Chapter 1

The Language of Statistical Mechanics

Additional Reading

See also McQuarrie Ch. 1, Dill and Bromberg Ch. 1

The Theory of Measurements

I. Objectives of Statistical Mechanics

   A. Describe *macroscopic* properties in terms of *microscopic* (single molecule, single atom) properties

   B. Derive the postulates of equilibrium thermodynamics

   C. Describe finite systems where thermodynamics fails

      i. Melting of small clusters

      ii. Nanoparticles

      iii. Single molecule experiments

   D. Describe fluctuations from equilibrium

   E. Macroscopic properties of non-equilibrium solutions

      i. Chemical reactions rates

      ii. Nucleation

II. Terminology

   A. **Macroscopic**: U, H, A, G, S, μ, p, V, T, C_p, C_V

   B. **Microscopic**: consider for example, an N particle monatomic gas (N non-interacting particles in a 3D box)

i. From classical mechanics: $\vec{p}_x$, $\vec{p}_y$, $\vec{p}_z$, $\vec{q}_x$, $\vec{q}_y$, $\vec{q}_z$ for each particle $(\vec{p}^{3N}, \vec{q}^{3N}) = 6N$ degrees of freedom

ii. From quantum mechanics: n_x, n_y, n_z for each particle $= 3N$ degrees of freedom

C. **Assembly**: collection of a large (i.e., N) number of particles

D. **State** [of an assembly]: a fully specified set of coordinates for every particle (i.e., $6N$ from CM or $3N$ from QM)

i. Two classical states, α and β, for an assembly of N particles

$$\begin{array}{c|l} \alpha & p_{1x},\ p_{1y},\ p_{1z},\ q_{1x},\ q_{1y},\ q_{1z}, \\ & p_{2x},\ p_{2y},\ p_{2z},\ q_{2x},\ q_{2y},\ q_{2z}, \\ & \ldots \\ & p_{Nx},\ p_{Ny},\ p_{Nz},\ q_{Nx},\ q_{Ny},\ q_{Nz} \\ \hline \beta & p'_{1x},\ p'_{1y},\ p'_{1z},\ q'_{1x},\ q'_{1y},\ q'_{1z}, \\ & p'_{2x},\ p'_{2y},\ p'_{2z},\ q'_{2x},\ q'_{2y},\ q'_{2z}, \\ & \ldots \\ & p'_{Nx},\ p'_{Ny},\ p'_{Nz},\ q'_{Nx},\ q'_{Ny},\ q'_{Nz} \end{array}$$

ii. Two quantum states, α and β, for an assembly of N particles

state	n_{1x}	n_{1y}	n_{1z}	n_{2x}	n_{2y}	n_{2z}	...	n_{Nx}	n_{Ny}	n_{Nz}
α	1	1	0	2	1	1		0	1	2
β	2	1	2	2	1	3		1	2	2

iii. In either description, states evolve in time. Classically,

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{1.1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{1.2}$$

from Hamilton's equations of motion (or equivalently Lagrange or Newton's equations of motion). Quantum mechanically, we have

$$i\hbar \frac{\partial}{\partial t} \Psi\left(x_i, y_i, z_i, t\right) = H\Psi\left(x_i, y_i, z_i, t\right) \tag{1.3}$$

E. **Degeneracy**: $\Omega(E, N)$ is the number of distinguishable states of an assembly whose energy is E and particle number is N.

F. **Ensemble**: a collection of all possible states of an assembly or all states sampled in an infinite amount of time.

G. **Ergodic Hypothesis**: The time average of the microscopic quantities gives the same macroscopic result as an ensemble average

III. Approaches to the Central Problem of Statistical Mechanics - how do we calculate macroscopic, time-averaged properties from rapidly fluctuating microscopic quantities?

A. The Brute Force Approach: Time-average over microscopic properties. In this approach, we watch in real time which states the assembly visits, monitor the variable of interest, and compute its average,

$$\langle f \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} f(t) dt, \tag{1.4}$$

where $\langle f \rangle$ is an observed macroscopic quantity and f is a microscopic mechanical variable associated with operator F. This calculation is difficult and often impossible because it requires knowledge of the time dependence of a very large number of positions and momenta or quantum numbers.

B. Ensemble Theory: compute an average over all feasible states of an assembly and rely on the **ergodic hypothesis**. Often we can enumerate the states possible for an assembly without watching them in real time. In lieu of this missing information, we employ statistics and probability.

IV. Important Concepts about Probability

A. Probability arises when we

i. Have a random or uncertain future event. For example, we are about to throw a die and the probability of getting 3 is $\frac{1}{6}$.

ii. Have non-random, incomplete information about an event. For example, the die has already been thrown and our best guess is "equal likelihood."

iii. Need statistical information about multiple events. For example, we throw 6000 dice or one die 6000 times. What is the fraction of 3s expected or measured?

B. Probability Distributions

Property	Discrete Distribution	Continuous Distribution
Distribution	P_i: $i = 1, 2, ..N$	$P(x)dx$
Normalization	$\sum_{i=1}^{N} P_i = 1$	$\int_{x_{min}}^{x_{max}} P(x)dx = 1$
Positivity	$P_i \geq 0 \; \forall i$	$P(x) \geq 0 \; \forall x$
Examples	dice, cards, Kronecker δ, binomial, polynomial, Poisson	Dirac δ, Gaussian, Fermi-Dirac, Boltzmann

Note that for continuous distributions, $P(x)$ is the *probability density* which gives the probability between x and $x + dx$.

C. Description of a probability distribution in terms of *moments* For a discrete variable, i, or a continuous variable, x, the n^{th} moment of the probability distribution is defined as,

$$\langle i^n \rangle = \overline{i^n} = \frac{\sum_{i=1}^{N} i^n P_i}{\sum_{i=1}^{N} P_i} \tag{1.5}$$

$$\langle x^n \rangle = \overline{x^n} = \frac{\int_{x_{min}}^{x_{max}} x^n P(x)dx}{\int_{x_{min}}^{x_{max}} P(x)dx}, \tag{1.6}$$

where the denominators are only necessary if the distributions have not been normalized.

i. 0^{th} moment (normalization)

$$\left\langle i^0 \right\rangle = \left\langle x^0 \right\rangle = 1 \tag{1.7}$$

ii. 1^{st} moment (mean value, statistical average, expectation value)

$$\langle i \rangle = \frac{1 \cdot P_1 + 2 \cdot P_2 + 3 \cdot P_3 + \ldots + N \cdot P_N}{P_1 + P_2 + P_3 + \ldots + P_N} \tag{1.8}$$

$$= \frac{\sum_{i=1}^{N} iP_i}{\sum_{i=1}^{N} P_i} \tag{1.9}$$

$$\langle x \rangle = \frac{\int_{x_{min}}^{x_{max}} xP(x)dx}{\int_{x_{min}}^{x_{max}} P(x)dx} \tag{1.10}$$

iii. 2^{nd} moment (variance, standard deviation, dispersion, mean squared deviation)

$$\left\langle i^2 \right\rangle = \frac{\sum_{i=1}^{N} i^2 P_i}{\sum_{i=1}^{N} P_i} \tag{1.11}$$

$$\left\langle x^2 \right\rangle = \frac{\int_{x_{min}}^{x_{max}} x^2 P(x)dx}{\int_{x_{min}}^{x_{max}} P(x)dx} \tag{1.12}$$

The variance is defined as the square of difference from the mean, which is shown below to be equal to the difference of 2^{nd} moment and the square of the 1^{st} moment,

$$Var(x) = \left\langle (x - \langle x \rangle)^2 \right\rangle \tag{1.13}$$

$$= \left\langle x^2 - 2x \langle x \rangle + \langle x \rangle^2 \right\rangle \tag{1.14}$$

$$= \left\langle x^2 \right\rangle - 2 \langle x \rangle \langle x \rangle + \langle x \rangle^2 \tag{1.15}$$

$$= < x^2 > - < x >^2 . \tag{1.16}$$

The standard deviation is the square root of the variance, and is sometimes preferred because it has the same units as the mean and original variable.

$$Std(x) = \sigma = \sqrt{Var(x)} = \sqrt{< x^2 > - < x >^2}. \tag{1.17}$$

D. Probability distributions are often used to evaluate the mean value of a function (expectation value, statistical average). This is

$$\langle F \rangle = \frac{F(1) \cdot P_1 + F(2) \cdot P_2 + ... + F(N) \cdot P_N}{P_1 + P_2 + \ldots + P_N}, \tag{1.18}$$

for a discrete distribution and

$$\langle F \rangle = \frac{\int_{x_{min}}^{x_{max}} F(x)P(x)dx}{\int_{x_{min}}^{x_{max}} P(x)dx} \quad (1.19)$$

for a continuous distribution.

E. Probability distributions are also generalizable to several variables and are called multivariate probability distributions. For example, $P(x, y)$ gives the probability density of measuring the first variable between x and $x+dx$ and simultaneously the second variable between y and $y + dy$.

Property	Multivariable Continuous Distribution
Distribution	$P(x, y)dxdy$
Normalization	$\int_{x_{min}}^{x_{max}} \int_{y_{min}}^{y_{max}} P(x, y)dxdy = 1$
Positivity	$P(x, y) \geq 0 \ \forall x, y$
Examples	hands in blackjack, outcome in rolling two dice, velocity and nearest neighbor distance in solution

The probability distribution can be factored in the case that the two variables are uncorrelated,

$$P(x, y) = P_x(x)P_y(y). \quad (1.20)$$