

10.40 Chapter 10 – Statistical Mechanics, Molecular Methods, and Simulation

There are three ways of looking at the material in this chapter—three levels of stat. mech., if you will:

1) *The theoretical level*

- Discovering new concepts and formulating new models
- Mastering the mechanics and techniques of deriving new relationships between variables

2) *The conceptual level*

- Understanding the relationship between molecular interactions and macroscopic thermodynamics
- Understanding the approximations used
- Understanding the components of theories, methods, or equations

3) *The practical level*

- How to use the equations
- How to run related software
- How to interpret the results of the above

This class is focused on 2 and 3—understanding how molecular interactions affect thermodynamics and how to use this understanding in real-world problems. With that in mind, the following is a brief summary of the important concepts and equations in Chapter 10.

Phase Space

The instantaneous state of a system can be defined in terms of the position of particles in the system and the physical properties and interactions of those particles. For N “real” particles interacting classically, *phase space* would be the $6N$ -dimensional vector of positions ($\mathbf{r}_1 \dots \mathbf{r}_N$) and momenta ($\mathbf{p}_1 \dots \mathbf{p}_N$). This can be subdivided into *configuration space* and *momentum space*, each of which are $3N$ vectors.

A statistical mechanical method that allows you to sample *all* regions of phase space, without barriers, dead-ends, loops, or “traps,” is referred to as *ergodic*. *Ergodic sampling* in this context means that a method samples from all possible states.

The Classical Approximation

At high temperatures, and/or when $\Delta E/kT \ll 1$, a classical description of a system can be used in place of a rigorous quantum-mechanical treatment. The probability that a system of N particles is in a particular energy state at $\underline{E}_i$ is defined as:

$$P_i(\underline{E}_i) = \frac{\exp(-\underline{E}_i/kT)}{\sum_j \exp(-\underline{E}_j/kT)}$$

The form of this equation, by no coincidence, adopts Boltzmann statistics for molecules at equilibrium.

Gibbs Ensembles

A particle, given access to all states in phase space, will occupy those states with a particular probability distribution. There are different ensembles, each designed to mirror different macroscopic constraints. The ones we are interested in include:

- 1) *microcanonical ensemble*, where N , $\underline{V}$, and $\underline{E}$ (total energy) are held constant. This suggests the motion of classical particles in space (Newton's laws of motion).
- 2) *canonical ensemble*, where N , $\underline{V}$, and T are held constant—a closed, isothermal system.
- 3) *grand canonical ensemble*, an open system with constant μ , $\underline{V}$, and T .
- 4) *isobaric/isothermal ensemble*, where, of course, N , P , and T are constant.

For an ensemble of N particles, we can calculate an ensemble average of any thermodynamic property B for all states k by multiplying B_k by the probability density and averaging the quantity:

$$B_{\text{observed}} = \langle B \rangle = \sum_k P_N(\mathbf{r}^N, \mathbf{p}^N) B_k$$

Canonical Partition Function

The denominator of P_N as defined above is an important expression. It normalizes the distribution by summing over all allowed states in phase space, and so inherently describes many properties of the system. The *canonical partition function*, which is this sum in $N\underline{V}T$ coordinates, is defined as:

$$Q_N \equiv \sum_i \exp(-\beta \underline{E}_i)$$

The *ergodic hypothesis* lets us equate time averages with ensemble average for *ergodically*-sampled ensembles. We can use the properties embedded in Q_N to calculate many important physical properties, for example:

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

We can also connect macroscopic thermodynamics directly to the canonical ensemble through the equation:

$$\underline{A} = -kT \ln Q_N$$

Section 10.1 and the first chapter of Hill show many more examples and derivation of these properties.

Classical Monatomic Ideal Gas

From the expression for P given above, it can be shown that for noninteracting particles ($Q_N \rightarrow Q_N^g$), the equation $P=NkT/\underline{V}$ appears directly from the stat. mech. relationships.

The Semiclassical Approximation

To make the partition function tractable for polyatomic molecules with rotations, vibrations, and electronic transitions as well as center-of-mass translation, we can factor Q_N into two components, *internal* and *center-of-mass*:

$$Q_N = Q_{int}(T, N, \text{structure}) Q_{cm}(T, \underline{V}, N)$$

For a single component system, Q_{int} can also be represented as the product of q_{int} raised to the N power, $Q_{int}=(q_{int})^N$. Each atomic q_{int} can be further decomposed into all of the internal contributions:

$$q_{int} = q_{rotation} q_{vibrations} q_{internal\ rotations} q_{electronic\ motions} q_{nuclear\ spin}$$

The center-of-mass component can also be simplified by separating the intermolecular effects into potential energy (PE) and kinetic energy (KE) effects, assuming molecules are rigid, and characterizing the interactions between molecules in an intermolecular potential energy function.

Intermolecular Forces

Forces between molecules can be characterized as *short range* (repulsive interactions between electron clouds), *intermediate range* (hydrogen bonds, molecular association) and *long range* (Coulombic, dispersion, induction, van der Waals, dipole-dipole). *Potential energy functions* attempt to capture the effects of all three through empirical or semi-empirical functional approximations. Table 10.3 lists many popular potential functions. A common approximation is *pairwise*

additivity, which assumes that many-body interactions can be represented as sum of pairwise *i-j* interactions.

Virial Equation of State and Van der Waals Theory

We can rigorously derive the virial equation of state in statistical mechanics, and show that the coefficients $B(T)$, $C(T)$, $D(T)$, etc. relate to 2-body, 3-body, and 4-body interactions, respectively. We can calculate $B(T)$ directly from pairwise potentials:

$$B(T) = -2\pi N_A \int_0^{\infty} [\exp(-\beta\Phi(r)) - 1] r^2 dr$$

and use the assumption of pairwise additivity and special cluster integral techniques to estimate $C(T)$.

We can also re-write the classic partition function in terms of fluid structure, locating clusters of parameters that correspond to *attractive* and *excluded volume* contributions and deriving the van der Waals a and b parameters from intermolecular interactions. This theoretically rationalizes the choice of the a and b parameters and shows the direct link between PVT properties and intermolecular forces.

Molecular Corresponding States

Corresponding states, widely used in traditional Chemical Engineering practice, also has roots in molecular-level effects. Just as we traditionally reduced physical properties by critical constants, we can similarly reduce properties by the parameters of the potential energy expression used to describe the system. This lets us write a reduced temperature, T^* , as $T^* = kT/\epsilon$, or reduced pressure as $P^* = P\sigma^3/\epsilon$ if we assume that a Lennard-Jones potential governs intermolecular interactions. These new reduced properties can be linearly correlated to traditional reduced properties such as T/T_c and P/P_c .

Radial Distribution Functions

The most convenient and intuitive way to characterize the structure of a uniform fluid is through a *radial distribution function*, $g(r)$. The RDF is defined as the ratio of local density to average density:

$$g(r) \equiv \frac{\rho(r)}{\rho} = \frac{\rho(r)}{\langle \rho \rangle}$$

This function gives a time-averaged picture of the distribution of neighbors around any given particle. By definition this function should decay to 1 as r becomes large, and should be 0 at small r (inside the excluded volume of the

particle). For a large number of particles, integrating the RDF over all space should give the total number of particles:

$$N \approx N - 1 = \int_0^{\infty} \langle \rho \rangle g(r) 4\pi r^2 dr$$

where $\langle \rho \rangle g(r) 4\pi r^2 dr$ is the probability of finding a neighbor within the spherical shell at a distance r with thickness dr . Representative RDFs for liquid, vapor, and solid phases are given in Figure 10.5.

Ensemble-averaged properties, dependent on structure, as well as the 2nd virial coefficient, can be calculated from radial distribution functions.

Molecular Simulation Applications

We can generate configurations—that is move through phase space—using computerized molecular simulations. Two types of simulation are discussed.

1) *Monte Carlo* simulations generate successive configurations through random molecular displacement. The *Metropolis Algorithm* determines which moves are accepted and which are rejected. The ensemble-averaged properties for this type of simulation are simply arithmetic means of those properties sampled at each configuration. Since time is not included, only equilibrium and structural properties can be calculated.

2) *Molecular Dynamics* simulations generate configurations through the numerical integration of Newton's Laws of Motion. Properties can then be derived through the microcanonical (*NVE*) ensemble. This allows the calculation of dynamic properties, such as kinetic temperature and diffusion coefficients.

Periodic boundary conditions are used in simulations to let a finite number of molecules mimic a macroscopic system. Simulations often involve generating 1,000 to 1,000,000 independent configurations for sets of 100 to 10,000 atoms or molecules. Statistical analysis is used to determine *equilibration*, that is whether equilibrium has been reached, before sampling of properties begins.

Critical Phenomena

In general there are two types of phase transitions, so-called discontinuous and continuous phase transitions. Discontinuous phase transitions are so named because they correspond to a discontinuity in the derivatives of free energy (actually the derivatives diverge). In continuous-phase transitions the first derivative of free energy is continuous (thus the derivative of free energy with

respect to pressure, which is the volume, is continuous across the vapor-liquid critical point).

Critical Phenomena are important in a number of chemical engineering applications:

- Structured fluids: micelles, liquid crystals (Professor Litster) etc.
- Fluid equilibria
- Surface phenomena
- Polymers

Critical phenomena can be expressed as:

$$\text{order parameter (e.g. } \rho_L - \rho_V \text{ or } \langle M \rangle) \propto |T - T_c|^\beta$$

Where $\langle M \rangle$ is the average magnetization and β is the critical exponent. Be careful, this β is not to be confused with $1/k_B T$.

For our purposes, an analysis of $\langle M \rangle$ is instructive. This is because magnetization and liquid-vapor critical points follow the same rules, that is they belong to the same “Universality Class”.

For our analysis of magnetization, with a system of N particles each with spin, S_i and with magnetic susceptibility μ , $\langle M \rangle$ can be written as:

$$\langle M \rangle = \sum_{i=1}^N \mu S_i$$

It has been observed (first by Curie) that even in the absence of a magnetic field that below some critical temperature (which is referred to as the Curie Temperature, T_C) spontaneous magnetization occurs (i.e. $\langle M \rangle$ is non-zero). This phenomenon of spontaneous magnetization which is analogous to the vapor-liquid critical point described in Chapter 6 of Tester and Modell. It is quite striking that the same physics underlie two apparently different phenomena. To understand how this is possible, we need to consider statistical thermodynamics.

From our study of statistical mechanics, we know that the partition function, Q , can be written as:

$$Q = \sum_{i=1}^N \exp(H_i / k_B T)$$

Where H_i is equal to E_i in the classical approximation. Furthermore, we know that Q contains all the thermodynamic information needed to describe the macroscopic state of a system. The question is, “How do we interpret Q to understand critical phenomena?”

The Ising Model

The Ising model is one means of interpreting Q . The basic idea is that the system can be divided as a lattice of N cells. Each of these cells is filled with a particle that has a spin (S_i) or either $+1$ or -1 . If an external field of magnitude h is applied to the system, the energy of state i can be written as:

$$E_i = -\sum_{i=1}^N h\mu S_i - \sum_{i,k} J S_i S_k$$

In this expression, J , is the coupling constant and represents the energy stabilization that occurs when like spins are nearest neighbors. The symbol $\sum'$ is a special notation which means a summation over nearest neighbors only.

Also, from statistical mechanics we know that:

$$Q_N = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N=\pm 1} \exp(Q_i) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N=\pm 1} \exp \left[\sum_{i=1}^N (\mu h S_i / k_B T + J S_i S_{i+1} / k_B T) \right]$$

Here, the summation of $S_i S_{i+1}$ has replaced the $\sum'$.

This expression for the partition function contains all the macroscopic thermodynamic information we need. It can be solved in one of two ways:

- 1) Direct Numerical Solution
- 2) Through the use of simplifying assumptions
 - a) reducing the dimensionality
 - b) "mean-field" theory.

Approach 1) is useful, predicting a value for the critical exponent, β , of approximately 0.31, quite close to the experimental value of approximately 0.33. This close agreement between experiment and theory is reassuring. Unfortunately, numerical solution does not provide physical insight. Let's discuss approach 2).

Solving the Ising Model

Reducing the Dimensionality:

First, what happens if we reduce the dimensionality of the Ising Model?

1D – analytically solvable, but does not predict spontaneous magnetization at T_c . Why? Physically, the failure of the 1D Ising Model to predict spontaneous

magnetization is due to the fact that as T approaches 0, the free energy (A) is dominated by the internal energy contribution (U). In turn, for macroscopic systems, U approaches infinite as N approaches infinite. Thus, there is no driving force for magnetization.

2D – Onsager solved the 2D Ising Model. The exact form of Onsager's model is not as important as the final result, that being an analytic result for the critical exponent of β of $1/8$. Unfortunately, the 2D Ising Model's prediction of β is not very close to the experimental value. This indicates that a second approach is needed.

Mean-Field Theory:

The basic idea in mean-field theory is that we can "tag" one particle in our system. The "tagged" particle then interacts with the remaining $N-1$ as an average system. From this approximation, we can write:

$$E_j = -\sum_{i=1}^N S_i h_i^{\text{eff}} = -\sum \mu_i S_i \left(h + \sum_k J_{ik} \langle S_k \rangle + \sum_k J_{ik} (S_k - \langle S_k \rangle) \right)$$

In this expression, the terms have the following meanings:

$\sum_i \mu_i S_i h \equiv$ magnetization due to an external field, of strength, h

$\sum_i \sum_k S_i J_{ik} \langle S_k \rangle \equiv$ magnetization due to interaction with mean field spin, $\langle S_k \rangle$

$\sum_k J_{ik} (S_k - \langle S_k \rangle) \equiv$ magnetization due to fluctuations from the mean field spin

The term h^{eff} is used to express all these contributions in one term.

Also, in this notation, $J_{ik} = J$ if i and k are nearest neighbors, else $J=0$.

If we ignore the contributions of fluctuations (i.e. if $S_k - \langle S_k \rangle = 0$) then our expression for energy simplifies to:

$$E_j = -\sum_i S_i (h + 2DJ \langle M \rangle) \quad \text{since} \quad \sum J_{ik} \langle S_k \rangle = 2DJ \langle M \rangle$$

And after a short derivation, which involves using the definition of an ensemble average for $\langle M \rangle$ and subsequent Taylor Series expansion, we find that:

$$\langle M \rangle \propto \left(\frac{T_c - T}{T_c} \right)^{1/2} \quad \text{i.e. } \beta = 1/2 \text{ (mean-field theory result)}$$

Why does mean-field theory fail to predict β more accurately?
Remember that we assumed that the contribution of fluctuations was ignored in our treatment. Far from the critical point, this assumption is justified, but close to the critical point ignoring fluctuations is a poor assumption. For this reason, our mean-field prediction is not extremely accurate.

In conclusion, our treatment of Critical Phenomena and the Ising Model is important because it lays the ground work for (a) a more rigorous understanding of a very important class of phase transitions and (b) thermodynamic models which are based on concepts similar to that of the Ising model such as the Lattice Gas and equations of state for polymers such as the Flory-Huggins equation of state.