Questions about solutions for Exam 1

Statistical Mechanics: Introduction

Classical Thermodynamics

- Macroscopic Theory

- Provides simple connections between different macroscopic properties of systems.

- It is independent of the atomistic interpretation of reality.

- In order to be useful, Thermodynamics requires experimental input.

- *TD* doesn't offer mechanistic interpretation of the system.

Statistical Mechanics

- Provides a microscopic description of systems.

- Statistical Mechanics constitutes a link between the Quantum Mechanical description of a system and its Thermodynamic Properties.

- Generates a more intuitive interpretation of system.

- Enables a *first principles* prediction of thermodynamic properties.

Degeneracy

Consider the energy states of a particle in a three-dimensional infinite well of dimensions $a \times a \times a$.

From quantum mechanics, the energy of such a system is defined as (eq. 1-33 of McQuarrie):

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} \left(n_x^2 + n_y^2 + n_z^2 \right) \tag{1}$$

where n_x, n_y, n_z are integers from 1 to infinity.

The degeneracy is given by the number of ways that the integer $M = frac8ma^2h^2$ can be written as the sum of the squares of three positive integers. If you consider a $3-D$ space spanned by n_x, n_y, n_z, Eq. 1 represents a sphere with radius $R = \left(\frac{8ma^2\varepsilon}{h^2} \right)^{1/2}$.

To calculate the degeneracy of this system, we need to calculate the number of states with energy ε, corresponding to the radius R of the sphere. For large numbers, it is possible to treat R as a continuous variable and then define the degeneracy of the system as the number of states within

the interval $\varepsilon, \varepsilon + \triangle\varepsilon$, where $\frac{\triangle\varepsilon}{\varepsilon} << 1$:

$$\omega\left(\varepsilon, \triangle\varepsilon\right) = \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}\varepsilon^{1/2}\triangle\varepsilon + O\left((\triangle\varepsilon)^2\right) \tag{2}$$

With $\varepsilon = 3kT/2$, $T = 300\,K$, $m = 10\times^{-22}\,g$, $a = 10\,cm$ and $\triangle\varepsilon = 0.01\varepsilon$, we obtain:

$$\omega\left(\varepsilon, \triangle\varepsilon\right) = O\left(10^{28}\right) \tag{3}$$

This is just for one particle!!!

For N particles $\sim 10^{23}$,

$$\Omega\left(E, \triangle E\right) = O\left(10^{10^{23}}\right) \tag{4}$$

The concept of degeneracy, $\Omega\left(E\right)$ is very important in statistical mechanics. As we will see later on, the *partition function* for a *Canonical Ensemble*, $Q(N, V, T)$ is given by:

$$Q\left(N, V, T\right) = \sum_E \Omega\left(N, V, E\right) e^{-\frac{E(N,V)}{kT}}$$

Ideas behind Stat. Mech. The observation time of macroscopic properties of system is much longer than the time-scale at which the atomic components of the system change their state.

Macroscopic Thermodynamic properties of systems are time averages of the *instantaneous* states of the system, considered from the microscopic point of view:

$$U = \bar{E} = \frac{1}{\Delta t}\int_{\Delta t} E\left(\vec{r}\left(t\right), \vec{p}\left(t\right)\right)dt$$

$$U = \bar{E} = \frac{1}{\Delta t}\int_{\Delta t} \langle\psi\left(\vec{q}, t\right)|H|\psi\left(\vec{q}, t\right)\rangle\,dt$$

The integrals above state that thermodynamically defined properties, such as the internal energy of a system U, are *time averages* of the instantaneous microscopic properties of the system.

In practice, however, the calculation of these time integrals is not possible ($N = O(10^{23})$). This is where Statistical Mechanics becomes useful.

POSTULATE I: Within $\triangle t$, all possible states that a system can take are sampled.

In this case, the time average of thermodynamic properties is equivalent to the weighted average over all possible states that the system can be in:

$$U = \bar{E} = \int_{\vec{r},\vec{p}} E(\vec{r},\vec{p}) P(\vec{r},\vec{p}) \, d\vec{r} d\vec{p}$$

where $P(\vec{r},\vec{p})$ is the probability distribution.

POSTULATE II: Every possible state for an *isolated* system is equally probable and it should be given equal weight.

The main problem of Statistical Mechanics is to find P_ν for the given thermodynamic boundary conditions imposed on the systems under study.

Mechanical/Non-mechanical Properties

Mechanical properties in statistical mechanics are defined as the properties that can be readily found from the solution of the Schrödinger equation $H\psi = E\psi$, such as E, p, etc. For these properties, the thermodynamic, macroscopic variables can be established through the time or phase-space integration of the microscopic, instantaneous properties:

$$U = \bar{E} = \int_{\vec{r},\vec{p}} E(\vec{r},\vec{p}) P(\vec{r},\vec{p}) \, d\vec{r} d\vec{p}$$

or

$$\bar{E} = \sum_\nu P_\nu E_\nu$$

Non-mechanical properties are those that require the introduction of temperature for their definition, such as S. In order to obtain the statistical mechanic definitions of these properties, it is necessary to establish the relationship between T.D. and S. M.

Ensembles

Collection of macroscopically identical systems. All the systems have the same thermodynamic boundary conditions, however, they can reside in different microstates.

If you assume that the ensemble consists of **A** systems, it is possible to define a_i as the number of systems in the ensemble that are in state i at any given time. Since the total number of systems is constant, the condition $\sum_i a_i = \mathbf{A}$ must be satisfied.

Sterling's Approximation

$$\ln N! = \sum_{m=1}^{N} \ln m$$

For large N, it is possible to replace the sum by a integral:

$$\ln N! = \int\limits_{x=1}^{N} \ln x \, dx = x \ln x - x \big|_1^N = N \ln N - N$$

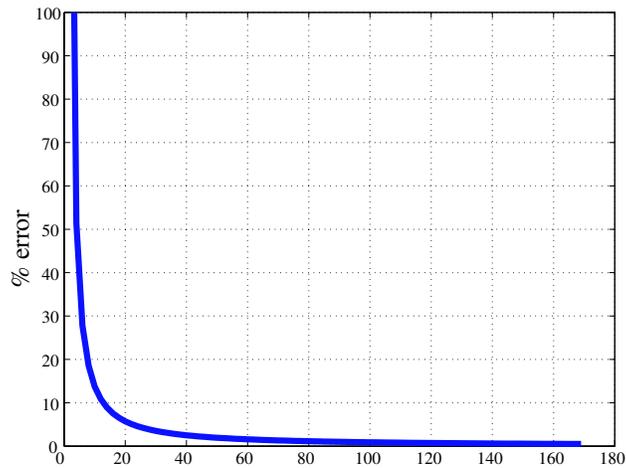This approximation is quite good, as can be seen in Fig. 1

Figure 1: Error between $ln\,(n!)$ and $nln(n) - n$, in $\%$

In Statistical Mechanics, we always deal with large numbers (systems, microstates, molecules, etc.) and the Sterling's Approximation is very useful for all the derivations that we will see in the next week.