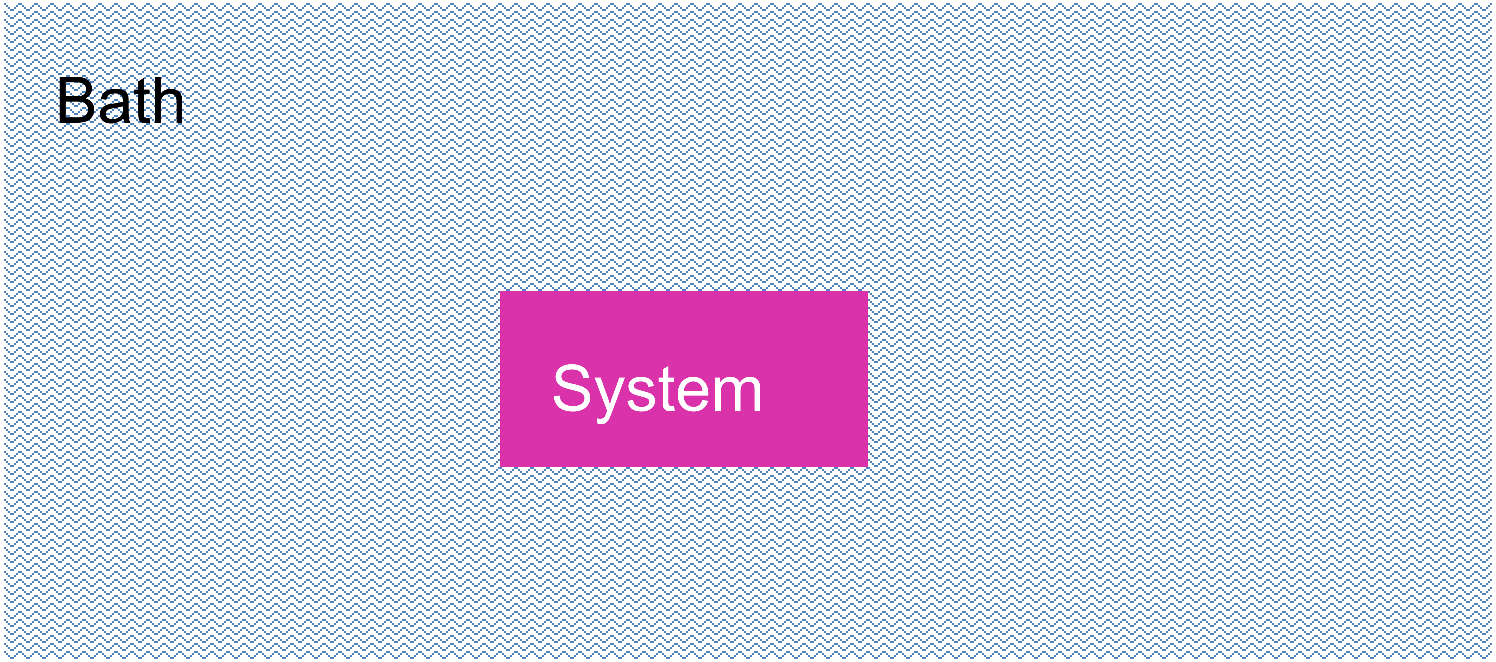
From Leon -- My question before class is how do we calculate the partition function as Zint(T,V)? I know that it equals to Zrot * Zvib, but for example when it comes to hw19 I got confused about what it is under that particular circumstance.

From Nick – correcting some typos in lecture notes.   The correct equations should read:b

$$Z(T,V,N) = \frac{1}{N!}\left(Z_1(T,V)\right)^N$$

$$\begin{aligned} F(T,V,N) &= -kTN\ln\left(Z_1(T,V)\right) + kT\ln N! \\ &\approx -kTN\ln\left(Z_1(T,V)\right) + kTN(\ln N - 1) \end{aligned}$$

Canonical ensemble for system in bath



$$\mathcal{P}_s = \frac{e^{-U_s/kT}}{Z} \quad \text{where } Z = \sum_s e^{-U_s/kT}$$

Examples for systems of single particles:

First consider a single atom of mass *m* in box of volume *V*

Its energy depends on only on its momentum **p** in terms of its kinetic energy

$$U_s \equiv U_{\mathbf{p}} = \frac{p^2}{2m}$$

$$\sum_s e^{-U_s/kT} \rightarrow \frac{1}{h^3}\int d^3r \int d^3p \; e^{-p^2/(2mkT)} = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} dp_x e^{-p_x^2/(2mkT)}\right)^3$$

$$= \frac{V}{h^3}\left(2\pi mkT\right)^{3/2}$$

V

Planck’s constant for compatibility with QM

See Appendix B

$$Z_{1\ \mathrm{trans}}(T,V) = \frac{V}{h^3}\left(2\pi mkT\right)^{3/2}$$

Digression -- If we had started with N non interacting particles you may wonder how we can avoid finding the system energy U_s.

$$Z=\sum_s e^{-U_s/kT} \qquad U_s=\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m}$$

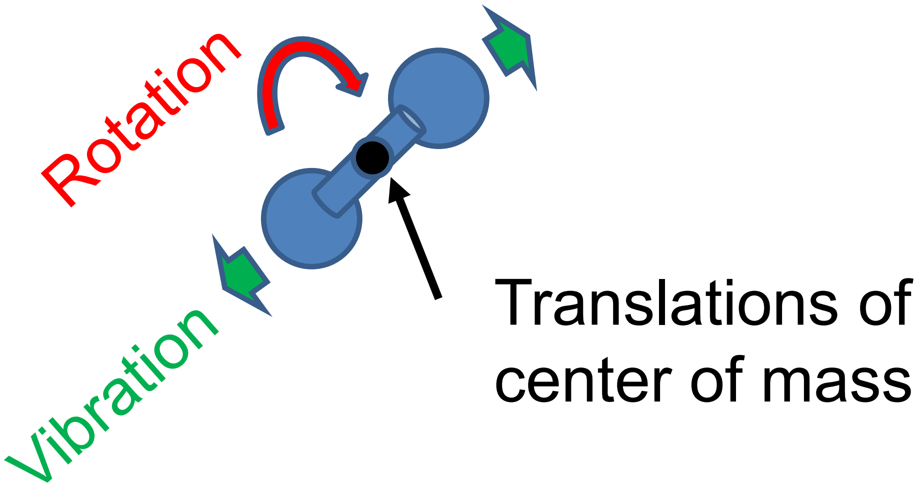
In this case U_s is a continuous variable so that

$$\sum_s e^{-U_s/kT} \rightarrow \int dU_s e^{-U_s/kT}$$

$$Z=\int dU_s\left(\int d^3r_1 d^3p_1\int d^3r_2 d^3p_2....\int d^3r_N d^3p_N e^{-(|\mathbf{p}_1|^2+|\mathbf{p}_2|^2.....)/(2mkT)}\right)\delta\left(U_s-\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m}\right)\frac{1}{N!}$$

$$=\frac{1}{N!}\left(\int d^3r_1 d^3p_1 e^{-|\mathbf{p}_1|^2/(2mkT)}\right)^N$$

Now consider the motions of a more complicated system such as a diatomic molecule



$$U_s = U_{trans}(\mathbf{p}) + U_{\text{int}}$$

Partition function for single molecule including translational and “internal” motions

$$Z_1(T,V) = Z_{1\,\text{trans}}(T,V)Z_{1\,\text{int}}(T)$$

Generalizing to N indistinguishable molecules:

$$Z(T,V,N) = \frac{1}{N!}\left(Z_1(T,V)\right)^N$$

$$F(T,V,N) = -kTN\ln\left(Z_1(T,V)\right) + kT\ln N!$$

$$\approx -kTN\ln\left(Z_1(T,V)\right) + kTN(\ln N - 1)$$

Returning to the concept of probability distribution for the case of an ideal gas particle of mass m:

$$\mathscr{P}_s = Ke^{-|\mathbf{p}_s|^2/(2mkT)}e^{-U_{\text{int}}/kT}$$

where K is a temperature dependent constant.

In terms of the particle velocity,

$$\mathbf{p}_s = m\mathbf{v}_s$$

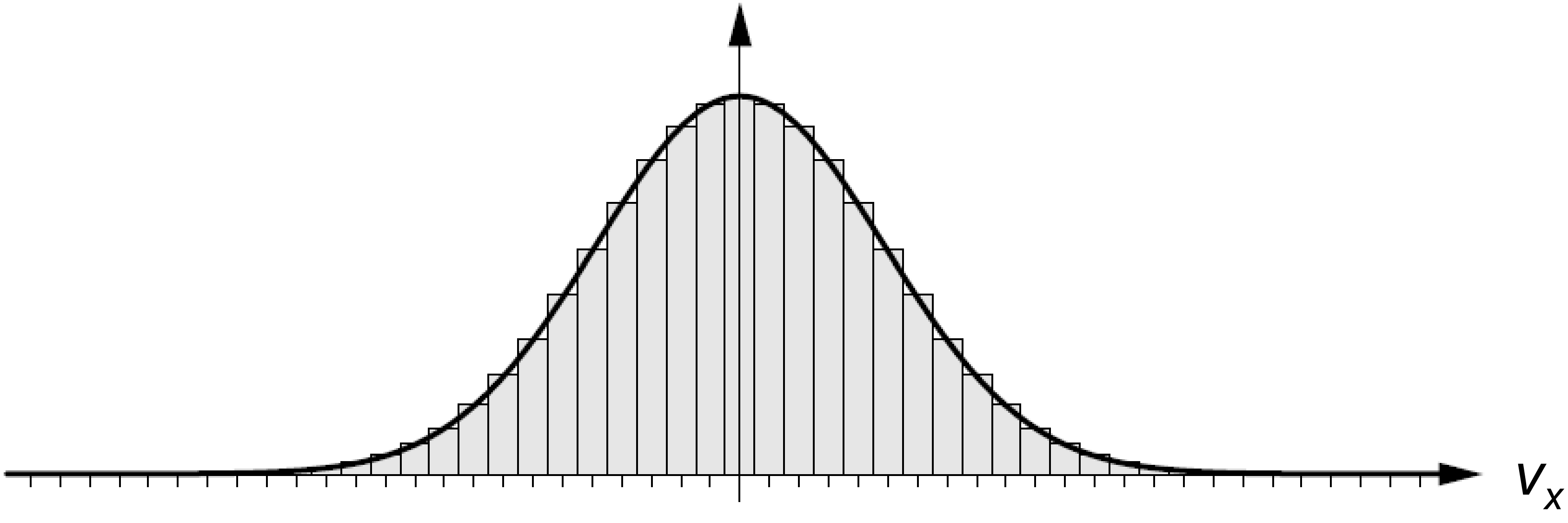
Dropping the index s, we can think of the probability in terms of the components

$$v_x, v_y, v_z$$

$$\mathscr{P}(v_x, v_y, v_z) = K'e^{-m(v_x^2+v_y^2+v_z^2)/2kT}$$

Velocity distribution function

$$\mathcal{P}(v_x, v_y, v_z) = K' e^{-m(v_x^2+v_y^2+v_z^2)/2kT}$$



Plotted for fixed v_y and v_z

Finding the average v_x

Finding the average values:

$$\mathcal{P}(v_x) = K'' e^{-mv_x^2/2kT}$$

$$\langle v_x \rangle = \frac{\int_{-\infty}^{\infty} v_x e^{-mv_x^2/2kT} dv_x}{\int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x} = 0$$

$$\langle v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x}{\int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x} = \frac{kT}{m}$$

Finding the average |*v*|

Using spherical polar coordinates $d^3v \rightarrow d\Omega v^2 dv$

Finding the average values:

$\mathcal{P}(|v|) = K''' \; v^2 \; e^{-mv^2/2kT}$

Note that the maximum probability:

$$v_{\max} = \sqrt{\frac{2kT}{m}}$$

$$\langle |v| \rangle = \frac{\int_0^\infty v^2 dv \; v e^{-mv^2/2kT}}{\int_0^\infty v^2 dv e^{-mv^2/2kT}} = \sqrt{\frac{8kT}{\pi m}}$$

$$v_{\max} = \sqrt{\frac{2kT}{m}} \qquad \langle |v| \rangle = \sqrt{\frac{8kT}{\pi m}}$$

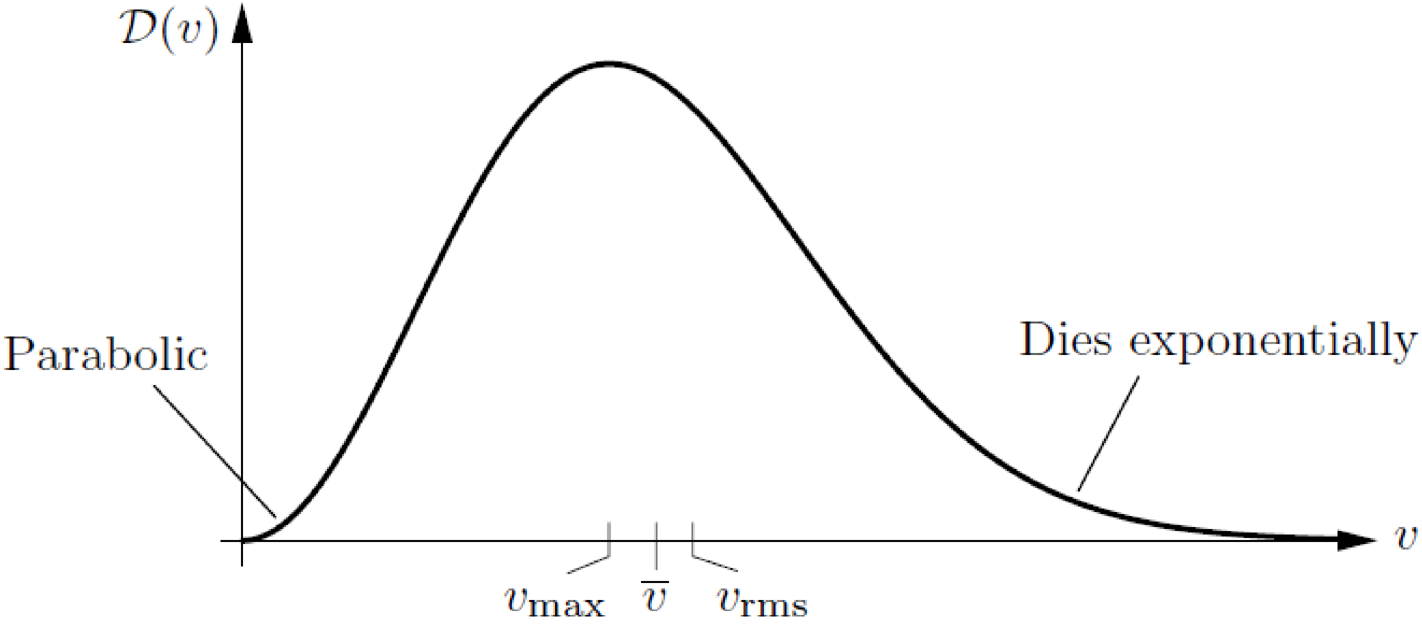


Figure 6.13. The Maxwell speed distribution falls off as $v \to 0$ and as $v \to \infty$. The average speed is slightly larger than the most likely speed, while the rms speed is a bit larger still. Copyright ©2000, Addison-Wesley.

Another example; this time based on particle spins aligned in a magnetic field B

$$U_s = \mu B(N_\downarrow - N_\uparrow)$$

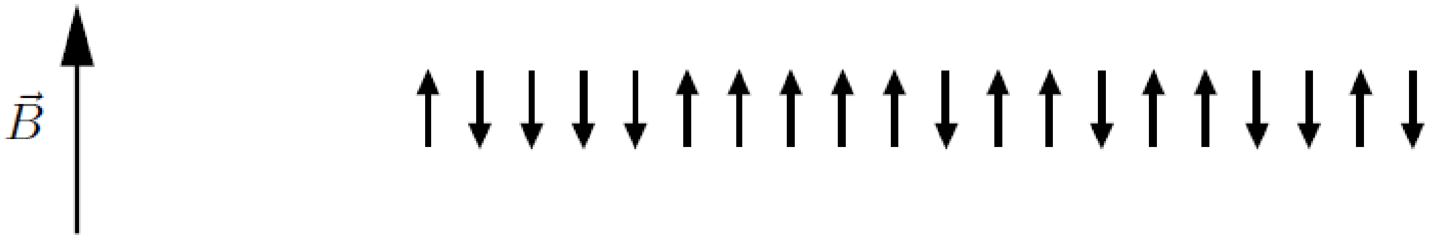
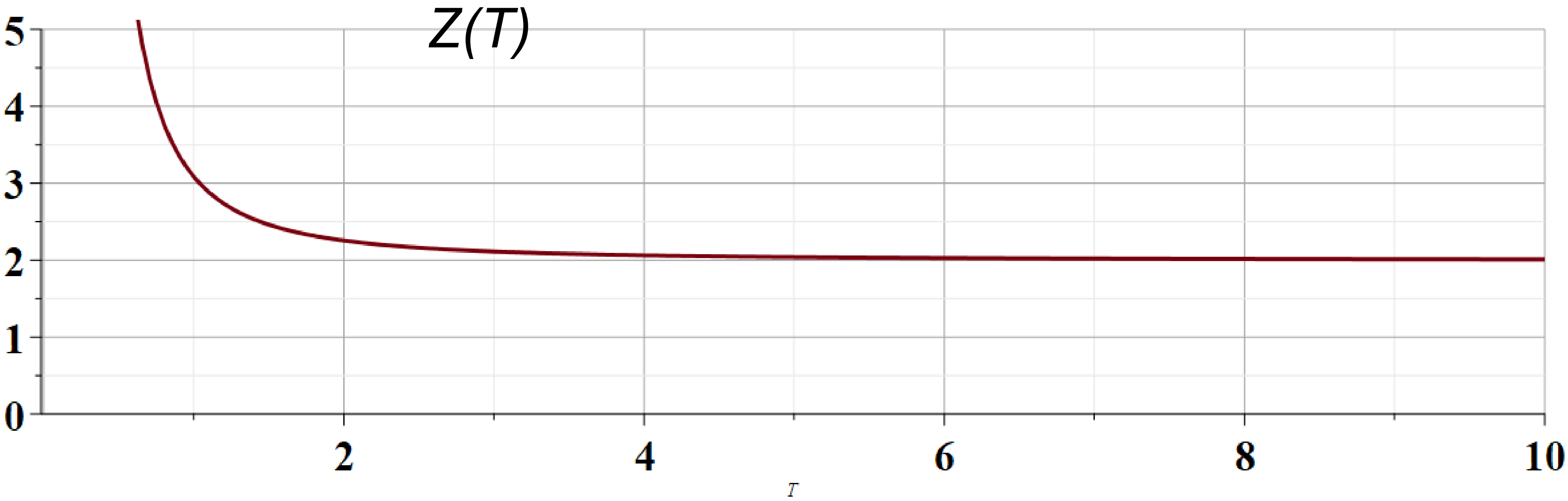


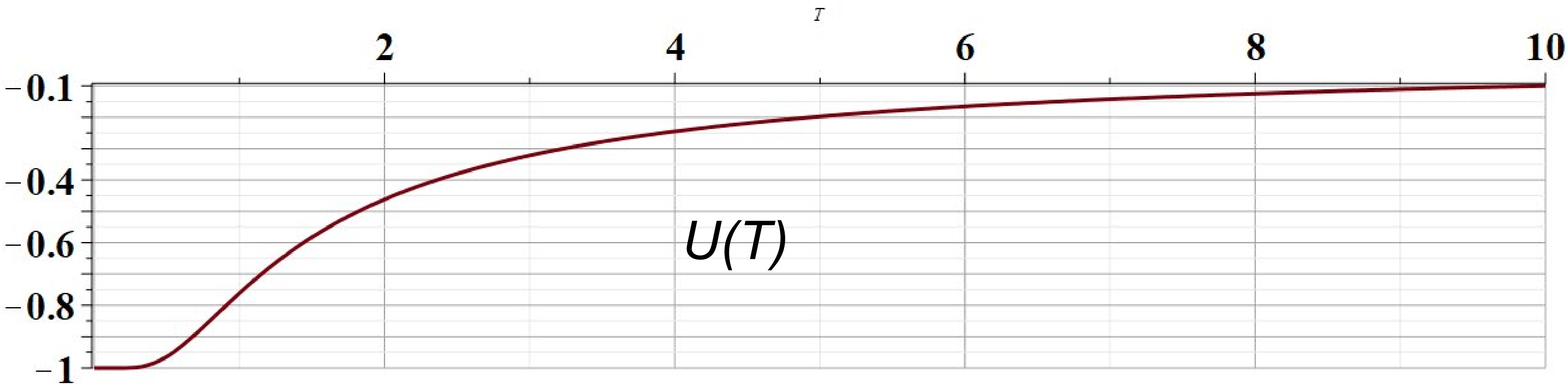
Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either "up" or "down" at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy). Copyright ©2000, Addison-Wesley.

For a single particle:

$$Z_1(T) = e^{\mu B/kT} + e^{-\mu B/kT} = 2\cosh\left(\frac{\mu B}{kT}\right)$$

$$\langle U \rangle = \frac{1}{Z_1}\left(-\mu B e^{\mu B/kT} + \mu B e^{-\mu B/kT}\right) = -\mu B \tanh\left(\frac{\mu B}{kT}\right)$$


Z(T)
5
4
3
2
1
0
2
4
6
8
10
T


T
2
4
6
8
10
−0.1
−0.4
−0.6
−0.8
−1
U(T)

Next time – Chapter 7 of your text book

Extending these ideas to quantum systems.