XV. Summary

- Statistical Mechanics is the microscopic theory of thermodynamics
- Equilibrium Statistical Mechanics is largely based on ensemble theories.
- Ensemble theory is based on the theory developed for isolated systems (microcanonical ensemble)

A. Microcanonical Ensemble

(E, V, N) fixed

$$S = k \ln W$$

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

$$\frac{1}{kT} = \left(\frac{\partial \ln W}{\partial E}\right)_{N,V}$$

$$\frac{p}{kT} = \left(\frac{\partial \ln W}{\partial V}\right)_{E,N}$$

$$\frac{\mu}{kT} = -\left(\frac{\partial \ln W}{\partial N}\right)_{V,E}$$

- Good for establishing the formulation
- Not so convenient in doing calculations

B. Canonical Ensemble

(T, V, N) fixed (E fluctuates)

$$P(E_r) = \frac{1}{Z} e^{-\beta E_r}$$

$$Z(T,V,N) = \sum_{\text{all N-particle states}} e^{-\beta E_r}$$

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

$$dF = -S\,dT - p\,dV + \mu\,dN$$

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

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

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

$$U = \langle E \rangle = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}$$

- Convenient in doing calculations
- Find $Z(T,V,N)$ and then take derivatives
- Become less convenient in treating fermions and bosons
- Macroscopic Systems: $\langle E \rangle$ is representative of the system's energy

C. Grand Canonical Ensemble

(T, μ, V) fixed (E fluctuates, N fluctuates)

$$P(E_r(N), N) = \frac{1}{Q} e^{-\beta E_r(N) + \beta \mu N}$$

$$Q(T,\mu,V) = \sum_N \sum_{N\text{-particle states}} e^{-\beta E_r(N)} e^{\beta \mu N} = \sum_N e^{\beta \mu N} Z(T,V,N)$$

$$\Omega = -kT \ln Q(T,\mu,V) \ ; \ \Omega = -pV$$

$$d\Omega = -S\,dT - \langle N \rangle d\mu - p\,dV$$

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V,\mu}$$

$$\langle N \rangle = kT \left(\frac{\ln Q}{\partial \mu} \right)_{T,V}$$

$$p = \frac{kT}{V} \ln Q$$

- Construct $Q(T,V,\mu)$ and then take derivatives
- Convenient in handling bosons and fermions
- For macroscopic systems, $\langle E \rangle$ is representative of the energy of the system and $\langle N \rangle$ is representative of the number of particles in the system. They are E and N in thermodynamics.

Mathematical Techniques

- Gaussian integrals
- Volume of a high-dimensional sphere
- Stirling's formula for $\ln N!$ $(N \gg 1)$
- Expressing fluctuations in terms of difference of means
- Method of Lagrange Multiplers
  - extremizing a function under constraints (Most probable distributions)
- Counting microstates
- Turning sums into integrals - Density of states
- Idea of single-particle states and occupation numbers
- Gamma functions and Zeta functions $(\Gamma(n), \zeta(n))$
- $\displaystyle\int_0^\infty \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon = \int_0^\mu f(\varepsilon) d\varepsilon + \frac{\pi^2}{6}(kT)^2 f'(\mu)$, $kT \ll \mu$
- Getting $\mu(T)$ for fermi and bose gases
- $f_n(\xi)$ functions (fermi gas) and $g_n(\xi)$ functions (bose gas)
- Corrections to $\frac{pV}{\langle N \rangle kT} = 1$ for non-interacting fermions and bosons at high temperatures and/or low densities

Mathematical Structure

(a) $$Z(T,V,N) = \sum_{\text{all N-particle states}} e^{-\beta E_i} = \sum_{\substack{\text{all N-particle}\\ \text{energy \underline{levels} } E}} \underbrace{W(E,V,N)}_{\text{this is what is needed in microcanonical ensemble}} e^{-\beta E}$$

i.e. Z "generates" $W(E,V,N)$

(b) $$Q(T,\mu,V) = \sum_N \sum_{\text{N-particle states}} e^{-\beta E_i(N)} e^{\beta\mu N}$$

$$= \sum_N e^{\beta\mu N} \sum_{\text{N-particle states}} e^{-\beta E_i(N)}$$

$$= \sum_N e^{\beta\mu N} \underbrace{Z(T,V,N)}_{\text{this is what is needed in canonical ensemble.}} = \sum_N \xi^N Z(T,V,N)$$

i.e. Q "generates" $Z(T,V,N)$

Standard Problems

- For an undergraduate statistical mechanics course, there are several standard problems.
- $\underbrace{\text{Non-interacting}}_{\text{easier}}$ vs $\underbrace{\text{interacting}}_{\text{hard}}$

  easier (e.g.: all other problems in the course)

  hard (e.g.: real gas, Ising model, phonon problem (solvable))

- $\boxed{\text{Gases}}$

  Classical → MCE, CE → $Z = \frac{1}{N!}(z)^N$

  Quantum → start with GCE or most probable distribution → Q_F and Fermi-Dirac distribution; → Q_B and Bose-Einstein distribution

Key factor is: $\underbrace{\left(\frac{V}{N}\right)\frac{1}{\lambda_{th}^3(T)}}$ $\sim \left(\frac{\text{particle separation}}{\text{thermal wavelength}}\right)^3$

large → classical limit

≈ 1 → need to consider fermions / bosons

$$\lambda_{th}(T) = \frac{h}{\sqrt{2\pi m kT}}$$

- 2-level systems (MCE, CE) or finite-level systems (per particle)
  - paramagnetism
- Collection of harmonic oscillators (MCE, CE)
  - heat capacity of solids (Einstein's model, Debye model)
  - Vibrational motion in molecules
- Rotational partition function of diatomic molecules
- When Z can be factorized into product of z's
- N-particle states vs single-particle states
  [interacting vs non-interacting system]
- Derivation of $f_{FD}(\varepsilon)$ and $f_{BE}(\varepsilon)$ and their meaning
- Using dimensionality and dispersion relation to derive the single-particle density of states
  [non-relativistic, relativistic dispersion relations]
- Derivation of $P(E_i)$ and $P(E_i(N), N)$, and the corresponding formalism.

- Interacting systems
  - coupled oscillators (exactly solvable, phonons)
  - Real gas (2^{nd} virial coefficient, van der Waals eqn.)
  - Law of corresponding states
  - Phenomena near critical point
  - 1D Ising (exactly solvable)
  - 2D Ising (mean field theory, critical behavior)
- Fermi Gas: Q_F, N-eqn, E-eqn, $pV = kT \ln Q_F$
  - $T=0$ physics (E_F, T_F, k_F) (Pauli Exclusion)
  - $T \ll T_F$ physics (order $\left(\frac{kT}{E_F}\right)^2$ corrections)
  - $T > T_F$ physics (correction to classical gas law)
  - Sommerfeld expansion and hand-waving argument for low-temperature physics

- Bose Gas : Q_B, N-eqn, E-eqn, $pV = kT \ln Q_B$
  - Meaning of $f_{BE}(\varepsilon) \Rightarrow \mu < \varepsilon_{lowest}$
  - Possibility of Bose-Einstein Condensation
  - Macroscopic Occupation of s.p. groundstate ($T<T_c$)
  - Determine T_c and N_0
  - Correction to classical gas law for $T \gg T_c$.

References

You should be able to read and work on problems in the following standard textbooks. Our course is at about the same level of these books.

1. Bowley and Sanchez : Ch.1-10 (out of 13 Chapters)
2. Mandl : Whole Book
3. Guénault : Ch.1-13+ (out of 15 Chapters)
4. Trevena : 10 chapters (out of 11)
5. Rosser : whole book

[Our treatments are more formal than 3 and 4. Our discussions on GCE, Fermi Gas, Bose Gas are more complete than 1 and 2.]

In preparing my lectures, I have continually consulted two graduate-level textbooks:

6. R.K. Pathria, "Statistical Mechanics" (2nd edition)
7. D.A. McQuarrie, "Statistical Mechanics"

We covered Ch.1-11 (out of 22 chapters) of 7 and Ch.1-8 (out of 14 chapters) of 6.

There are a few recently published† books that cover very similiar topics at the same level...

8. Ian Ford, "Statistical Physics: An Entropic Approach"

9. L.G. Benguigui, "Statistical Mechanics for Beginners: A textbook for undergraduates"

10. J.D. Walecka, "Introduction to Statistical Mechanics"

If you want to have one book that covers both thermodynamics and statistical mechanics and works everything out in detail, read

11. W. Greiner, L. Neise, H. Stöcker, "Thermodynamics and Statistical Mechanics"

† These books were published after I had prepared the class notes. They happened to cover similar topics at the same level.

Moving on...

- For those who want to learn more statistical mechanics, possible topics are
  - Interacting systems
    - classical systems (cluster expansion)
    - quantum systems (many-body formalism)
  - Phase transition and critical phenomena
  - Kinetic theory of gases and Boltzmann Equation
  - Transport Processes
  - Time-correlation function
  - Brownian Motion, fluctuations

A good way to start is to study the other chapters in Refs. 6 and 7 that are not covered in our course.