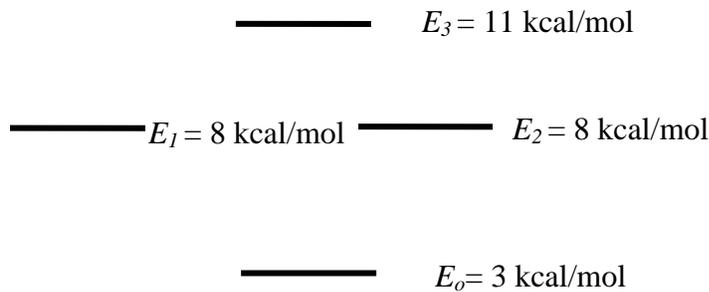
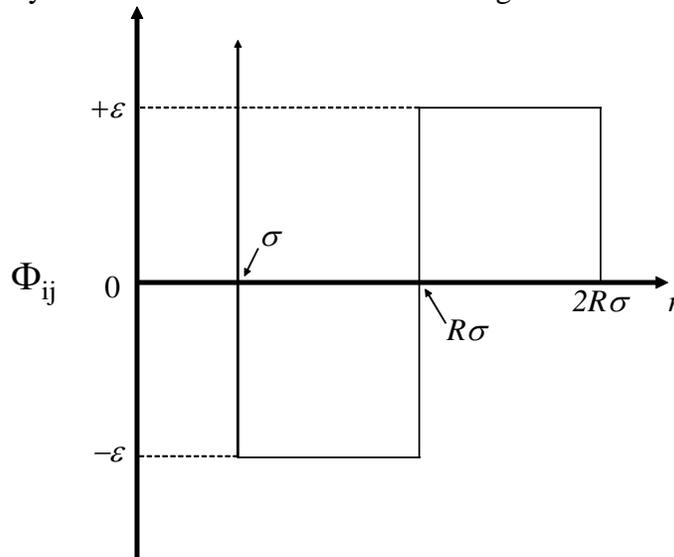

Use of *Thermodynamics and Its Applications*, 3rd ed. and 10.40 class notes and handouts and a hand calculator are permitted. No other aids or documents are permitted. Please answer each question in a separate exam book. Be careful about managing your time and be aware of the maximum points allotted to each part of the 6 problems.

1. (20 points) For a 1 mole molecular system that can only occupy any of 4 different states:



- (a) (4 points) What is U at $T = 300 \text{ K}$?
- (b) (4 points) What is the probability that a given snapshot of the system will have an energy of 3 kcal/mol at 300 K ?
- (c) (4 points) If each energy state is increased by 2 kcal/mol , what is the probability that a given snapshot of the system will have an energy of 3 kcal/mol at 300 K ?
- (d) (4 points) What is U as T gets very large?
- (e) (4 points) What is U as T gets very small?
2. (10 points) Imagine a lattice consisting of 10000 sites filled with 3000 indistinguishable particles at temperature T . Only one particle can reside at each lattice site and there is no energy of interaction between particles of any type. The initial state is such that the 3000 particles occupy 30% of the lattice volume separated by a partition from the rest of the lattice. Compute the change in \underline{G} from the initial state to a final equilibrium state.

3. (15 points) In terms of the grand partition function, Ξ , the PVT equation of state is expressed explicitly in molecular units in Equation (10-57) as $PV = kT \ln \Xi$.
 Recalling our discussion in class of the Virial equation of state, develop an analysis to determine under what conditions Eq(10-57) would reduce to the ideal gas equation of state for a range of densities. Describe the nature of the intermolecular interactions that exist that will yield this result.
4. (20 points) For a fluid whose intermolecular interactions follow the Sutherland potential described in Problem Set 8 (Problem 10.12 of the text):
- (a) (10 points) Can $B(T)$, the second virial coefficient, be positive or negative or zero? Justify your answer and explain its significance in terms of molecular interactions.
- (b) (10 points) Do you expect that this fluid will exhibit a Zeno point condition at high density ($\rho \gg 0$) where the compressibility factor $Z = PV/RT$ equals unity? Explain the rationale behind your answer.
5. (20 points) A set of different polyatomic, multi-polar molecules all have similar intermolecular potential functions for their binary interactions, as described approximately by the functional form shown in the figure below.



- (a) (10 points) Develop an expression for $B(T)$, the second virial coefficient, for a particular pure component species.
- (b) (10 points) Would you expect all pure fluids in this set of compounds to follow the Law of Corresponding States? What are the appropriate scaling parameters to non-dimensionalize T , P , and V for each fluid that you could use to test your answer with a set of experimental volumetric data? Briefly explain the rationale behind your choice of scaling parameters.

6. (15 points) The direct evaluation of the partition function for a liquid is difficult to achieve in practice. Fortunately a range of approximations are available. In the simple cell model for liquids, a unit cell is envisioned to be composed of a single molecule “engaged” inside a rigid lattice formed by the nearest neighbor molecules surrounding the trapped molecule. This entrapped molecule is allowed to wander inside the cell volume (see figure below). Although it is not possible to characterize the interaction energy of the wandering molecule by a single value, the mean field approximation and free volume concepts can be applied. If we bring N molecules together from infinite mutual separations to form a lattice, the system loses potential energy due to attractive forces which can be equated to the “lattice energy” $= \Phi_L$. Now we assume that all molecules are at fixed locations in the lattice, except for the wandering molecule which is assumed to preferentially want to locate at the cell center. Thus, on a per molecule basis the attractive part of the potential energy is Φ_L/N . In general, Φ_L depends on lattice spacing and hence on the volume. Note that while all molecules have the same size described by spheres of diameter σ , the lattice on the other hand has characteristic nearest neighbor distance of a as shown in the figure below.

- (a) (8 points) Develop an expression for the configurational integral for the cell in the liquid model.
- (b) (7 points) If Φ_L/N can be approximated by $\Phi_L = - a/V$, where $a = a(T)$ is only a function of temperature, develop a pressure-explicit EOS form in terms of $P = f(T, V, V_o, a(T))$.

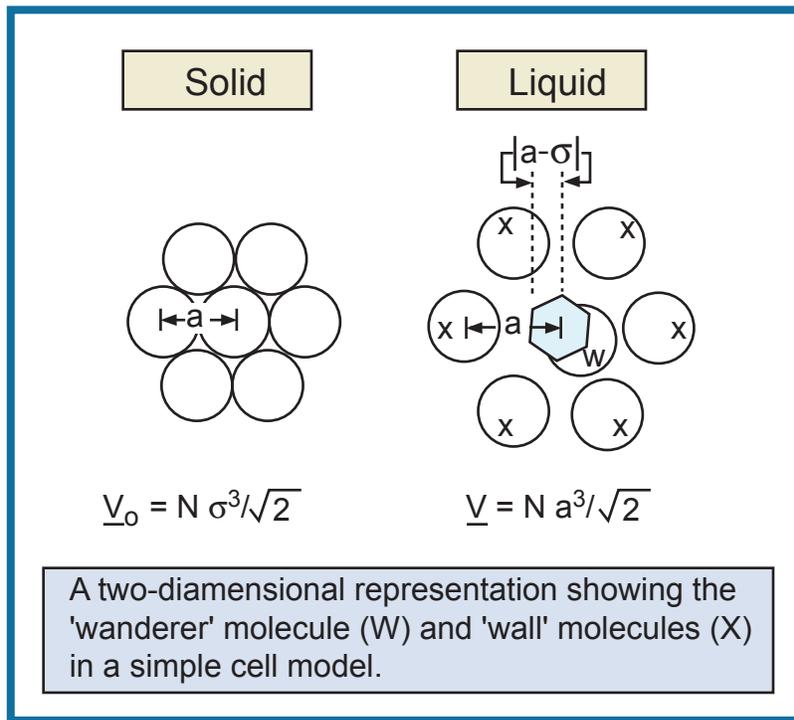


Image by MIT OCW.