

Equilibrium Statistical Mechanics

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Chapter I

Introduction

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Energy

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Introduction

- ▶ What is Statistical Mechanics?
- ▶ Microscopic and macroscopic descriptions.
 - ▶ Statistical mechanics is used to describe systems with a large ($\sim 10^{23}$) number of degrees of freedom
 - ▶ particles, spins, neurons, investors, animal populations, early universe, processors...
 - ▶ Gas ($\sim 10^{23}$ particles) continual collisions with each other and container walls. Classical (Chapt. 2)
 - ▶ Newton's equations + initial conditions \rightarrow evolution of \vec{r} , \vec{p} is known for all time
 - ▶ This implies that we know the density $n(\vec{r}, t)$ where

$$n(\vec{r}, t) = \frac{1}{\Delta V} \int_{\Delta V} d^3 r_j \sum_{j=1}^N \delta(\vec{r} - \vec{r}_j(t)) \quad (1)$$

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- ▶ The density counts the number of particles in the volume ΔV in a time interval Δt around t
- ▶ ΔV is small compared to the system size but large compared to a particle size \rightarrow large number of particles in $\Delta V (\sim 10^2 - 10^3)$
- ▶ Δt is large compared to microscopic times.
- ▶ We will refer to quantities such as \vec{r} and \vec{p} as microscopic variables and those like $n(\vec{r}, t)$ as macroscopic variables.
- ▶ Knowing the value of all 10^{23} microscopic variables is technically not feasible. Chaos. Molecular dynamics.
- ▶ Quantum mechanics is worse. Wave function (Schrodinger equation) for 10^{23} particles is harder.
- ▶ We will refer to systems that have a microscopic description as having a microstate. (models)
- ▶ Other macroscopic variables-energy, pressure, magnetization...

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- ▶ Since the microscopic description is not viable we adopt a macroscopic approach.
 - ▶ Coarse grained(macroscopic) variables leave out information \rightarrow statistical description.
 - ▶ Thermodynamics-relation between macroscopic variables is deterministic however it requires entropy.
 - ▶ Entropy is a measure of statistical uncertainty.
 - ▶ Entropy is not definable in terms of microscopic variables.

Walls

- ▶ Important variable-Energy

$$E = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j) \quad (2)$$

- ▶ We assume forces are conservative (derivable from a potential)
- ▶ Potential is only a function of the particle position and is pairwise additive.
- ▶ Also assume that all masses are the same and molecules have no internal structure.
- ▶ In an isolated system the energy is conserved.
- ▶ The classical Hamiltonian \rightarrow the quantum in the usual way.

- ▶ Energy can be supplied to or taken from a system in the form of heat or work.
- ▶ Once the energy is in the system we cannot tell in which form it was added.
- ▶ Mechanical energy(work) is added by changing the external parameters.
- ▶ Heat by radiation or conduction.
- ▶ We control how energy is added by the use of walls.
 - ▶ Adiabatic wall - allows no heat transfer
 - ▶ Diathermic wall allows heat transfer
 - ▶ Work is generated by the change of the external parameters, piston, electric field· · ·
 - ▶ Rigid walls allow no work to be done by changing system shape. (no piston)
 - ▶ Permeable walls allow only particles to enter or leave. Semi-permeable-selective as to particle type.
 - ▶ Isolated system exchanges no energy with surroundings

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Work, Heat Internal Energy

Quantitative development of general concepts discussed above.

- ▶ Consider a cylinder with a piston. The position of the piston is specified by x coordinate.(figure1)
- ▶ If $F(x)$ is the component of the force applied by the piston parallel to the x axis then

$$dW = F(x)dx \quad (3)$$

$$W_{A \rightarrow B} = \int_{x_A}^{x_B} dx F(x) \quad (4)$$

- ▶ We assume the process is quasi-static (discussed more fully shortly) \rightarrow Macroscopic (e.g. E) variables independent of path.

- ▶ The total energy then is the sum of the two forms of energy available - work and heat.

$$E_B - E_A = Q_{A \rightarrow B} + W_{A \rightarrow B} \quad (5)$$

- ▶ $Q_{A \rightarrow B}$ is the heat supplied in going from $A \rightarrow B$.
- ▶ $W_{A \rightarrow B}$ is the work done going from $A \rightarrow B$.

This is often written in differential form

$$dQ = dE - dW \quad (6)$$

This is the first law of thermodynamics.

- ▶ ΔE is independent of path whereas ΔQ and ΔW is not.

This can be seen for the work in analogy to mechanical work

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$$W_{A \rightarrow B} = \int_A^B \vec{F} \cdot d\vec{l} \quad (7)$$

which clearly depends on the path.

Discussion of Thermal Equilibrium

If we wait long enough the system will evolve to a state that is independent of the past history and time

This will be referred to as the EQUILIBRIUM state

- ▶ Systems in equilibrium will be our focus this semester.
 - ▶ There are systems such as glasses that are not in equilibrium but are relaxing over thousands of years. State depends on history.

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- ▶ There are also systems that appear to be in equilibrium but are metastable. If we wait long enough they will spontaneously decay to a different (usually equilibrium) state.
- ▶ Metastable states also exhibit hysteresis (figure 2)
- ▶ For systems of particles with no structure (point particles) the equilibrium state is specified by E , V and $\{N_i\}$ where V is the volume and N_i the number of particles of type i .
 - ▶ This is a statement based on experiment and will be justified by comparison of theory with experiments.
 - ▶ Often we will restrict ourselves to one kind of particle so that the system is specified by E , V and N .
- ▶ The quantities E , V and N are extensive. That is they are proportional to the volume V .

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Postulate of Maximum Entropy

Consider an isolated system divided into two subsystems 1 and 2.(figure3) separated by a piston.

- ▶ The subsystems are large enough that any interaction with the walls is negligible.
- ▶ The subsystems are characterized by $E_1, V_1, N_1, E_2, V_2, N_2$
 - ▶ $E = E_1 + E_2, V = V_1 + V_2, N = N_1 + N_2$
- ▶ The piston creates the following internal constraints.
 - ▶ If fixed no energy is transmitted from one subsystem to the other in the form of work.
 - ▶ If adiabatic, no heat flow.
 - ▶ Impermeable, no particle flow.
- ▶ We lift the constraint by making the wall mobile, permeable, diathermic or any combination.

We begin with a fixed, adiabatic, impermeable piston with both sides in equilibrium and remove one or more constraints and ask what happens and how can we describe it.

The following postulates are equivalent to the usual statement of the second law of thermodynamics.

- ▶ 1. For any system at equilibrium, there exists a positive differential entropy function $S(E, V, N^{(1)} \dots N^{(r)})$ which is an increasing function of E for a fixed V and $\{N^{(i)}\}$.
- ▶ 2. For a system made up of M subsystems, S is additive, or extensive: the total entropy, S_{tot} , is the sum of the entropies of the subsystems.

$$S_{tot} = \sum_{m=1}^M S(E_m, V_m, \{N^{(i)}\}) \quad (8)$$

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- ▶ 3. Suppose the global isolated system is initially divided by internal constraints into subsystems that are separately at equilibrium: if we lift one (or more) constraint the final entropy, after the re-establishment of equilibrium, must be greater or equal to the initial entropy. The new values of E_m , V_m , N_m^i are such that the entropy is increased or remains the same. In summary: the entropy of an isolated system cannot decrease.
- ▶ Rigorously, the entropy is only defined for a system in equilibrium.
 - ▶ If we have a system that is globally not in equilibrium, but we can divide it into subsystems that are almost at equilibrium with whom they interact weakly, we can define a global entropy via equation ???. This is important in non-equilibrium statistical mechanics.

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Quasi-static process Transformation $A \rightarrow B$ is quasi-static if the system stays infinitesimally close to equilibrium.

- ▶ Process is infinitely slow since we need to wait after each step for the system to come back into equilibrium.
 - ▶ Idealization-change in control parameters slow compared to relaxation time.

If the transformation is (in the real world) slow enough that the system can be thought of as going from one equilibrium state to the other then we can define the entropy for each time step. $S_{tot}(t)$

- ▶ $S_{tot}(t)$ will be an increasing function of time if the system is isolated.

For a homogeneous system the entropy is a concave function of the extensive variables E, V, N .

- ▶ Concave function $f(x)$ has $f''(x) \leq 0$ and

$$f\left(\frac{x_1 + x_2}{2}\right) \geq \frac{f(x_1) + f(x_2)}{2} \quad (9)$$

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- ▶ Convex function $f''(x) \geq 0$ and

$$f\left(\frac{x_1 + x_2}{2}\right) \leq \frac{f(x_1) + f(x_2)}{2} \quad (10)$$

Suppose for a homogeneous system S were a **strictly** convex function of E instead of concave. Then from eq.??

$$2S(E) < S(E - \Delta E) + S(E + \Delta E) \quad (11)$$

From eq.?? (additivity of the entropy) we have $2S(E) = S(2E)$.

Then

$$S(2E) < S(E - \Delta E) + S(E + \Delta E) \quad (12)$$

- ▶ If the system were inhomogeneous with the energies $E - \Delta E$ and $E + \Delta E$ it would have a higher entropy (by the entropy maximum postulate) and hence the equilibrium state would not be homogeneous contrary to our assumption.

- ▶ The breakdown of the concavity is a signature of a phase transition where the system goes from homogeneous to heterogeneous.

Intensive Variables: Temperature, Pressure, Chemical Potential

$$\left. \frac{\partial S}{\partial E} \right|_{V, N^i} = \frac{1}{T} \quad (13)$$

$$\left. \frac{\partial S}{\partial V} \right|_{E, N^i} = \frac{P}{T} \quad (14)$$

$$\left. \frac{\partial S}{\partial N^i} \right|_{E, V, N^{j \neq i}} = -\frac{\mu^i}{T} \quad (15)$$

- ▶ The variables T, P, μ^i are called intensive variables.

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- ▶ Double system size extensive variables (E, V, N^i) double; intensive remain the same.

- ▶ These are definitions. We need to show that they correspond to our physical intuition.

Temperature

Does eq.(??) \rightarrow thermal equilibrium?

- ▶ Assume an system divided by a fixed, impermeable, adiabatic wall. The two subsystems have entropies $S_1(E_1, V_1)$ and $S_2(E_2, V_2)$.
 - ▶ We have suppressed the N dependence since it will remain fixed.
 - ▶ Both sides are assumed to be in equilibrium independently since they do not interact.
- ▶ We now make the wall between subsystems diathermic so that heat can be exchanged.
- ▶ The system will now come into equilibrium such that the total $S = S_1 + S_2$ is maximized.

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$$dS = \left. \frac{\partial S_1}{\partial E_1} \right|_{V_1} dE_1 + \left. \frac{\partial S_2}{\partial E_2} \right|_{V_2} dE_2 = 0 \quad (16)$$

- ▶ Since the total system (1 + 2) is isolated
 $dE = dE_1 + dE_2 = 0$.
- ▶ From energy conservation and the definition of temperature (eq.??)

$$dS = \left[\frac{1}{T_1} - \frac{1}{T_2} \right] dE_1 = 0 \quad (17)$$

- ▶ Since dE_1 is arbitrary we must have that the final temperatures of both sides are equal; $T_1 = T_2 = T$

When two systems are in thermal contact equilibrium implies that they come into the same temperature defined by eq.??

- ▶ Does heat energy flow from hot to cold?

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- ▶ Compartment 1 is initially colder than compartment 2, $[T'_1 < T'_2]$ - prime denotes initial state.
- ▶ (a) Since $\frac{\partial^2 S}{\partial E^2} < 0 \rightarrow \frac{\partial T}{\partial E} > 0$ and the process is quasi-static.
- ▶ (b) The system will come to equilibrium with $T_1 = T_2$
- ▶ Suppose energy flows from system 1 to system 2. Then from (a) above T_1 will decrease and T_2 will increase.
- ▶ This will make the equilibration of the temperature in item (b) impossible.
- ▶ It will only be possible if heat flows from system (2)(hotter) to system (1)colder.
- ▶ This implies that our definition of temperature corresponds to what we expect physically.
Suppose that $\frac{\partial^2 S}{\partial E^2} = 0$ over some interval of E
(function not strictly concave)

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- ▶ In this range the exchange of energy causes no temperature change.
- ▶ Physically this corresponds to a phase transition with a latent heat.

Pressure

Does eq.(??) \rightarrow mechanical equilibrium?

- ▶ We start again with a two chamber system with each side isolated from the other in in equilibrium.
- ▶ We now make the wall diathermic and mobile and apply the entropy maximum principle.

$$dS = \left[\frac{\partial S_1}{\partial E_1} \Big|_{V_1} dE_1 + \frac{\partial S_2}{\partial E_2} \Big|_{V_2} dE_2 \right] + \left[\frac{\partial S_1}{\partial V_1} \Big|_{E_1} dV_1 + \frac{\partial S_2}{\partial V_2} \Big|_{E_2} dV_2 \right] = 0 \quad (18)$$

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- ▶ $dE_1 = -dE_2$ and $dV_1 = -dV_2$ since the total system is isolated.
- ▶ Using these relations and eqs.(??) and (??) we obtain

$$dS = \left[\frac{1}{T_1} - \frac{1}{T_2} \right] dE_1 + \left[\frac{P_1}{T_1} - \frac{P_2}{T_2} \right] dV_1 = 0 \quad (19)$$

- ▶ As before dE_1 and dV_1 are arbitrary $\rightarrow T_1 = T_2$ and $P_1 = P_2$.
- ▶ Suppose $T_1 = T_2 = T$ then from eq.(??)

$$dS = (P_1 - P_2) \frac{dV_1}{T} = 0 \quad (20)$$

- ▶ If P_1 is slightly bigger than P_2 then from $dS > 0$, $dV_1 > 0$

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If two systems are at the same T and in mechanical contact then the one at higher pressure expands

Chemical potential; equilibrium of particle flux

Finally, the piston is made diathermic, fixed and permeable to particles of type i .

$$dS = \left[\frac{\partial S}{\partial E_1} dE_1 + \frac{\partial S}{\partial E_2} dE_2 \right] + \left[\frac{\partial S}{\partial N_1^i} dN_1^i + \frac{\partial S}{\partial N_2^i} dN_2^i \right] = 0 \quad (21)$$

- ▶ The obvious quantities are held constant including the N^j for the other species than the i th.
- ▶ Again $dE_1 = -dE_2$ and $dN_1^i = -dN_2^i$ so we have

$$dS = \left[\frac{1}{T_1} - \frac{1}{T_2} \right] dE_1 - \left[\frac{\mu_1^{(i)}}{T_1} - \frac{\mu_2^{(i)}}{T_2} \right] dN_1^i = 0 \quad (22)$$

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- ▶ Using the same reasoning as before we find that in equilibrium $\mu_1^{(i)} = \mu_2^{(i)}$ and that particles of type i go from higher chemical potential to lower.

Equation of state

- ▶ Assuming N is a constant (only one species of particle) and eqs.(??) and (??) we have

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V = f_T(E, V) \quad (23)$$

$$\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_E = f_P(E, V) \quad (24)$$

- ▶ Since f_T is a strictly decreasing function of E for a homogeneous system (concavity of S) we can determine E as a function of T at fixed V .
 - ▶ $E = g(T, V)$
- ▶ Substituting E into eq.(??) we obtain

$$P = T f_P(g(T, V), V) = h(T, V) \quad (25)$$

- ▶ The relation $P = h(T, V)$ is the equation of state.

Ideal gas - one mole

$$P = \frac{RT}{V} = \frac{N_A k_B T}{V} = n k_B T \quad (26)$$

- ▶ R is the ideal gas constant, k_B is Boltzmann's constant, N_A is Avagadro's constatnt and n the density.
 - ▶ Experimental equation - dilute gas. Will derive from Stat. Mech.

Quasi-static and reversible processes

- ▶ Using equations (??) - (??) we have (one kind of particle)

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN \quad (27)$$

or

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$$TdS = dE + PdV - \mu dN \quad (28)$$

- ▶ Since S is an increasing function of E the mapping is one to one so there is $E(S)$ so we can write

$$dE = TdS - PdV + \mu dN \quad (29)$$

- ▶ If there is no work because $dV = 0$ and there is no change in N then $dE = TdS$
- ▶ From the first law of thermodynamics (eq.(??))

$$dQ = TdS \quad (30)$$

- ▶ This is a special case of the second law of thermodynamics which we will discuss in greater detail later. This form is only valid for quasi static processes.
- ▶ The pressure can be thought of as force per unit area $F/A \rightarrow$ for piston $dW = -PdV$. Pressure \rightarrow quasi-static process.

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From eq.(??) if we divide both sides with respect to dV and keep S and N constant

$$\frac{dE}{dV} = -P \quad (31)$$

or , since S and N are held constant

$$\left. \frac{\partial E}{\partial V} \right|_{S,N} \quad (32)$$

- ▶ This gives physical backing to our definition of the pressure which we could also obtain from eq.(??).
- ▶ We want to stress that

$$dE = dQ + dW \quad (33)$$

is always valid

- ▶ However

$$dE = TdS + dW \quad (34)$$

depends on the notion of entropy which needs a quasi static process.

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Reversible transformation

- ▶ A quasi-static transformation is reversible if it takes place at constant total entropy.
 - ▶ In general lifting one or more constraints on a system increases the entropy.
 - ▶ Re-imposing the constraints cannot return the system to its original state.
 - ▶ Hence the process is **irreversible**.
- ▶ For an isolated system removing the constraint causes the entropy to rise until a new equilibrium is established.
- ▶ For a reversible transition we can restore the original state by manipulating the **internal** constraints.
- ▶ If a homogeneous system is isolated and the total volume is fixed $dV = dQ = 0$. → if the process is quasi-static it is reversible.
- ▶ It is possible that parts of an isolated system will have an entropy decrease, whatever the process, compensated by an increase in other parts.

Maximum Work and Heat Engines

A device χ is connected to two heat sources at $T_1 > T_2$
The device supplies work to the outside.

Theorem of maximum work

- ▶ Suppose that χ receives a quantity of energy Q from a heat source, S , at temperature T .
 - ▶ We assume that S is big enough so that Q is infinitesimal compared to the total energy in S so that T remains unchanged.
 - ▶ The process is quasi-static so the entropy change of S is $-Q/T$. Such a source is called a **heat reservoir**
 - ▶ The system χ supplies an amount of work W to the outside world.
 - ▶ The combination $[\chi + S]$ is thermally isolated.
 - ▶ The energy change for χ is

$$\Delta E = Q - W \quad (35)$$

- ▶ This means that the change in energy of χ is equal to the energy added in heat minus the energy expended in work done by χ .

- ▶ The total entropy change, ΔS_{tot} , of $[\chi + S]$ (which is isolated) must be greater than or equal to zero. This is equal to the entropy change of χ (ΔS) minus the entropy change of the reservoir S . Hence

$$\Delta S_{tot} = \Delta S - \frac{Q}{T} \geq 0 \quad (36)$$

or

$$Q \leq T\Delta S \quad (37)$$

Finally using eqs(??) and (??)

$$W \leq T\Delta S - \Delta E \quad (38)$$

- ▶ Note that the maximum work is obtained when the work process is reversible so that $\Delta S_{tot} = 0$

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The device χ functions in a cycle. It returns to the same state.

- ▶ To obtain a cycle we will need the two heat reservoirs at T_1 and T_2 with $T_1 > T_2$

Let W be the work supplied by χ during one such cycle, Q_1 the heat given to χ by the hot reservoir and Q_2 the heat given to the cold reservoir.

- ▶ During this process χ is successively in contact with the two reservoirs. The transformations in the cycle are assumed to be reversible.
- ▶ The entropy of χ does not change since it returns to the same state. Hence in a cycle the entropy change in χ is given by

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad (39)$$

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- ▶ Since the work done is equal to the difference in the energy obtained from the hot reservoir minus the energy deposited into the cold reservoir by conservation of energy we have using eq.(??)

$$W = Q_1 - Q_2 = Q_1 \left(1 - \frac{T_2}{T_1} \right) \quad (40)$$

- ▶ Note that if $T_2 = T_1$ there is no work done. If we define the efficiency η as

$$\eta = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1} \quad (41)$$

- ▶ The entropy and hence the temperature is defined up to a constant. This is consistent with the fact that we can have many temperature scales. Fixing the constant fixes the temperature scale.

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Thermodynamic potentials Assume N is constant so that E is a function of S and V only.

- ▶ It is often convenient to have the system described by functions of T and P rather than S and V
- ▶ The variable changes are implemented using potentials or Massieu functions.
 - ▶ These functions are Legendre transforms of the energy and entropy.

We begin by showing how to go from the energy to the temperature.

Remembering that N is constant we have from eq.(??)

$$\left. \frac{\partial E}{\partial S} \right|_V = T \quad (42)$$

- ▶ The Legendre transform, F of E with respect to S is given by

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$$F(T, V) = E - TS \quad (43)$$

Note again from eqs.(??) and (??) we have with N fixed

$$dF(T, V) = dE - TdS - SdT \quad (44)$$

$$dF(T, V) = dE - T \left(\frac{1}{T} dE - \frac{P}{T} dV \right) - SdT \quad (45)$$

$$\left. \frac{\partial F}{\partial T} \right|_V = -S \quad (46)$$

- ▶ From eq(??) the first two terms cancel and the third term is zero since V is constant.

$$\left. \frac{dF}{dT} \right|_{(V, N) \text{ constant}} = -S \quad (47)$$

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Again from eq.(??)

$$dF(T, V) = TdS - PdV - TdS - SdT \quad (48)$$

If we keep T fixed and divide both sides by dV we have

$$\left. \frac{\partial F}{\partial V} \right|_T = -P \quad (49)$$

- ▶ Remember that N is held constant.
- ▶ The function F is called the free energy.
 - ▶ Going from E to F allows us to use the temperature rather than the entropy.
- ▶ There are other thermodynamic potentials two of which are

$$\bar{H}(S, P) = E + PV \quad (50)$$

which is called the **enthalpy**

We have

$$\left. \frac{\partial \bar{H}}{\partial S} \right|_P = T \quad (51)$$

and

$$\left. \frac{\partial \bar{H}}{\partial P} \right|_S = V \quad (52)$$

► Gibbs potential

$$G(T, P) = E - TS + PV \quad (53)$$

From arguments similar to those above.

$$\left. \frac{\partial G}{\partial T} \right|_P = -S \quad (54)$$

$$\left. \frac{\partial G}{\partial P} \right|_T = V \quad (55)$$

- ▶ These definitions and the fact that the functions (potentials) we consider have continuous second derivatives lead to the **Maxwell relations**
 - ▶ The continuous second derivatives implies that the order of the mixed partial derivatives is irrelevant.

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \quad (56)$$

From eqs.(??) and (??) eq.(??) implies

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V \quad (57)$$

- ▶ Similar reasoning applied to the Gibbs potential gives

$$\left. \frac{\partial S}{\partial P} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_P \quad (58)$$

- ▶ Instead of taking the Legendre transform of the energy we can take those of the entropy and obtain the Massieu functions.
- ▶ From eq.(??) and reasoning identical to that above we have

$$\left. \frac{\partial S}{\partial E} \right|_V = \frac{1}{T} \quad (59)$$

We define the Massieu function Φ_1

$$\Phi_1\left(\frac{1}{T}, V\right) = S - \frac{E}{T} = -\frac{1}{T}F \quad (60)$$

If we keep V fixed and N (as before) then $dS = \frac{1}{T}dE$. Hence

$$d\Phi_1 = dS - \frac{1}{T}dE - Ed\left(\frac{1}{T}\right) \quad (61)$$

or

$$\frac{\partial \Phi_1}{\partial 1/T} = -E \quad (62)$$

Remember $dS = \frac{1}{T}dE + \frac{P}{T}dV$ with fixed N .

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$$\left. \frac{\partial \Phi_1}{\partial V} \right|_{1/T} = \frac{P}{T} \quad (63)$$

- ▶ In thermodynamics the free energy F is more commonly used than the Massieu functions and T more commonly than $1/T$. However, in statistical mechanics we will see that $1/T$ and Φ_1 are the more natural functions.
- ▶ In fact Φ_1 will be seen as the log of the partition function.

Specific heats

- ▶ Suppose we give a system a quantity of heat dQ , in a quasi-static process, while keeping one or more of the thermodynamic variables fixed, say y . If dT is the increase in temperature the **specific heat** (or heat capacity) at fixed y is given by

$$C_y = \left. \frac{dQ}{dT} \right|_y = T \left. \frac{\partial S}{\partial T} \right|_y \quad (64)$$

where we have assumed a quasi-static process.

Moreover

- ▶ Note that $dE = dQ + dW$ and (for fixed N)
 $dE = TdS - PdV$
- ▶ Since $dW = -PdV$ it follows that $dQ = TdS$.
- ▶ The classic cases are the specific heat at constant volume C_V and the specific heat at constant pressure C_P .

$$C_V = \left. \frac{dQ}{dT} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V \quad (65)$$

$$C_P = \left. \frac{dQ}{dT} \right|_P = T \left. \frac{\partial S}{\partial T} \right|_P = \left. \frac{\partial \bar{H}}{\partial T} \right|_P \quad (66)$$

- ▶ The appearance of the enthalpy \bar{H} follows from $\bar{H} = E + PV$
- ▶ The quantities C_V and C_P are not independent. To derive the relation we need to define the following coefficients.
- ▶ **Expansion coefficient at constant pressure**

$$\alpha = \left. \frac{1}{V} \frac{\partial V}{\partial T} \right|_P \quad (67)$$

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► **Coefficient of isothermal compressibility**

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \quad (68)$$

► **Coefficient of adiabatic compressibility**
(constant entropy)

$$\kappa_S = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_S \quad (69)$$

We now need the following relation between partial derivatives. Consider a function $z(x, y)$ and its differential

$$dz = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy \quad (70)$$

► We now restrict ourselves to a surface of constant $z \rightarrow dz = 0$ so

$$\left. \frac{\partial z}{\partial x} \right|_y dx = - \left. \frac{\partial z}{\partial y} \right|_x dy \quad (71)$$

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We can write this as

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1 \quad (72)$$

- This is dependent on the fact that z is a constant.
As an example let $z^2 = x^2 + y^2$.

$$\left. \frac{\partial z}{\partial x} \right|_y = \frac{x}{z}$$

$$\left. \frac{\partial z}{\partial y} \right|_x = \frac{y}{z}$$

$$\left. \frac{\partial x}{\partial y} \right|_z = -\frac{y}{x}$$

Using

$$\left[\left. \frac{\partial z}{\partial y} \right|_x \right]^{-1} = \left. \frac{\partial y}{\partial z} \right|_x$$

we get the result in eq.(??).

- ▶ These equations also apply under cyclic permutations of the variables.

We apply the result to the variables T, V, P which are related through the equations of state.

$$\left. \frac{\partial T}{\partial P} \right|_V \left. \frac{\partial P}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P = -1 \quad (73)$$

We now use

$$dS(T, P) = \left. \frac{\partial S}{\partial T} \right|_P dT + \left. \frac{\partial S}{\partial P} \right|_T dP \quad (74)$$

where we have kept N constant. Using eq.(??)

$$TdS = C_P dT + T \left. \frac{\partial S}{\partial P} \right|_T dP \quad (75)$$

Using eq.(??) we have

$$TdS = C_P dT - T \left. \frac{\partial V}{\partial T} \right|_P dP = C_P dT - TV\alpha dP \quad (76)$$

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Where we have used eq.(??).

Dividing both sides of eq.(??) by dT

$$T \left. \frac{\partial S}{\partial T} \right|_V = C_P - TV\alpha \left. \frac{\partial P}{\partial T} \right|_V \quad (77)$$

where we have kept V constant.

Using eq.(??) we replace $\left. \frac{\partial P}{\partial T} \right|_V$ by $-\left. \frac{\partial P}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P$

But

$$\left. \frac{\partial P}{\partial V} \right|_T = -\frac{1}{V\kappa_T}$$

and

$$\left. \frac{\partial V}{\partial T} \right|_P = V\alpha$$

► Using these relations in eq.(??) we obtain

$$T \left. \frac{\partial S}{\partial T} \right|_V = C_P - TV \frac{\alpha^2}{\kappa_T} \quad (78)$$

Remembering that

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V$$

we obtain

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T} \quad (79)$$

Another relation which will be assigned for homework is

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \quad (80)$$

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Gibbs-Duhem

We now consider the situation where the number of particles can change.

If we scale all the extensive variables by the factor λ we obtain

$$E \rightarrow \lambda E \quad V \rightarrow \lambda V \quad N \rightarrow \lambda N \quad (81)$$

The entropy is also extensive will also scale $S \rightarrow \lambda S$.

Hence

$$\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \quad (82)$$

We now differentiate both sides of eq.(??) with respect to λ to obtain

$$S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T} \quad (83)$$

or remembering the Gibbs potential G eq.(??)

$$\mu N = E - TS + PV = G \quad (84)$$

Therefore the chemical potential μ is the Gibbs potential per particle.

From eqs.(??) - (??) and eq.(??) we have

$$-SdT + VdP + \mu dN = \mu dN + Nd\mu \quad (85)$$

or

$$Nd\mu + SdT - VdP = 0 \quad (86)$$

which is known as the Gibbs-Duhem relation.

If we take $dT = 0$, from eq.(??) we have

$$\left. \frac{\partial P}{\partial \mu} \right|_T = n \quad (87)$$

where n is the density.

- The volume per particle $v = V/N = 1/n$

$$\frac{1}{\kappa_T} = -v \left. \frac{\partial P}{\partial v} \right|_T = n \left. \frac{\partial P}{\partial n} \right|_T = n \left. \frac{\partial P}{\partial \mu} \right|_T \left. \frac{\partial \mu}{\partial n} \right|_T \quad (88)$$

Hence

$$\frac{1}{\kappa_T} = n^2 \left. \frac{\partial \mu}{\partial n} \right|_T \quad (89)$$

where we have used eq.(??).

Therefore

$$\left. \frac{\partial \mu}{\partial n} \right|_T = \frac{1}{n^2 \kappa_T} \quad (90)$$

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Concavity of entropy and convexity of energy

We now discuss the conditions under which thermodynamic systems are stable. For simplicity we will take N constant for this analysis.

- ▶ Let $S(2E, 2V)$ be the entropy of an isolated, homogeneous system at equilibrium.
- ▶ We divide the system into two subsystems with energy $E \pm \Delta E$ and volumes $V \pm \Delta V$.
- ▶ Suppose that the entropy is convex.(see eqs.(??) and (??).)

$$S(E + \Delta E, V + \Delta V) + S(E - \Delta E, V - \Delta V) > 2S(E, V) = S(2E, 2V) \quad (91)$$

- ▶ If the entropy were convex this would imply that the inhomogeneous system would have a lower entropy than the homogeneous system. That is the removal of an internal constraint would lower the entropy. This means that the entropy must be concave.

- ▶ Note that there is a special case $\Delta E/E = \Delta V/V$ where the energy density does not become inhomogeneous.
- ▶ Concavity means

$$S(E + \Delta E, V + \Delta V) + S(E - \Delta E, V - \Delta V) \leq 2S(E, V) \quad (92)$$

The condition can also be written

$$(\Delta S)_{(E, V)} \leq 0 \quad (93)$$

which denotes that the imposition of internal constraints on a system of fixed E and V can only decrease the entropy.

- ▶ To look at the linear stability of the system we expand the entropy to second order in ΔE and ΔV

$$S(E \pm \Delta E, V \pm \Delta V) \sim S(E, V) \pm \Delta E \frac{\partial S}{\partial E} \pm \Delta V \frac{\partial S}{\partial V} \\ + \frac{1}{2}(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + \frac{1}{2}(\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + \Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V^2} \quad (94)$$

Inserting the expansion into eq.(??)

$$(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + (\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + 2\Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V} \leq 0 \quad (95)$$

- The concavity condition on the entropy can be transformed to a convexity condition on the energy. Consider an isolated system with energy E and a volume V - divide into two subsystems.

$$E = E_1 + E_2 \quad V = V_1 + V_2 \quad (96)$$

We now apply an internal constraint where

$$E_1 \rightarrow E_1 + \Delta E \quad E_2 \rightarrow E_2 - \Delta E \quad (97)$$

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$$V_1 \rightarrow V_1 + \Delta V \quad V_2 \rightarrow V_2 - \Delta V \quad (98)$$

Remembering eq.(??)

$$S(E_1 + \Delta E, V_1 + \Delta V) + S(E_2 - \Delta E, V_2 - \Delta V) \leq S(E, V) \quad (99)$$

We expect (except at some phase transitions) that the entropy is a continuous and increasing function of E .

Hence there is a value of $E = \tilde{E}$ where

$$S(E_1 + \Delta E, V_1 + \Delta V) + S(E_2 - \Delta E, V_2 - \Delta V) = S(\tilde{E}, V) \quad (100)$$

- ▶ If we now release the internal constraints to go back to the homogeneous system in equilibrium the entropy and energy return to their original values. Hence the entropy returns to

$$S(E_1 + E_2, V_1 + V_2) = S(E, V)$$

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where

$$E \geq \tilde{E}$$

This means that the energy is a convex function of S and V i.e.

$$(\Delta E)_{(S,V)} \geq 0 \quad (101)$$

Stability conditions and their consequences

The convexity condition can be expressed as

$$\begin{aligned} E(S_1 + \Delta S, V_1 + \Delta V) + E(S_2 - \Delta S, V_2 - \Delta V) \\ \geq E(S, V) \end{aligned} \quad (102)$$

where

$$S_1 + S_2 = S \quad V_1 + V_2 = V \quad (103)$$

- ▶ As we did with the entropy we can expand $E(S \pm \Delta S, V \pm \Delta V)$ in a power series in ΔS and ΔV to second order and insert it into the convexity equation written as

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$$E(S + \Delta S, V + \Delta V) + E(S - \Delta S, V - \Delta V) \geq 2E(S, V) \quad (104)$$

to obtain

$$(\Delta S)^2 \frac{\partial^2 E}{\partial S^2} + (\Delta V)^2 \frac{\partial^2 E}{\partial V^2} + 2\Delta S \Delta V \frac{\partial^2 E}{\partial S \partial V} \geq 0 \quad (105)$$

This can be more conveniently expressed in matrix form. We introduce

$$\varepsilon = \begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial V} \\ \frac{\partial^2 E}{\partial V \partial S} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix} = \begin{pmatrix} E''_{SS} & E''_{SV} \\ E''_{VS} & E''_{VV} \end{pmatrix} \quad (106)$$

- ▶ Since $E(S, V)$ is continuous and differentiable, $E''_{SV} = E''_{VS}$ in eq.(??) and ε is real and symmetric.

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We introduce the two component vector

$$x = (\Delta S, \Delta V) \quad (107)$$

and its transpose x^T . The stability condition in eq.(??) can be written as

$$x^T \varepsilon x \geq 0 \quad (108)$$

Since ΔS and ΔV are arbitrary this implies that ε is a positive definite matrix.

- ▶ A positive definite matrix satisfies eq.(??) for any vector.
- ▶ Since ε is Hermetian (real and symmetric) all its eigenvalues are real and it can be diagonalized by a unitary transformation R where

$$R^T R = R R^T = 1 \quad (109)$$

We have

$$x^T R R^T \varepsilon R R^T x \geq 0 \quad (110)$$

Since $\Lambda = R^T \varepsilon R$ is diagonal and $y = R^T x$ is arbitrary

$$y^T \Lambda y = \sum_j^N \lambda_j y_j^2 \geq 0 \quad (111)$$

implies that the eigenvalues $\lambda_j \geq 0$.

Consider an arbitrary real 2×2 symmetric matrix

$$A = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \quad (112)$$

The eigenvalues are defined from the usual determinant and must satisfy the equation

$$(a - \lambda)(c - \lambda) - b^2 = 0 \quad (113)$$

- A is Hermetian so λ_j is real

The solution for the eigenvalues is

$$2\lambda = (a + c) \pm [(a + c)^2 - 4(ac - b^2)]^{1/2} \quad (114)$$

- ▶ Since λ is real we know that the interior of the bracket is positive.
- ▶ Hence $a + c \geq 0$ or choosing the - sign from the \pm would generate a negative .
- ▶ We must have $ac - b^2 \geq 0$ or choosing the - sign will again make λ negative.
- ▶ These two conditions imply that both $a \geq 0$ and $c \geq 0$.
- ▶ In this case $a = \frac{\partial^2 E}{\partial S^2}$ and $c = \frac{\partial^2 E}{\partial V^2}$ are positive.

► For $\frac{\partial^2 E}{\partial S^2}$, V is held constant for both derivatives. N is assumed constant.

► Since $\left. \frac{\partial E}{\partial S} \right|_{V,N} = T$,

$$a = \left. \frac{\partial T}{\partial S} \right|_{V,N} = \frac{T}{C_V} \geq 0 \rightarrow C_V \geq 0 \text{ from eq.(??).}$$

► Since $\left. \frac{\partial^2 E}{\partial V^2} \right|_{S,V} \geq 0$ and $\left. \frac{\partial E}{\partial V} \right|_{S,V} = -P$ from eq.(??)

we have $\kappa_S \geq 0$

As we have seen the entropy S is concave in both E and V and the energy E is convex in both S and V . For the free energy F we have at constant T

$$F(V + \Delta V) + F(V - \Delta V) =$$

$$E(V + \Delta V) + E(V - \Delta V) - T[S(V + \Delta V) + S(V - \Delta V)] \quad (115)$$

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From the convexity of the energy

$$E(V + \Delta V) + E(V - \Delta V) \geq E(2V) \quad (116)$$

From the concavity of the entropy

$$-T[S(V + \Delta V) + S(V - \Delta V)] \geq -TS(2V) \quad (117)$$

- ▶ From eqs.(??), (??) and (??)

$$F(V + \Delta V) + F(V - \Delta V) \geq F(2V) \quad (118)$$

- ▶ Remember that T is fixed.
- ▶ The convexity implies that

$$\frac{\partial^2 F}{\partial V^2} = -\left. \frac{\partial P}{\partial V} \right|_T = \frac{1}{V\kappa_T} \geq 0 \quad (119)$$

- ▶ Therefore the isothermal compressibility $\kappa_T \geq 0$ for stability.

We have shown for that for stability

$$C_V \geq 0 \quad \kappa_T \geq 0 \quad \kappa_S \geq 0 \quad (120)$$

However eq.(??) is

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \rightarrow C_P \geq 0$$

► From eq.(??)

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T}$$

and the positivity conditions we obtain

$$C_P \geq C_V \quad (121)$$

Finally, solving for $\frac{C_P}{C_V}$ in eq.(??) and using eq.(??) we have

$$\frac{\kappa_T}{\kappa_S} - 1 = \frac{TV\alpha^2}{\kappa_T} \quad (122)$$

Since the right hand side is positive we have

$$\kappa_T \geq \kappa_S \quad (123)$$

We have the following potentials and their convexity (concavity) properties.

- ▶ $\bar{H}(S, P) = E + PV$ convex in E - concave in P
 - ▶ $F = E - TS$ concave in T - convex in V
 - ▶ $G = E - TS + PV$ concave in T - concave in P
- Note that the Legendre transformation changes the convex(concave) property of the potential.

General discussion

Suppose we have a function $f(x)$ which is convex in x . That is

$$f''(x) \geq 0 \quad (124)$$

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The Legendre transformation to $g(u)$ is given by

$$g(u) = f(x(u)) - ux(u) \quad (125)$$

where $f'(x) = u$. To obtain the derivative of $g(u)$ we write

$$dg = f' dx - x du - u dx \quad (126)$$

Since $f'(x) = u \rightarrow$

$$\frac{dg}{du} = -x(u) \quad (127)$$

$$\frac{d^2g(u)}{du^2} = -x'(u) = -\frac{1}{f''(x(u))} \leq 0 \quad (128)$$

The relation between x' and f'' above follows from $f'(x) = u$

This implies that the Legendre transformation of a convex function ($f(x)$) is concave in the transform variable.

- ▶ This result implies the results we saw above on the relation between thermodynamic potentials and their Legendre transforms.

Third law of thermodynamics

The statement of the third law is

$$(\lim T \rightarrow 0)(\lim V \rightarrow \infty) \frac{1}{V} S(V) = 0 \quad (129)$$

- ▶ The first limit is the thermodynamic limit which takes the $V \rightarrow \infty$ keeping the density and other intensive variables constant.
- ▶ Thermodynamics and statistical physics of systems such as liquids gases and solids deal with the physics of electrons

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- ▶ There is a residual entropy at the nuclear level at the temperatures we normally reach.
- ▶ This implies that a more useful statement of the third law is.

$$(\lim T \rightarrow 0)(\lim V \rightarrow \infty) \frac{1}{V} S(V) = S_o \quad (130)$$

- ▶ S_o is a reference entropy that is independent of chemical composition, pressure, crystalline form ...
 - ▶ Nuclear spins are insensitive to these parameters at the temperatures we are discussing.

Application to metastable states

Consider a system that can exist in two crystalline forms (a) and (b) one stable and one metastable.

What is a metastable state?

Consider a system that can exist in the solid, liquid and gas phase.

- ▶ For a fixed temperature the equilibrium state minimizes the free energy.

- ▶ The free energy is

$$F = E - TS$$

- ▶ Since the energy is a minimum and the entropy a maximum for a fixed temperature (T) F is a minimum.
- ▶ Suppose $T = 0 \rightarrow F = E$ and the only consideration is minimizing the energy.
- ▶ Suppose $T = \infty \rightarrow F = -TS$ and the only consideration is maximizing the entropy.
- ▶ For a finite temperature (not zero or infinity) there is a competition between maximizing the entropy and minimizing the energy.
 - ▶ Consider a simple substance in the liquid phase. Lowering the temperature enough causes freezing into a crystal (lower energy-lower entropy)
 - ▶ Raising T enough will cause the solid to melt.
- ▶ This phase transition is represented mathematically by the switch from (solid) minimizing energy at low T to (liquid) maximizing the entropy at high T .

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- ▶ The equilibrium phase transition (for fixed pressure and density) will always occur at the same temperature.
- ▶ What does a system at the phase transition temperature T_P look like?
At the phase transition both phases are equally likely since we expect the low temperature phase(solid) slightly below T_P and the high temperature phase(liquid) slightly above T_P .
- ▶ The free energy then must have two minima at the phase transition temperature.
 - ▶ One minimum represents the solid phase and one the liquid.

What happens to the liquid(solid) minimum when the temperature is raised(lowered)?

- ▶ Since we expect the free energy to be a continuous function of the temperature one minimum will be higher than the other.(figure4)

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- ▶ Since the stable state is the free energy minimum; What is the relative minimum correspond to? - **metastable state**
- ▶ Metastable states exist between all phases
 - ▶ liquid-solid
 - ▶ liquid-gas
 - ▶ gas-solidHow do we understand metastability?
- ▶ Suppose the system is in a metastable state. → There exists a lower minimum corresponding to the stable state.
We make the following assumptions .
 - ▶ The metastable state can be treated with equilibrium methods.(we will return to this)
 - ▶ Fluctuations about the mean value of say the density (think liquid-gas) are compact - have a well defined surface and volume.
 - ▶ The metastable and stable minima are at about the same depth. The stable minimum is only slightly lower.

- ▶ Probability of a droplet is low so we can assume that they are independent.
- ▶ The free energy cost of creating the surface between the droplet and the background metastable state is independent of the “distance” into the metastable state.(quench depth) (figure5)
- ▶ The free energy density (Δf) in the interior of the droplet is the same as that of the stable state.

What is the free energy cost of a droplet?

$$F_D = -|\Delta f|l^d + \sigma l^{d-1} \quad (131)$$

- ▶ The first term is the contribution from the droplet interior. Since the stable phase has a lower free energy $\Delta f < 0$.
- ▶ The second term is the free energy cost of creating the surface between the interior of the droplet and the metastable state. The surface free energy density (σ) is usually called the surface tension. $\sigma > 0$

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- ▶ Since the volume term is negative and the surface term is positive the free energy cost increases and then decreases as l increases.(figure6)
- ▶ The maximum of the $F_D(l)$ curve is found by differentiating $F_D(l)$ with respect to l and setting it equal to zero.

$$l_c = \frac{d-1}{d} \frac{\sigma}{|\Delta f|} \quad (132)$$

- ▶ The probability of a critical droplet $P_{CD}(\Delta f, \sigma)$ is

$$P_{CD}(\Delta f, \sigma) \propto \exp[-\beta F_D(l_c)] = \exp\left[-\beta \frac{1}{d} \left[\frac{d-1}{d}\right]^{d-1} \frac{\sigma^d}{|\Delta f|^{d-1}}\right] \quad (133)$$

- ▶ The probability that there is a droplet being proportional to the exponential of the negative of the free energy will be discussed later.

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- ▶ The fact that the probability of the droplet is independent of interaction of droplets comes from the assumption of low probability. This will be true if $|\Delta f| \ll 1$.
- ▶ In this regime the metastable state is long lived and can be treated as an equilibrium state.

Latent heat

If we lower the temperature by removing heat from liquid water the system will be totally liquid water at 0 degrees centigrade if we remove no more heat once we reach 0 degrees.

- ▶ For a quasi static process $dQ = TdS$ so if we have a latent heat L we have

$$\frac{L}{T_P} = S^{(b)} - S^{(a)} \quad (134)$$

where $S^{(a)}(T)$ and $S^{(b)}(T)$ are the entropies of the states (a) and (b) at temperature T .

- ▶ To calculate the entropy at T_P of each phase we can integrate the specific heats at fixed y from 0 to T_P .

$$S^{(a)}(T_P) = S_o + \int_0^{T_P} dT \frac{C_y^{(a)}(T)}{T} \quad (135)$$

and

$$S^{(b)}(T_P) = S_o + \int_0^{T_P} dT \frac{C_y^{(b)}(T)}{T} \quad (136)$$

Remember S_o is the residual entropy at $T = 0$ which is independent of the crystalline form.

- ▶ We can measure the entropy difference in two ways.
 - ▶ Measure the latent heat and calculate the entropy difference from eq.(??).
 - ▶ calculate the specific heat integrals and subtract.
- ▶ If the two methods give the same result this is evidence that two crystalline structures indeed have the same residual entropy S_o
- ▶ This has been verified by measurements. See example in book: grey tin.

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Low temperature behavior of specific heats

- ▶ The third law constrains the behavior of the specific heats as $T \rightarrow 0$. We begin with

$$S(T; P, V) - S_o = \int_0^T dT' \frac{C_{P,V}(T')}{T'} \quad (137)$$

where the P or V is held constant. Note that $C_{P,V}$ is referred to as the specific heat but it is often referred to as the heat capacity. The specific heat is the heat capacity divided by V . Hence the heat capacity is extensive as is the entropy.

- ▶ If we divide both sides of eq.(??) by V , S/V must be finite \rightarrow the integral must converge.
- ▶ This, in turn, implies that the specific heat go to zero as $T \rightarrow 0$

Without proof we state three other results that follow from the third law as $T \rightarrow 0$

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \rightarrow 0 \quad \left. \frac{\partial P}{\partial T} \right|_V \rightarrow \quad (138)$$

$$\frac{C_P - C_V}{C_P} \sim \alpha T \quad (139)$$

Ideal gas

We want to consider some properties of the gas-liquid system as described by the equation of state.

- ▶ First we look at the ideal gas equation.
- ▶ From experiment on low density-high temperature gases lead(as we have seen earlier) to the following equation of state

$$PV = NK_B T \quad (140)$$

or

$$Pv = K_B T \quad (141)$$

where v is the volume per particle.

- ▶ As we will see when we do statistical mechanics this is an equation that describes a system of particles

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What kind of interactions can we expect in realistic systems?

- ▶ Hard core repulsion at short range and an attraction at longer ranges.
- ▶ The hard core reduces the volume per particle v .
 - ▶ The reduction of volume per particle is represented by $v \rightarrow (v - b)$ where b is a positive constant.
- ▶ The attractive part of the potential reduces the pressure.
 - ▶ The pressure reduction is represented by $P \rightarrow (P + a\rho^2) = (P + \frac{a}{v^2})$.

Putting these terms together we have the van der Waals equation

$$(P + \frac{a}{v^2})(v - b) = K_B T \quad (142)$$

We can rewrite this as

$$P = \frac{\rho K_B T}{1 - \rho b} - a\rho^2 \quad (143)$$

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We plot the pressure P as a function of the density ρ for a fixed temperature T .

- ▶ For low temperature there is a maximum and minimum in the pressure vs the density
- ▶ When the temperature is high the maximum and minimum disappear.
- ▶ The temperature at which the maximum and minimum disappear is a critical point.(second order phase transition)
 - ▶ It is also the end point of a line of first order phase transitions.

To understand this we go back to the Gibbs potential eq.(??) and the Gibbs-Duhem relation eq.(??)

- ▶ Gibbs potential

$$G = \mu N = E - TS + PV$$

- ▶ Gibbs-Duhem

$$Nd\mu + SdT - VdP = 0$$

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From the Gibbs-Duhem for constant T we have

$$\left. \frac{\partial \mu}{\partial P} \right|_T = v \quad (144)$$

The chemical potential μ then is

$$\mu(P) = \int_0^P dP' v(P') \quad (145)$$

- ▶ The figure7 is μ vs P . From the figure7 we see that G is a concave function of P over $A \rightarrow B \rightarrow C$.
- ▶ From the figure7 G is convex from $D \rightarrow E$

What is the meaning of the part of the curve $B \rightarrow D$ or $E \rightarrow B$?

Let's look again at

$$G = \mu N = E - TS + PV = F + PV$$

- ▶ For a fixed P and V , F is a minimum in the stable phase $\rightarrow G$ is a minimum.

- ▶ This implies that the $B \rightarrow D$ and $E \rightarrow B$ parts of the curve are metastable states. (concave G but not the lowest value of G in a concave region)
- ▶ The circuit $B \rightarrow E \rightarrow B$ returns the system to the same value of the Gibbs potential G .
- ▶ In the P vs v or P vs ρ diagram this is the equal area construction.
- ▶ In the figure8 we plot the locus of the ends of the Maxwell construction as a function of temperature.
 - ▶ This is the coexistence curve.
- ▶ In the figure8 we plot the locus of the maximum and minimum of the P vs ρ curve as a function of T .
 - ▶ This is the spinodal curve.
- ▶ Inside the spinodal the system is on the curve $D \rightarrow E$ and is convex \rightarrow unstable.

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- ▶ As the spinodal is approached

$$\frac{1}{\kappa_T} = -v \left. \frac{\partial P}{\partial v} \right|_T \rightarrow 0 \quad (146)$$

- ▶ This implies that the isothermal compressibility diverges as the spinodal is approached

If we want to stay in stable equilibrium then the path $B \rightarrow D \rightarrow E$ must be avoided.

- ▶ This implies that we follow the Maxwell construction. \rightarrow The density has a jump with no change in the pressure.
- ▶ This is referred to as a **first order phase transition**
 - ▶ It is called first order because there is a discontinuity in the order parameter as a function of the pressure.
- ▶ As the temperature is raised the size of the jump in the density decreases and vanishes at T_c the critical point.
- ▶ At the critical point the minimum and maximum in P vs ρ coalesce and there is an inflection point at the critical point.

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We have then

$$\left. \frac{\partial P}{\partial \rho} \right|_{T_C, \rho_C} = 0 \quad \left. \frac{\partial^2 P}{\partial \rho^2} \right|_{T_C, \rho_C} = 0 \quad (147)$$

From eq.(??) we have

$$\frac{K_B T_C}{(1 - \rho_C b)^2} = 2a\rho_C \quad (148)$$

and

$$\frac{2bK_B T_C}{(1 - \rho_C b)^3} = 2a \quad (149)$$

Solving for a and b

$$a = \frac{9}{8} \frac{K_B T_C}{\rho_C} \quad b = \frac{1}{3\rho_C} \quad (150)$$

The van der Waals equation can be written as

$$P = \frac{3\rho\rho_C K_B T}{3\rho_C - \rho} - \frac{9}{8} \frac{K_B T_C \rho^2}{\rho_C} \quad (151)$$

Taking the derivative of P with respect to ρ and setting $\rho = \rho_C$ we obtain

$$\left. \frac{\partial P}{\partial \rho} \right|_{\rho_C} = \frac{9}{4} K_B (T - T_C) \quad (152)$$

- ▶ From eq.(??) and some simple manipulation we have that the isothermal compressibility diverges as

$$\kappa_T \sim |T - T_C|^{-1} \quad (153)$$

- ▶ This is an example of a critical exponent that characterizes the physics at the critical point.
 - ▶ There are several other critical exponents that we will encounter later in the semester.
 - ▶ The van der Waals equation is a meanfield description of a system. We will also discuss this later in the semester.

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