

## Thermal Physics: Problem Set #6

### Statistical Mechanics: Canonical Ensemble

$$P_s(T) = \frac{1}{Z(T)} e^{-\beta E_s} ; Z(T) = \sum_s e^{-\beta E_s} ; \bar{E} = \frac{1}{Z(T)} \sum_s E_s e^{-\beta E_s} ; F = -kT \ln Z ; U = kT^2 \frac{\partial \ln Z}{\partial T}$$

"Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously." from "States of Matter" by David Goodstein

Due: Friday Feb. 20 by 6 pm

**Note:** We will have class on **Saturday Feb. 21, 10:00-2:00** to make up for the week of March 2-6.

**Reading Assignment:** for Mon, 6.2-6.3 (12 pgs) (Average values from the partition function)  
 for Wed, 6.4-6.6 (9 pgs) (Thermodynamics from the partition function)  
 for Fri, 6.7 (5 pgs) (Ideal gas partition function)  
 for Sat, 7.1-7.3 (29 pgs) (Gibbs factor and Quantum statistics)

**Overview:** The subject of statistical mechanics finds its origins in Boltzmann's proposal that the entropy  $S = k \ln \Omega$ . This equation provides the link between the microscopic concept of the number of accessible states  $\Omega(N, V, U)$  and the thermodynamic (i.e., macroscopic) quantity entropy  $S(N, V, U)$ . Boltzmann's entropy expression is useful when working with a system at fixed energy (this is known as the micro-canonical ensemble). We simply count the number of accessible states with energy  $U$  and then we assert that the probability of observing a specific state  $s$  is simply  $P_s(N, V, U) = 1/\Omega$ , i.e., we assume that all states are equally likely. This latter assumption is the postulate of equal *a priori* probabilities and is the fundamental postulate of statistical mechanics. In most cases we are interested in working with a system at fixed temperature rather than fixed energy. This is known as working in the canonical ensemble. By studying a small system in thermal contact with a large fixed  $U$  system, such that the small system can exchange energy with the large system, we arrive at the canonical probability distribution function  $P_s(N, V, T)$  given above. (The idea of ensembles and partition functions was introduced by the great American physicist Gibbs, who luckily didn't do himself in, although Ehrenfest tried to do him in with harsh criticism of his approach). For a fixed  $T$  system, the probability of observing state  $s$  is now given by the so called Boltzmann factor  $\exp(-\beta E_s)$  [defining  $\beta = 1/kT$ ] divided by the partition function  $Z(N, V, T)$ . The partition function is a weighted sum over all states of the system and actually contains ALL thermodynamic information about the system. In particular, the Helmholtz free energy is simply given by  $F = -kT \ln Z(T)$ . Thus, the central goal of statistical mechanics becomes calculation of the partition function. We will be following such a program for the next few weeks as we apply the machinery we develop this week to problems of photons, phonons, fermions, bosons, and good old classical non-ideal fluids.

**Problem Assignment:** (10 problems total)

- 6.6 (probability to find hydrogen in first excited state)
- 6.12 (temperature of interstellar space)
- 6.13 (nucleons in the early universe)
- \*6.15 (a ten atom system) [ Su ]
- 6.16 (average energy as a derivative of Z)
- 6.18 (energy fluctuations and heat capacity)

\*denotes a problem to be presented in class

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### 6.23 (rotational partition function for CO)

\*6.31 (equipartition for linear terms in the energy) [ Ryogo ]

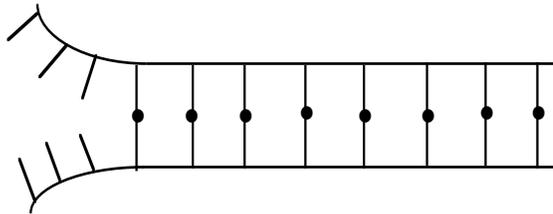
#### A1) Partition function for the van der Waals gas

One model for an interacting or "real" gas (versus a non-interacting ideal gas) is provided by the van der Waals equation of state. The canonical partition function for this model is

$$Z(N, V, T) = \frac{(V - Nb)^N}{N!} \lambda_{th}^{-3N} e^{\frac{aN^2}{V^2kT}}$$

where  $\lambda_{th} = h/\sqrt{2\pi mkT}$  and  $a$  and  $b$  are positive constants that depend on the particular gas being modeled.

- Compute the pressure equation of state for this model and explain under what conditions it reduces to the ideal gas result.
- Compute the internal energy of this model and compare with the ideal gas result.



#### A2) Zipper model for DNA

Consider a zipper with  $N$  links. Each link has a state in which it is closed with energy 0 and a state in which it is open with energy  $\epsilon$ . We require that the zipper only unzip from one side (say from the left) and that link  $n$  can only open if all links to the left of it (1, 2, ... ,  $n-1$ ) are already open.

- Find the canonical partition function for this model.
- Write an expression for the average number of open links  $\langle n \rangle$  at temperature  $T$ .
- Show that for low temperatures (i.e.,  $kT \ll \epsilon$ )  $\langle n \rangle$  is independent of  $N$  in the limit of large  $N$ .
- Show that for high temperatures (i.e.,  $kT \gg \epsilon$ )  $\langle n \rangle \rightarrow N/2$ .
- Plot  $\langle n \rangle/N$  vs  $kT/\epsilon$  (with  $0 \leq kT/\epsilon \leq 300$ ) for  $N=100$ .