

Notes on Statistical Mechanics

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These notes are based off of my time in CHEM 5220. *Advanced Physical Chemistry II: Statistical Mechanics* taught by Professor Kateri DuBay of the University of Virginia in Fall, 2023. Upon doing some reading for the motivation of this field, I would like to provide some here. The following comes from David Tong's own notes for statistical physics, available here: <https://www.damtp.cam.ac.uk/user/tong/statphys.html>.

Statistical mechanics is the art of turning the microscopic laws of physics into a description of Nature on a macroscopic scale.

Suppose you've got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us? More concretely, if I give you a box containing 10^{23} particles and tell you their mass, their charge, their interactions, and so on, what can you tell me about the stuff in the box?

There's one strategy that definitely won't work: writing down the Schrödinger equation for 10^{23} particles and solving it. That's typically not possible for 23 particles, let alone 10^{23} . What's more, even if you could find the wavefunction of the system, what would you do with it? The positions of individual particles are of little interest to anyone. We want answers to much more basic, almost childish, questions about the contents of the box. Is it wet? Is it hot? What colour is it? Is the box in danger of exploding? What happens if we squeeze it, pull it, heat it up? How can we begin to answer these kind of questions starting from the fundamental laws of physics?

Put less eloquently, Statistical Mechanics is mankind's greatest attempt to answer questions about phenomena that, when treated in its totality and at the smallest scale, becomes unwieldy.

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0 Introduction

0.1 August 24th, 2023

The main goal of today's class was to discuss the definition of equilibrium while also working through useful mathematical topics.

0.1.1 Equilibrium

There are many types of equilibrium (thermal, chemical, dynamic, etc). Equilibrium is a property over some time window rather than a particular microstate.

Equilibrium

Equilibrium: A condition of a system* over a given window of time where the probability of each microstate is as probable over that time window (when making an observation) as it would be over an infinite time window.

* no net matter or energy flow

States around/below $k_B T$ are likely to be populated while states above $k_B T$ are unlikely to be populated

Ergodicity

Ergodicity: one state is accessible from another \rightarrow long-time measurements look the same as multiple measurements.

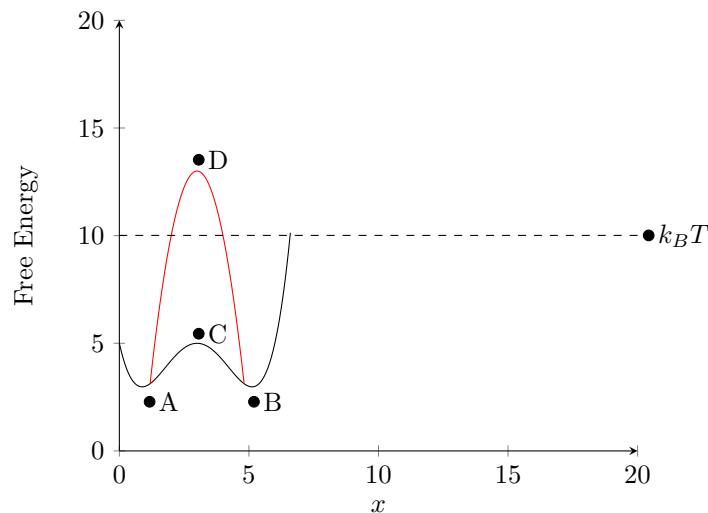


Figure 1: Diagram of arbitrary ergodic and non-ergodic states.

Since A, B, and C are below $k_B T$, you are likely to see interconversion between those states (they are ergodic). State D, on the other hand, is above $k_B T$, so it is unlikely for one to observe that state being populated.

0.1.2 Math Review

Stirling's Approximation: $\ln(n!) \approx n \log(n)$ for large n

Expectation Values:

$$\langle x \rangle_{\text{ensemble}} = \int_{\text{all } x} x \cdot P_{\text{ensemble}}(x) dx$$

where P is the probability of seeing some outcome, x

$$\text{if ergodic} \implies \frac{1}{T_{\text{large}}} \sum_{t=1}^{T_{\text{large}}} x(t)$$

$$\langle E_{\text{tot}} \rangle = \langle E_1 + E_2 + E_3 \rangle = \langle E_1 \rangle + \langle E_2 \rangle + \langle E_3 \rangle$$

Note: The above operation would not be permissible if it was multiplicative rather than additive.

Permutations:

$$P(n, r) = \frac{n!}{(n-r)!}$$

n in r distinguishable spots

Combinations:

$$C(n, r) = \frac{n!}{(n-r)!r!}$$

n in r indistinguishable spots

(0.1.1)

Taylor Series:

f(x) expanded about x = a


$$f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \dots \quad (0.1.2)$$

$$\Delta f(x-a) = f(x) - f(a) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \dots \begin{cases} f'(a)(x-a) = \delta f|_a = \left(\frac{\partial f}{\partial x}\right) \delta x \\ \frac{f''(a)}{2!}(x-a)^2 = \delta^2 f|_a = \frac{1}{2} \left(\frac{\partial^2 f}{\partial x^2}\right) \delta x \\ \delta x = (x-a) \end{cases}$$

Note $\delta f|_a$ can be referred to as the first order variational displacement and $\delta^2 f|_a$ the second order variational displacement

Triple Product Rule:

$$f(x, y, z) = 0 \implies \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

First Law of Thermodynamics 

Internal energy of an isolated system is held constant

$$dE = \delta Q + \delta W$$

where heat (Q) and work (W) are path dependent while internal energy (E) is path independent \longrightarrow a state quantity

Second Law of Thermodynamics 

Entropy is always increasing or constant for any spontaneous process in an isolated system

These two laws and the things we can derive from them will be incredibly important as we continue throughout the semester. In fact, the questions posed on the title page will be answered using these two laws.

1 Introduction to Thermodynamics

1.1 August 29th, 2023

The general topics today were:

1. Types of Systems
2. Macroscopic Variables
3. First Law of Thermodynamics
4. Second Law of Thermodynamics

1.1.1 Types of Systems

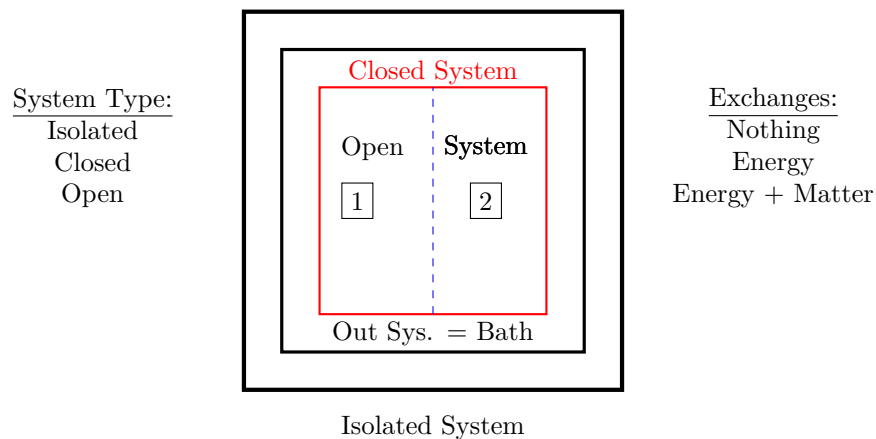


Figure 2: Different types of systems and their properties.

If adiabatic \rightarrow can't conduct energy as heat

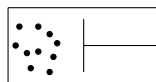
1.1.2 Macroscopic Variables

$$E + \vec{X}$$

where E is internal energy and \vec{X} is a set of mechanical extensive variables $\{V, N, L, \dots\}$

Assume energy is extensive (treat energy as additive) but this isn't always true. Imagine magnets; putting two together would have some repulsive force thus $E \neq E_1 + E_2$.

A process is reversible if it occurs so slowly that at each infinitesimal step, the system equilibrates (thus a truly irreversible process takes infinite time). Approximate as a small Δ to a very large system.



$$P_{int} = P_{ext} + \varepsilon$$

for an irreversible process ($\varepsilon \sim 0$)

1.1.3 First Law of Thermodynamics

Internal energy of an isolated system is constant. Energy changes through heat or work.

Visualizing path dependence:

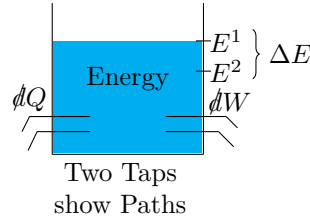


Figure 3: Visualization of path dependence.

$$dE = \delta Q + \delta W \implies \Delta U = q + w \begin{cases} \delta Q \equiv \text{heat flow into system} \\ \delta W \equiv \text{work done on system} \end{cases}$$

LHS is path independent while the RHS is path dependent. If adiabatic, $dE = \delta W$. Closing one “tap” means energy can only escape through the other while closing both taps means energy can’t escape, hence the RHS is path dependent.

Work:

$$\delta W = \vec{f} \cdot d\vec{X} \begin{cases} \vec{f} \equiv \text{set of forces applied to system} \\ d\vec{X} \equiv \text{corresponding set of mechanical extensive variables: } P_{ext}dV, fdL, \mu dN, \text{ etc.} \end{cases}$$

1.1.4 Second Law

Postulate: Entropy is an extensive function that increases monotonically with energy.

Remark. We are operating at the *thermodynamic limit* meaning many particles and high temperature.

$$\text{Entropy: } S = S(E, \vec{X}, \text{inter. constr}) \quad (1.1.1)$$

$S_B \geq S_A$ if macrostate B is adiabatically (no work done as well) accessible from macrostate A

$$\Delta S_{\text{isolated}} \geq 0 \quad (1.1.2)$$

Entropy is path independent (state function) and macroscopically extensive

$\Delta S = 0$ if irreversible b/c the system is always in equilibrium

$$dS = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} dE + \left(\frac{\partial S}{\partial \vec{X}} \right)_E d\vec{X} \quad (1.1.3)$$

$$\text{where } dE = \delta Q + \vec{f}_{ext} \cdot d\vec{X}$$

Note $\vec{f}_{ext} = \vec{f}_{int}$ at equilibrium

$$dS = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} [\delta Q + \vec{f}_{ext} \cdot d\vec{X}] + \left(\frac{\partial S}{\partial \vec{X}} \right)_E \cdot d\vec{X} \quad (1.1.4)$$

Choose adiabatic ($\delta Q = 0$) and reversible ($dS = 0$)

$$0 = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} \vec{f}_{int} \cdot d\vec{X} + \left(\frac{\partial S}{\partial \vec{X}} \right)_E \cdot d\vec{X} \quad (1.1.5)$$

$$- \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} \vec{f}_{int} = \left(\frac{\partial S}{\partial \vec{X}} \right)_E$$

$$T \equiv \left(\frac{\partial E}{\partial S} \right)_{\vec{X}} \geq 0 \quad (1.1.6)$$

Using this definition of temperature:

$$-\frac{\vec{f}_{sys}}{T} = \left(\frac{\partial S}{\partial \vec{X}} \right)_E \quad (1.1.7)$$

It's important to note S monotonically increases with E, so **T is always positive**.

1.2 August 31st, 2023

The general topics today were:

1. Review of 1.1
2. Variational Second Law
3. Energy Minimization
4. Hot Things Cool
5. Free Energies and Legendre Transformations

1.2.1 Review of Lecture 1.1

From last class:

$$dS = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} dE + \left(\frac{\partial S}{\partial \vec{X}} \right)_E d\vec{X} \quad (1.2.1)$$

where

$$T \equiv \left(\frac{\partial E}{\partial S} \right)_{\vec{X}} \quad (1.2.2)$$

and

$$-\frac{\vec{f}_{sys}}{T} = \left(\frac{\partial S}{\partial \vec{X}} \right)_E \quad (1.2.3)$$

which is true for any path

Today: substitute Eqn. 1.2.2 and Eqn. 1.2.3 into Eqn. 1.2.1

$$dS = \left(\frac{1}{T} \right) dE - \left(\frac{\vec{f}_{sys}}{T} \right) \cdot d\vec{X} \quad (1.2.4)$$

rearranging

$$dE = TdS + \vec{f} \cdot d\vec{X} \quad (1.2.5)$$

thus $E(S, \vec{X})$ ∴ E is a natural function of S and \vec{X} . Natural functions are ones where the differential of one variable can be written in terms of the differentials of others.

$$dE = \underbrace{\left(\frac{\partial E}{\partial S} \right)_{\vec{X}}}_T dS + \underbrace{\left(\frac{\partial E}{\partial \vec{X}} \right)_{\vec{X}}}_{solve} d\vec{X}$$

$$-\vec{f} = T \left(\frac{\partial S}{\partial \vec{X}} \right)_E$$

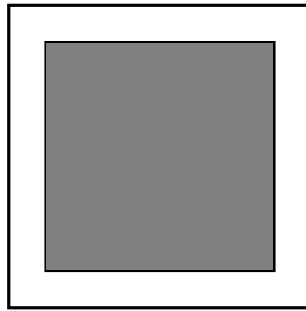
Referring to the definition for T and using the triple product rule:

$$\left(\frac{\partial E}{\partial S} \right)_{\vec{X}} \left(\frac{\partial S}{\partial \vec{X}} \right)_E = - \left(\frac{\partial E}{\partial \vec{X}} \right)_S \implies \vec{f} = \left(\frac{\partial E}{\partial \vec{X}} \right)_{\vec{S}} \checkmark$$

thus Eqn. 1.2.1 is consistent.

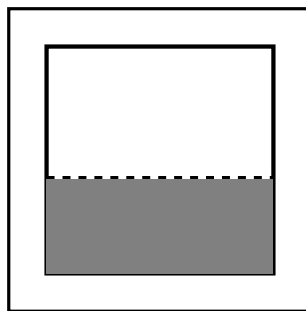
1.2.2 Variational Second Law

Return to the ink in water isolated system



Define equilibrium entropy $S = S(E, \vec{X})$

Add internal constraint, y (here, it's a membrane impermeable to ink but not water)



Define new equilibrium entropy with internal constraint $S' = S(E, \vec{X}, y)$

More accessible microstates means more entropy

Introducing an internal constraint excludes microstates \therefore entropy decreases

Consequently, $S' < S$ or more generally:

$$S(E, \vec{X}) > S'(E, \vec{X}, \text{internal constraint}) \quad (1.2.6)$$

Here, y could be thought of as the “height” of the membrane. In the first system, $y = 0$ thus there is no constraint.

Variational Principle of Entropy

$(\delta S)_{E, \vec{X}} \leq 0$ when at equilibrium. That is, increasing internal constraints decreases entropy.

1.2.3 Energy Minimization

$S(E, \vec{X})$ at equilibrium

$S(E, \vec{X}, \text{int. constr } \{y\})$ { note $y = 0$ at equilibrium

The second law states that at equilibrium, if reversible:

$$\left(\frac{\partial S}{\partial y} \right)_{E, \vec{X}} = 0 \text{ [extremum]} \quad (1.2.7)$$

$$\left(\frac{\partial^2 S}{\partial y^2} \right)_{E, \vec{X}} < 0 \text{ [global max]} \quad (1.2.8)$$

S decrease as y increase hence the sign of the second order partial derivative

Consider $E(S, \vec{X}, \text{Int. Constr.})$ at **Equilibrium**

Using the triple product rule:

$$\begin{aligned} \left(\frac{\partial E}{\partial y}\right)_{\vec{x},S} &= ? = - \underbrace{\left(\frac{\partial E}{\partial S}\right)_{\vec{x},y}}_T \underbrace{\left(\frac{\partial S}{\partial y}\right)_{\vec{x},E}}_0 \\ \left(\frac{\partial E}{\partial y}\right)_{\vec{x},S} &= 0 \text{ [extremum]} \\ \left(\frac{\partial^2 E}{\partial y^2}\right)_{\vec{x},S} &= - \left[\underbrace{T}_+ \underbrace{\left(\frac{\partial^2 S}{\partial y^2}\right)_{\vec{x},E}}_- + \left(\frac{\partial T}{\partial y}\right)_{\vec{x},S} \underbrace{\left(\frac{\partial S}{\partial y}\right)_{\vec{x},E}}_0 \right] \end{aligned} \tag{1.2.9}$$

thus

$$\left(\frac{\partial^2 E}{\partial y^2}\right)_{\vec{x},S} > 0 \therefore \text{energy is min. at equilibrium.} \tag{1.2.10}$$

Energy Minimization Principle >>>

$(\delta E)_{S,\vec{X}} \geq 0$ for any move away from equilibrium

1.2.4 Hot Things Cool

Imagine a system in thermal contact but is otherwise isolated (hold \vec{X} constant)

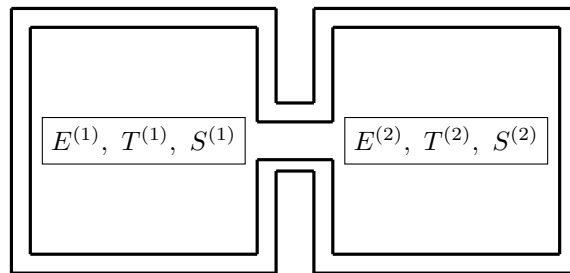


Figure 4: Isolated system in thermal equilibrium.

Q1: At equilibrium, how do $T^{(1)}$ and $T^{(2)}$ relate?

Using the variational second law $[(\delta S)_{E,\vec{X}} \leq 0 \text{ when at equilibrium}]$

Take

$$\begin{aligned} E &= E^{(1)} + E^{(2)} \text{ and } \underbrace{\delta E = 0}_{\text{1st Law}} \implies \delta E^{(1)} = -\delta E^{(2)} \\ S &= S^{(1)} + S^{(2)} \implies \delta S = \delta S^{(1)} + \delta S^{(2)} = \underbrace{\left(\frac{\partial S^{(1)}}{\partial E^{(1)}}\right)}_{\frac{1}{T^{(1)}}} \delta E^{(1)} + \underbrace{\left(\frac{\partial S^{(2)}}{\partial E^{(2)}}\right)}_{\frac{1}{T^{(2)}}} \underbrace{\delta E^{(2)}}_{-\delta E^{(1)}} \\ \delta S &= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \delta E^{(1)} \leq 0 \text{ for all } \pm \text{ values of } \delta E^{(1)} \end{aligned} \tag{1.2.11}$$

The above statement only holds true if $T^{(1)} = T^{(2)}$, thus $T^{(1)} = T^{(2)}$ at equilibrium

What if $T^{(1)} \neq T^{(2)}$ initially?

$S \equiv$ fluctuations away from equilibrium

$\Delta \equiv$ a large change towards equilibrium

$\Delta S_{\text{isolated}} > 0$ for a Δ towards equilibrium

$$\Delta S = \Delta S^{(1)} + \Delta S^{(2)}; \Delta E^{(1)} = -\Delta E^{(2)}$$

$$\left(\frac{\partial S^{(1)}}{\partial E^{(1)}}\right)_{\vec{x}} \Delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}}\right)_{\vec{x}} \Delta E^{(2)} > 0 \quad (1.2.12)$$

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \Delta E^{(1)} > 0$$

If $T^{(1)} > T^{(2)}$ initially: $\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}$ is negative $\rightarrow \Delta E^{(1)} < 0$ and energy flows to subsystem 2 while equilibrating

1.2.5 Free Energies and Legendre Transformations

$$dE = TdS - PdV + \mu dN \left\{ \text{think } +(-P) dV; \text{ i.e. negative pressure} \right. \quad (1.2.13)$$

If we know $dS, dV, dN \rightarrow E = E(S, V, N)$ is the natural function

What if we want E in terms of different variables? Use a Legendre transform.

Conjugate Variables: $ST, -PV, \mu N$

$$A \equiv E - TS \quad (1.2.14)$$

$$dA = dE - TdS - SdT \left\{ \text{recall } dE = TdS - PdV + \mu dN \right.$$

$$dA = -SdT - PdV + \mu dN \quad (1.2.15)$$

$A = A(T, V, N) \rightarrow$ Helmholtz Free Energy

$$G \equiv E - TS - (-PV) \quad (1.2.16)$$

$$dG = dE - TdS - SdT + PdV + VdP \left\{ \text{recall } dE = TdS - PdV + \mu dN \right.$$

$$dG = VdP - SdT + \mu dN \quad (1.2.17)$$

$G = G(T, P, N) \rightarrow$ Gibbs Free Energy

1.3 September 5th, 2023

The general topics today were:

1. Free Energy, the Variational Principle, and Claussius Inequality
2. Where are We?
3. Schwartz's Theorem \rightarrow Maxwell Relations
4. Heat Capacity
5. First Order Homogeneous Functions (Extensive)

1.3.1 Free Energy, the Variational Principle, and Claussius Inequality

$$dG = VdP - SdT + \mu dN \quad (1.3.1)$$

We normally see $\Delta G = \Delta H - T\Delta S$, but where does it come from?

$$H - (-PV) \implies dH = dE + VdP + PdV \left\{ \text{recall } dE = TdS - PdV + \mu dN \right.$$

$$\begin{aligned} dH &= TdS + VdP + \mu dN \\ H &= H(S, P, N) \end{aligned} \quad (1.3.2)$$

$$\Delta G = -S\Delta T + V\Delta P + \mu dN$$

and

$$\Delta H = T\Delta S + V\Delta P + \mu dN$$

therefore

$$\Delta G = \Delta H - T\Delta S - S\Delta T \left\{ \Delta T = 0 \text{ due to constant T} \right. \quad (1.3.3)$$

Variational Principle:

$(\delta E)_{S,V,N} \geq 0$ at equilibrium. We can similarly show $(\delta H)_{S,P,N} \geq 0$ at equilibrium.

Use the Claussius Inequality to show something similar for G and A

$$\text{Thermo Definition of Entropy: } \Delta S_{sys} = \frac{q_{rev}}{T} \implies T\Delta S_{sys} \geq q_{rev} \text{ if irrev.}$$

For A(T, V, N)

$$A = E - TS \implies \Delta A = \Delta E - T\Delta S - S\Delta T$$

we know $\Delta E = w + q$ so where δW is 0 so

$$\Delta A = q - T\Delta S$$

when considering constant T, V, N .:

$$\Delta A = q - T\Delta S \begin{cases} \Delta A = 0 \text{ if rev. (at eq. already)} \\ \Delta A < 0 \text{ if irrev. (move to eq.)} \end{cases}$$

One can show the same for Gibbs, but that is left as an exercise

1.3.2 Where are We?

First Law:

- $(dE)_{isolated} = 0$
- $dE = \delta Q + \delta W$
- $(\delta E)_{S,\vec{X}} \geq 0$ at equilibrium

Second Law:

- $(\Delta S)_{isolated} \geq 0$
- $(\delta E)_{S,\vec{X}} \leq 0$ at equilibrium

$$E(S, V, N) \xrightarrow{\text{L.T.}} H(S, P, N); A(T, V, N); G(T, P, N)$$

Free energy? G is the amount of energy available ('free') to do non-expansive work at constant T, P, N.

1.3.3 Schwartz's Theorem \rightarrow Maxwell Relations

Given $f(x, y)$ is well-differentiable:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial}{\partial y} \right)_x \right)_y = \left(\frac{\partial}{\partial y} \left(\frac{\partial}{\partial x} \right)_y \right)_x$$

General Case:

$$df = adx + bdy \begin{cases} a = \left(\frac{\partial f}{\partial x} \right)_y \\ b = \left(\frac{\partial f}{\partial y} \right)_x \end{cases} \implies \left(\frac{\partial a}{\partial y} \right)_x = \left(\frac{\partial b}{\partial x} \right)_y$$

Ex: $dA = -SdT - PdV + \mu dN$

$$-S = \left(\frac{\partial A}{\partial T} \right)_{V,N} \quad -P = \left(\frac{\partial A}{\partial V} \right)_{T,N} \quad \mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

therefore

$$\left(\frac{\partial(-S)}{\partial V} \right)_{T,N} = \left(\frac{\partial(-P)}{\partial T} \right)_{V,N}$$

note that N is constant for both sides in this Maxwell relation

1.3.4 Heat Capacity

$$C \equiv \frac{dQ}{dT} \simeq \frac{q}{\Delta T} \quad (1.3.4)$$

$$C = \frac{T}{T} \frac{dQ}{dT} = T \left(\frac{\partial S}{\partial T} \right) \left\{ \text{recall } \frac{1}{T} = \left(\frac{\partial S}{\partial T} \right) \right.$$

$$C_{\vec{f}/\vec{x}} = T \left(\frac{\partial S}{\partial T} \right)_{\vec{f}/\vec{x}} \quad (1.3.5)$$

Constant \vec{f} or \vec{x} where the former is any constant force (in most cases, pressure) and the latter is a constant extensive variable (in most cases, volume).

$$C_p - C_v = -T \left(\frac{\partial P}{\partial V} \right)_{T,N} \left[\left(\frac{\partial V}{\partial T} \right)_{P,N} \right]^2 \begin{cases} \left(\frac{\partial P}{\partial V} \right)_{T,N} = \text{isothermal compressibility} \\ \left(\frac{\partial V}{\partial T} \right)_{P,N} = \text{coeff. of thermal expansion} \end{cases}$$

$(dS)_n$ means differentiate with constant moles; if N , constant number of particles. Lastly, $v = \frac{V}{n}$ and $\chi_i = \frac{n_i}{n}$ is the mole fraction of i .

Consider an Ideal Gas:

$$PV = nRT \rightarrow \left(\frac{\partial P}{\partial v} \right)_{T,n} = -\frac{nRT}{V^2}; \left(\frac{\partial V}{\partial T} \right) = \frac{nR}{P}$$

$$C_P - C_V = -T \left[-\frac{nRT}{V^2} \right] \left[\frac{nR}{P} \right]^2$$

$$C_P - C_V = (nR)^3 \left(\frac{T}{PV} \right)^2$$

where $\frac{T}{PV} = \frac{1}{nR}$ so the above expression simplifies to:

$$R = \frac{C_P - C_V}{n} \quad (1.3.6)$$

1.3.5 First Order Homogeneous Functions (Extensive)

Extensive if First Order Homogenous Function:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda f(x_1, x_2, \dots, x_N) \quad (1.3.7)$$

Euler's Theorem for F.O.H. Functions

$$f(x_1, x_2, \dots, x_N) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} x_i \quad (1.3.8)$$

$$dE = TdS + \vec{f} \cdot d\vec{x} \text{ for } E \text{ which is extensive}$$

so Euler's Theorem says:

$$E = TS - PV + \mu N \longrightarrow dE = TdS + SdT - PdV - VdP + \mu dN + nd\mu$$

reconcile math and physical observations by saying:

$$0 = SdT - VdP + Nd\mu \quad (1.3.9)$$

which is the Gibbs-Duhem Relation

1.4 September 7th, 2023

The general topics today were:

1. Zero-Order Homogenous Function (Intensive)
2. Chapter 1 Summary
3. Multiphase Equilibria
4. Chemical Potential (μ)
5. Stability

1.4.1 Zero-Order Homogenous Function (Intensive)

Intensive if Zeroth Order Homogenous Function:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda^0 f(x_1, x_2, \dots, x_N) \quad (1.4.1)$$

Take pressure:

$$P(S, V, n, \dots, n_r) = P(\lambda S, \lambda V, \lambda n, \dots, \lambda n_r)$$

consider a useful value of λ

$$\lambda = \frac{1}{n_1 + n_2 + \dots + n_r} = \frac{1}{n} \longrightarrow P = P(S/n, V/n, \chi_1, \dots, \chi_{r-1}, 1 - \chi_1, \dots, 1 - \chi_r)$$

Since $\sum_{i=1}^r \chi_i = 1$, one less variable than the total system size, r , is needed for an intensive function. It's important to note conjugate variables in a function are not independent of one another: (P, V, N) are really two variables since P and V are conjugate while (P, T, N) does have three.

1.4.2 Chapter 1 Summary

First and Second Laws of Thermodynamics. From 2nd Law: variational principles stemming from entropy maximization and energy minimization. Zeroeth Law of Thermodynamics: If $T^{(1)} = T^{(2)}$ and $T^{(2)} = T^{(3)} \rightarrow T^{(1)} = T^{(3)}$.

$T \equiv \left(\frac{\partial E}{\partial S}\right)_{\bar{x}}$; $dE = TdS - PdV + \mu dN$. Math tools like Maxwell relations, Gibbs-Duhem equation, intensive and extensive functions, and the Legendre Transform.

1.4.3 Multiphase Equilibria

Consider 2 Phase (α), one component system (i):

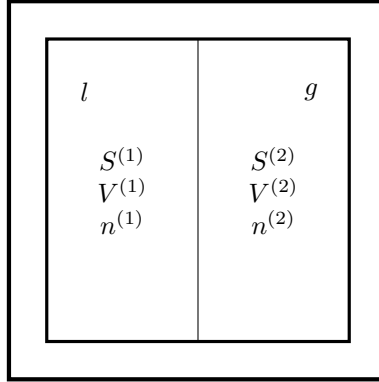


Figure 5: Example system for multi-phase equilibrium.

$dE = TdS - PdV + \mu dN$. All extensive so:

$$\delta S^{(1)} = -\delta S^{(2)} \quad \delta V^{(1)} = -\delta V^{(2)} \quad \delta n^{(1)} = -\delta n^{(2)}$$

At equilibrium, $(\delta E)_{S,V,N} \geq 0$

$$(\delta E)_{S,V,N} = \left[T^{(1)} \delta S^{(1)} - P^{(1)} \delta V^{(1)} + \mu^{(1)} \delta n^{(1)} \right] + \left[T^{(2)} \delta S^{(2)} - P^{(2)} \delta V^{(2)} + \mu^{(2)} \delta n^{(2)} \right] \geq 0$$

An equation to show how the various intensive quantities must relate at equilibrium:

$$(\delta E)_{S,V,N} = \left(\underbrace{T^{(1)} - T^{(2)}}_0 \right) \delta S^{(1)} - \left(\underbrace{P^{(1)} - P^{(2)}}_0 \right) \delta V^{(1)} + \left(\underbrace{\mu^{(1)} - \mu^{(2)}}_0 \right) \delta n^{(1)} \geq 0 \quad (1.4.2)$$

The above relationships must hold true for any \pm variation in $S^{(1)}, V^{(1)}, n^{(1)}$ \therefore the following is true to hold:

$$T^{(1)} = T^{(2)}, \quad V^{(1)} = V^{(2)}, \quad \mu^{(1)} = \mu^{(2)}$$

1.4.4 Chemical Potential (μ)

If $\mu^{(1)} > \mu^{(2)}$ initially, $\mu^{(1)} = \mu^{(2)}$ at equilibrium. The system is isolated $\therefore \Delta S > 0$.

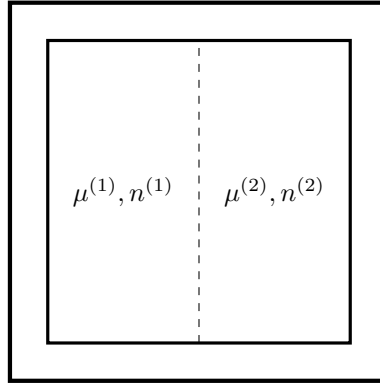


Figure 6: Example system for chemical potential at equilibrium.

$$\Delta S = -\frac{\mu^{(1)}}{T}\Delta n^{(1)} - \frac{\mu^{(2)}}{T}\Delta n^{(2)}$$

$$\underbrace{dE}_0 = TdS - \underbrace{PdV}_{\text{no dV}} + \mu^{(1)}dn^{(1)} + \mu^{(2)}dn^{(2)}$$

so rearranging produces:

$$dS = -\frac{\mu^{(1)}}{T}dn^{(1)} - \frac{\mu^{(2)}}{T}dn^{(2)} > 0$$

Lastly, $\Delta n^{(1)} = -\Delta n^{(2)}$ so

$$\Delta S = -\left(\underbrace{\frac{\mu^{(1)}}{T} - \frac{\mu^{(2)}}{T}}_{+ \text{ given init. cond.}}\right)\Delta n^{(1)} > 0 \quad (1.4.3)$$

Given these conditions, $\Delta n^{(1)}$ must be negative \therefore particles flow towards the lower μ

1.4.5 Stability

$(\Delta E)_{S,V,N} > 0$ is a stability requirement at equilibrium. Note that Δ here refers to any fluctuation away from equilibrium while at equilibrium. That is to say, the fluctuation must raise energy when at **equilibrium** as that is the state where **energy is minimized**.

Taylor Expand $(\Delta E)_{S,V,N}$:

$$(\Delta E)_{S,V,N} = (\delta E)_{S,V,N} + (\delta^2 E)_{S,V,N} + (\delta^3 E)_{S,V,N} + \dots > 0$$

We have already shown that the first order variation in E is zero for any \pm fluctuations in an unconstrained system $\therefore (\delta^2 E)_{S,V,N} \geq 0$ which is where we will derive our stability criteria from. Note: if $(\delta^2 E)_{S,V,N} = 0$, look at next highest order variation.

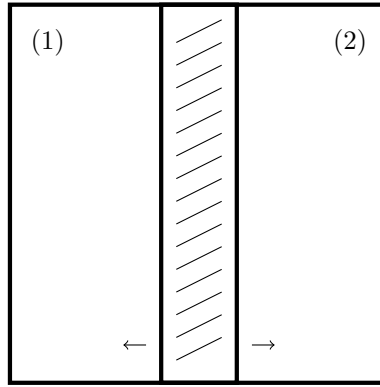


Figure 7: Example system for chemical potential at equilibrium.

$$A(T, V, n) \implies dA = -SdT - PdV + \mu dn$$

Only consider repartitions in $V^{(1)}$ and $V^{(2)}$ for this system. $(\Delta A)_{T,V,n} > 0$ for all deviations from equilibrium. If \pm fluctuations are allowed (i.e. wall moves left or right), then $(\delta A)_{T,V,n} = 0$ so $(\delta^2 A)_{T,V,N} \geq 0$.

We know $(\delta^2 A)_{T,V,N} = (\delta^2 A^{(1)})_{T,V,N} + (\delta^2 A^{(2)})_{T,V,N}$ due to extensivity.

$$(\delta^2 A)_{T,V,N} = \frac{1}{2} (\delta V^{(1)})^2 \left(\frac{\partial^2 A^{(1)}}{\partial V^{(1)2}} \right)_{T,N} + \frac{1}{2} (\delta V^{(2)})^2 \left(\frac{\partial^2 A^{(2)}}{\partial V^{(1)2}} \right)_{T,N} \geq 0$$

We know $\delta V^{(1)} = -\delta V^{(2)}$ $\therefore (\delta V^{(1)})^2 = (-\delta V^{(2)})^2$

$$= \frac{1}{2} (\delta V^{(1)})^2 \left[\left(\frac{\partial^2 A^{(1)}}{\partial V^{(1)2}} \right)_{T,N} + \left(\frac{\partial^2 A^{(2)}}{\partial V^{(2)2}} \right)_{T,N} \right] \geq 0$$

Note $\left(\frac{\partial^2 A}{\partial V^2} \right)_{T,N} = \left(\frac{\partial(-P)}{\partial V} \right)_{T,N}$ since $\left(\frac{\partial A}{\partial V} \right)_{T,N} = -P$

Lastly, we arrive at the following equation with which we derive stability criteria:

$$(\delta^2 A)_{T,V,N} = \frac{1}{2} \underbrace{(\delta V^{(1)})^2}_+ \left[- \underbrace{\left\{ \left(\frac{\partial A}{\partial V} \right)_{T,N}^{(1)} + \left(\frac{\partial A}{\partial V} \right)_{T,N}^{(2)} \right\}}_{\text{must be -}} \right] \geq 0 \quad (1.4.4)$$

thus $\left(\frac{\partial P}{\partial V} \right) \leq 0$

Note: $I = -P$ for pressure hence $\left(\frac{\partial P}{\partial V} \right)_{T,N} \leq 0$

Stability Criteria

$$\left(\frac{\partial I_i}{\partial X_i} \right)_{x_j \neq i} \geq 0$$

for intensive/extensive conjugate pairs I_i, X_i

1.5 September 12th, 2023

The general topics today were:

1. Gibbs Phase Rule

- 2. Phase Transitions
- 3. Maxwell Constructions

1.5.1 Gibbs Phase Rule

Stability at phase co-existence requires: $\mu_i^\alpha = \mu_i^\gamma$ for all i components in phases α, γ at equilibrium

For $1 \leq \alpha \leq \gamma \leq \nu$ (i.e. only two phases α, γ out of ν possible phases) and $1 \leq i \leq r$ where r is the total # of possible components

$$\mu_i^\alpha (T, P, x_1^\alpha, \dots, x_{r-1}^\alpha) = \mu_i^\gamma (T, P, x_1^\gamma, \dots, x_{r-1}^\gamma)$$

Note that $T^\alpha = T^\gamma$ and $P^\alpha = P^\gamma$ for each component and phase so there's no need for sub/super scripts. Write out combinations for all $\alpha + \gamma + i$ combinations using the above expression.

Ex:

$$\begin{aligned} &\text{if } \nu = 2 : \alpha = 1, \gamma = 2 \\ &\text{if } \nu = 3 : \alpha = 1, \gamma = 2; \alpha = 2, \gamma = 3 \end{aligned}$$

then we have $r(\nu - 1)$ independent equations that relate $2 + \nu(r - 1)$ intensive variables

$$D.O.F. = \underbrace{\{2 + \nu(r - 1)\}}_{\# \text{ var}} - \underbrace{\{r(\nu - 1)\}}_{\# \text{ indep. eqns.}} \tag{1.5.1}$$

Gibbs Phase Rule

$D.O.F. = 2 + r - \nu$ where r is the number of components and ν the number of phases

For $r = 1$, one component system: $f = 2 + r - \nu = 3 - \nu$

# Phases	ν	f	for given X_i	P, T
Single	1	2	System exists with multiple P, T	Areas on phase diagram
Two	2	1	Fix one or the other	Lines on phase diagram
Three	3	0	All X_i, T, P fixed	Points on phase diagram

Table 1: *Phase Diagram for n-Phase One-Component System*

Example:

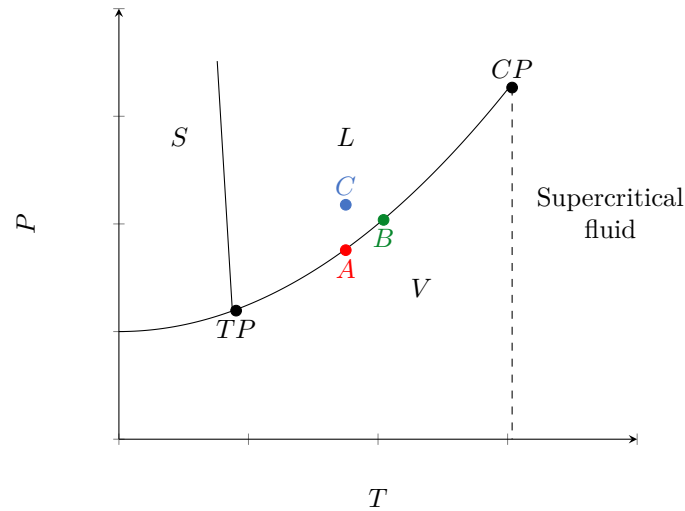


Figure 8: H_2O , single component. Note that you can still have distinct phases at the critical point, but it is continuous in s, v (molar quantities S/n and V/n).

Thought experiment: You have an isolated bottle with only H_2O , and you pick a point of co-existence between liquid and vapor, Point A. If you add more yet a sufficiently small amount of H_2O to the bottle, which point in Figure 8 would then describe the system?

Answer: Still Point A because adding more H_2O would only change the ratios between the phases.

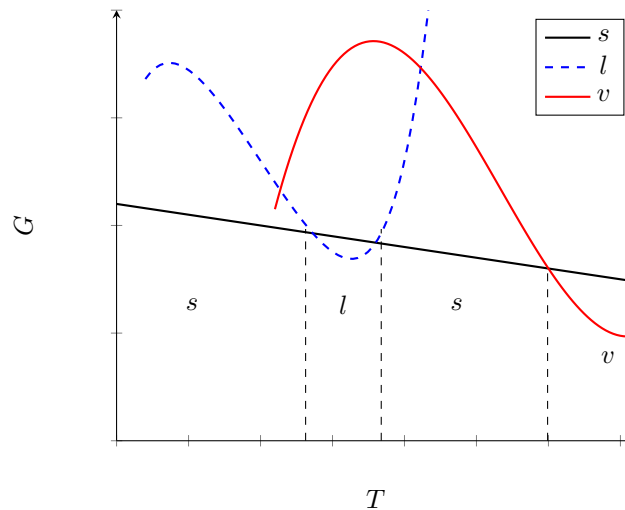


Figure 9: Example phase diagram of Gibbs Free Energy vs. Temperature. The free energies are very *unphysical* to get the point across regarding minimum free energy governing what phase we see.

Check what phase you're in for a given temperature based on where G is lowest. Recall $dG = -SdT + \dots$ so $-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$. Slope is $-S$ so solid steepness $<$ liquid steepness $<$ gas steepness.

1.5.2 Phase Transitions

Gibbs-Duhem: $d\mu = -sdT + vdP$ where s, v are molar (i.e. $s = S/N, v = V/N$) \therefore

$$\left(\frac{d\mu}{dP}\right)_T = v \ \& \ \left(\frac{d\mu}{dT}\right)_v = -s$$

If these partial derivatives are continuous, the phase transition is second order or higher. Ex: liquid to gas is a 1st order phase transition.

1. Volume per mol of the liquid phase is very different than volume per mol of the vapor phase
2. Qualitatively, consider how different the densities are

At the critical point, phases are continuous in entropy and molar volume. Along co-existence lines which pass through different pressures and temperatures:

$$\mu^{(\alpha)}(T, P) = \mu^{(\gamma)}(T, P) \implies d\mu^{(\alpha)} = d\mu^{(\gamma)}$$

Substitute in the Gibbs-Duhem relation:

$$-s^{(\alpha)}dT + v^{(\alpha)}dP = -s^{(\gamma)}dT + v^{(\gamma)}dP$$

Remark. Δ (*variations away from equilibrium, I believe*) increase as the discontinuity increases. $\Delta s(T)/\Delta v(T) = dP/dT$. Lastly, $\Delta s(T)$ and $\Delta v(T)$ approach 0 so dP/dT is ill-defined for ≥ 2 nd order transitions.

1.5.3 Maxwell Constructions

The Maxwell Construction leverages many principles discussed prior in order to create a diagram that quantitatively defines where co-existence will occur.

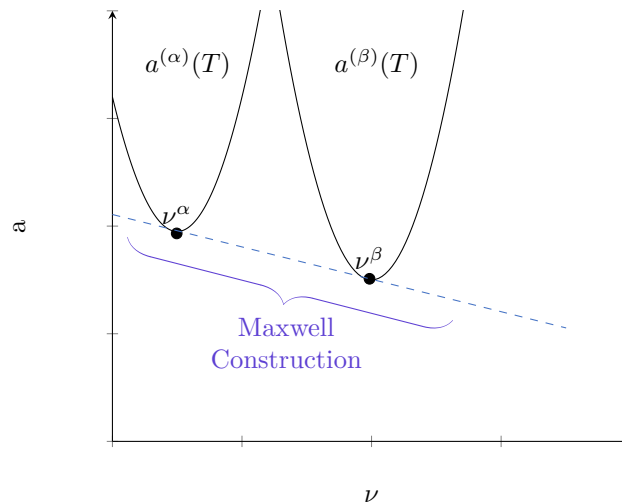


Figure 10: Maxwell Construction: Perfect double tangent line where a mixture of two phases co-exist. Energy is minimized at equilibrium, hence the double tangent is at the base of the two parabolas.

Note: $A = A(T, V, n)$; $a = A/n$; $v = V/n$.

A tie-line is a horizontal (i.e., constant-temperature) line through the chosen point, which intersects the phase boundary lines on either side. An example of one is shown below.

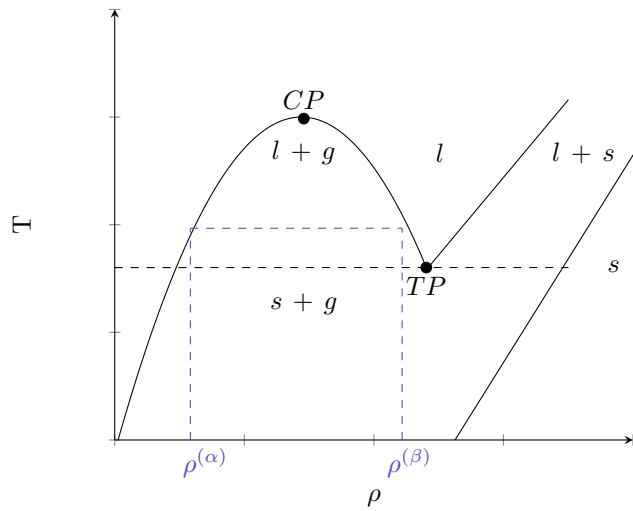


Figure 11: The dashed horizontal line in purple is an example of a tie line.

Tie lines occur where there are discontinuities in an axis, indicating a first order transition.

Spinodal: For $r = 1$, one-component system. $f = + r - \nu = 3 - \nu$

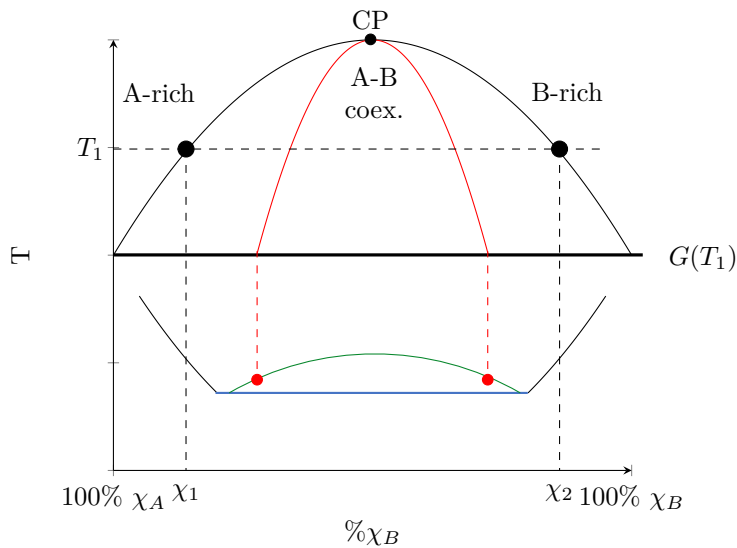


Figure 12: L-L Phase diagram for Immiscible Liquids. The black line denotes the binodal region. The green line is for a mixture not at equilibrium at χ_B from χ_1 to χ_2 . The red dots are inflection points that map back up to T_i , and the red line indicates the spinodal region. Lastly, the blue line denotes a Maxwell construction.

How do phases un-mix? Between the binodal and spinodal is the metastable region: $\left(\frac{\partial^2 G}{\partial \chi^2}\right) > 0$ resulting in a barrier to phase separation. Inside the spinodal, all fluctuations are downhill $\left(\frac{\partial^2 G}{\partial \chi^2}\right) < 0$.

1.6 September 14th, 2023

1.6.1 Interfaces

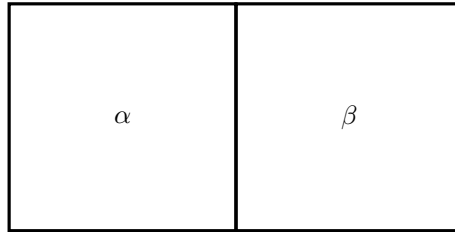


Figure 13: Example of an Interface

$$E = E^{(\alpha)} + E^{(\beta)} + E^{(surface)}$$

$$f \cdot dx \text{ for surface energy; } \gamma d\sigma \begin{cases} \gamma = \text{surface tension [intensive]} \\ \sigma = \text{surface area [extensive]} \end{cases}$$

$$\gamma = \left(\frac{\partial E}{\partial \sigma} \right)_{S,V,N} \geq 0$$

Energy must increase with σ to actually have a surface

$$dE = \underbrace{TdS - PdV + \mu dN}_{\text{phases}} + \underbrace{\gamma d\sigma}_{\text{surface}}$$

Euler's Theorem says $E = TS - PV + \mu N + \gamma\sigma$ where the first three terms are $\sim N$ and the surface term is $\sim N^{2/3}$. That is, they are all extensive properties. $N^{2/3}$ because we lose one dimension when taking a slice as a surface is inherently two-dimensional.

Consider the following two-component system:

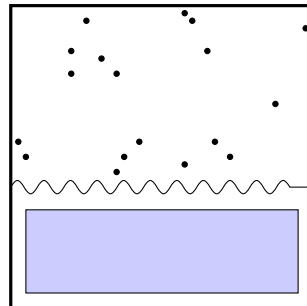


Figure 14: Dividing surface between phases of 1 component (H_2O). Liquid in the bottom, vapor above with no (H_2O) on the dividing surface.

$$\underbrace{dE^{(s)}}_{\text{for div. surf.}} = TdS^{(s)} + \gamma d\sigma + \mu_2 dn_2^{(s)}$$

Note that there is no μ_1 because of our definition. Using Euler's

$$E^{(s)} = TS^{(s)} + \gamma\sigma + \mu_2 n_2^{(s)}$$

$$0 = S^{(s)}dT + \sigma d\gamma + n_2^{(s)}d\mu_2 \xrightarrow{\text{for isotherm}} \sigma d\gamma = -n_2 d\mu_2 \longrightarrow \underbrace{\left(\frac{n_2^{(s)}}{\sigma} \right)}_{SA, n_2 \text{ is } +} = - \left(\frac{\partial \gamma}{\partial \mu_2} \right)_T$$

$$\begin{aligned} \left(\frac{n_2^{(s)}}{\sigma} \right) &= - \left(\frac{\partial \gamma}{\partial \mu_2} \right) \\ &= - \left(\frac{d\gamma}{\partial \rho_2^{(s)}} \right) \underbrace{\left(\frac{\partial \rho_2^{(s)}}{\partial \mu_2} \right)_T}_{\text{sign via stability}} \\ \rho &= \frac{n}{V} \implies \left(\frac{\partial \mu}{\partial n} \right) \geq 0 \quad \therefore + \end{aligned}$$

We conclude

$$\left(\frac{\partial \gamma}{\partial \rho_2^{(s)}} \right)_T < 0 \quad (1.6.1)$$

i.e. surface tension decreases as density of component 2 increases

1.6.2 CH. 2 Review

CH I:

- 1st & 2nd Laws + how to use them
- E(S, V, N), H(S, P, N), A(T, V, N), G(T, P, N) as natural functions of different variables
- Maxwell's & Gibbs-Duhem

CH II: Equilibrium, Stability, Phases

- Multiphase equilibria showed:

- $T^{(1)} = T^{(2)}$
- $P^{(1)} = P^{(2)}$
- $\mu_i^{(1)} = \mu_i^{(2)}$ if mass transport is allowed

- Stability Criteria: $\left(\frac{\partial I_i}{\partial X_i} \right)_{x_j \neq i} \geq 0$

- Phase Diagrams and Transitions

- Lower $\mu_i^{(\alpha)}$ determines which phase is stable at equilibrium
- $G = \mu n$ so minimize G

- Gibbs Phase Rule + C-C; first-order phase transition if there's a discontinuity (particularly in S or V)

1.6.3 Equilibrium Ensembles and $\langle G \rangle$

Consider an equilibrium measurement of some observable quantity, G

$$\langle G \rangle = \sum_{\nu} P_{\nu} G_{\nu} \quad \left\{ \begin{array}{l} \nu = \text{some microstate} \\ P_{\nu} = \text{probability of microstate } \nu \\ G_{\nu} = \text{value of G in microstate } \nu \end{array} \right.$$

This is a sum over state space and will remain static for all P_{ν} at equilibrium.

$$G_{obs} = \frac{1}{n} \sum_{\alpha=1}^n G_{\alpha}$$

for n observations if n is enough to get representative statistics (i.e. equilibrium statistics).

Either/Or

Long Enough Observations:

$$\tau_{\text{measure}} \gg \tau_{\text{relax}}$$

+ ergodic

Large Enough Sample Size:

Number of replicas
or

System Size $L \gg L_{\text{correlation}}$

1.6.4 Foundation of Stat Mech

Consider an ensemble (i.e. a collection of microstates) that contains all possible microstates (ν) subject to the requirement that all ν have a specified N, V, E . This collection is called the **microcanonical ensemble**. If we could all microstates:

$$\sum_{\nu} \nu = \Omega = \Omega(N, V, E)$$

That is, Ω is the total number of microstates with constant $\{N, V, E\}$

Foundation of Stat Mech

$$P_{\nu} = \frac{1}{\Omega(N, V, E)} \tag{1.6.2}$$

Every microstate in the microcanonical ensemble is **equally likely**.

For any isolated system, same N, V, E therefore it is part of the microcanonical ensemble:

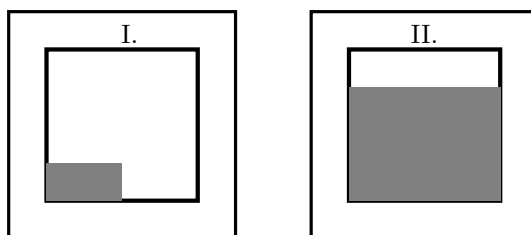


Figure 15: Ink in water. The probability of microstate I and II are **equal**, but there are more microstates that look like II.

System II of Figure 11 shows the results of entropy!

$$S_{\text{Boltzmann}} = k_B \ln\{\Omega(N, V, E)\}$$

Recall the 2nd Law says $S(N, V, E) > S(N, V, E, \text{ internal constraint(s)})$ since having internal constraints decreases $\Omega(N, V, E)$.

1.7 September 19th, 2023

1.7.1 Review of Microcanonical Ensemble

Collection of microstates at fixed N, V, E and $\Omega(N, V, E) =$ number of microstates w/ N, V, E

$$P_{\nu} = \frac{1}{\Omega(N, V, E)}$$

which is the foundational assumption of Statistical Mechanics

1.7.2 Review of Entropy

$$S_{\text{Boltzmann}} = k_B \ln\{\Omega(N, V, E)\}$$

Second Law: isolated system moves towards states with larger $\Omega(N, V, E)$

1.7.3 Entropy Properties and Gibbs Entropy

Entropy should be extensive. $S_{A+B} \stackrel{?}{=} S_A + S_B$

Example:

$$\begin{aligned} \Omega_A &= 3(1, 2, 3) \\ \Omega_B &= 3(1, 2, 3) \end{aligned} \quad \left\{ \begin{array}{l} 1 \rightarrow 1, 2, 3 \\ 2 \rightarrow 1, 2, 3 \\ 3 \rightarrow 1, 2, 3 \end{array} \right.$$

Here, you pick a number from each tuple to find the total number of permutations. The possibilities are:

$$\begin{array}{ccc} (1, 1) & (1, 2) & (1, 3) \\ (2, 1) & (2, 2) & (2, 3) \\ (3, 1) & (3, 2) & (3, 3) \end{array}$$

Thus $\Omega_{A+B} = 9$. How can we make this extensive? Consider the natural log.

$$\ln(9) = \ln(3)^2 = 2\ln(3) = \ln(3) + \ln(3)$$

which matches the extensivity property we wish for entropy to have.

Recall:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} \implies k_B \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V}$$

thus

$$\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V}$$

Here, we set the following definition: $\beta \equiv \frac{1}{k_B T}$ which is sometimes called “inverse temperature.”

General Definition for Entropy

$$S_{\text{Gibbs}} = -k_B \sum_{\nu} P_{\nu} \ln(P_{\nu}) \quad (1.7.1)$$

1.7.4 Canonical Ensemble {N, V, T}

Things change when our system no longer has consistent energy for each state. If the canonical ensemble applies, it can be considered as a subsystem of the microcanonical ensemble.

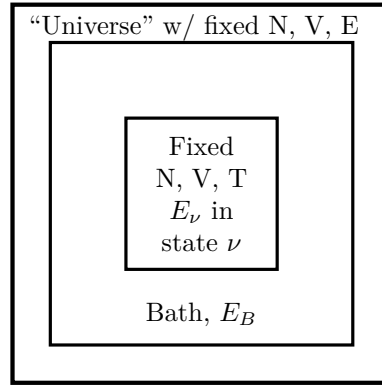


Figure 16: Visualization of a canonical ensemble as a subsystem of an isolated system.

Here, $E = E_B + E_\nu$ where changing E_ν changes E_B because E is fixed. Since the system is isolated, $\Delta E = 0$. We can also state $E_\nu \ll E$ since the subsystem is small. We want to know the probability of ν in the subsystem (i.e. P_ν in the canonical ensemble).

The **key** is to re-frame the question by asking “what is the size of the set of all microstates of the universe (isolated system) when the subsystem is in state ν ?”

We know

$$P_\nu \text{ in canonical} \propto P \text{ the set of all microstates of the “universe” w/ subsystem in microstate } \nu \\ \propto \Omega_{\text{bath}}(N, V, E_B) \underbrace{\Omega_{\text{sys. in } \nu}(N, V, E_\nu)}_{1 \text{ b/c fixed in } \nu} \propto \exp[\ln\{\Omega(N, V, E - E_\nu)\}]$$

We will now Taylor Expand $\ln\{\Omega(N, V, E - E_\nu)\}$ following Eqn. 0.1.2

$$\ln\{\Omega(E - E_\nu)\} = \ln\{\Omega(E)\} + (-E_\nu) \underbrace{\left(\frac{\partial \ln \Omega(E)}{\partial E}\right)}_{\beta}_{N, V} + \mathcal{O}(E_\nu)^2 \quad (1.7.2)$$

To make the relationships of the Taylor Expansion clear:

$$f(a + \varepsilon) = f(a) + f'(a) \frac{x - a}{1!} + f''(a) \frac{(x - a)^2}{2!} + \dots \begin{cases} x = E_B \\ a = E \\ \varepsilon = -E_\nu \end{cases}$$

That is, we imagine a Taylor Expansion of $f(E_B)$ about the “point” where $E_B = E$ to match the pattern we see in Eqn. 0.1.2 ($f(x)$ expanded about $x = a \rightarrow f(E_B) = f(E) + \underbrace{\frac{f'(E)}{1!}}_{\beta} \underbrace{(E_B - E)}_{-E_\nu} + \mathcal{O}(E_\nu)^2$)

This leaves us with

$$\ln \Omega(E - E_\nu) = \ln \Omega(E) - \beta E_\nu + \mathcal{O}^2 \quad (1.7.3)$$

Higher order terms go to 0 because $\frac{\partial \beta}{\partial E} \rightarrow 0$ if in an infinite thermal reservoir.

Remark. From Section 1.3 of David Tong’s notes: The term “reservoir” means that the energy of the subsystem is negligible compared with that of the reservoir. In particular, the subsystem can happily absorb or donate energy from or to the reservoir without changing the ambient temperature T .

We are now left with

$$P_\nu \text{ in canonical} \propto \exp[\ln\{\Omega(E)\} - \beta E_\nu] = \underbrace{\Omega(E)}_{\text{no } \nu} e^{-\beta E_\nu} \rightarrow P_\nu \text{ in canonical} \propto e^{-\beta E_\nu}$$

We must normalize such that $\sum_\nu P_\nu = 1$ so the probability for a microstate in the canonical ensemble is

$$P_\nu = \frac{e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}} = \frac{e^{-\beta E_\nu}}{Q} \quad (1.7.4)$$

Here,

$$Q = \sum_{\nu \text{ states}} e^{-\beta E_\nu} = \sum_l \Omega(E_l) e^{-\beta E_l}$$

energy levels

Consequently, you can think of **each** energy level l being its own microcanonical ensemble.

1.8 September 21st, 2023

1.8.1 Gibbs Entropy Continued

Still a microscopic based definition where

$$S_{\text{boltz}} = k_B \ln(\Omega) \implies S_{\text{Gibbs}} = -k_B \sum_\nu P_\nu \ln(P_\nu) \text{ and } P_\nu \text{ for } \{N, V, E\} = \frac{1}{\Omega}$$

Checking to see if we can reconcile Boltzmann Entropy with Gibbs, we substitute $\frac{1}{\Omega}$ into Gibbs' formula:

$$-k_B \sum_\nu \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k_B \ln\left(\frac{1}{\Omega}\right) \sum_\nu \frac{1}{\Omega} = -k_B \ln\left(\frac{1}{\Omega}\right) = k_B \ln(\Omega) \blacksquare$$

We can remove $\ln(1/\Omega)$ from the sum since it has no ν dependence. $\sum_\nu 1/\Omega = 1$, and using log rules, switching signs is equivalent to taking the reciprocal.

We want Gibbs entropy to be extensive as well. Check if S_{Gibbs} obeys $S_{A+B} = S_A + S_B$ if A and B are uncoupled systems (i.e. $P_{\nu_A} P_{\nu_B} = P_{\nu_A} P_{\nu_B}$)

$$\begin{aligned} S_{A+B} &= -k_B \sum_{\nu_A} \sum_{\nu_B} P_{AB}(\nu_A, \nu_B) \ln(P_{AB}(\nu_A, \nu_B)) \\ &= -k_B \sum_{\nu_A} \sum_{\nu_B} P_{\nu_A} P_{\nu_B} [\ln(P_{\nu_A}) + \ln(P_{\nu_B})] \\ &= -k_B \left[\sum_{\nu_A} P_{\nu_A} \ln(P_{\nu_A}) \underbrace{\sum_{\nu_B} P_{\nu_B}}_1 + \sum_{\nu_B} P_{\nu_B} \ln(P_{\nu_B}) \underbrace{\sum_{\nu_A} P_{\nu_A}}_1 \right] \\ &= -k_B \left[\sum_{\nu_A} P_{\nu_A} \ln(P_{\nu_A}) + \sum_{\nu_B} P_{\nu_B} \ln(P_{\nu_B}) \right] \blacksquare \end{aligned}$$

For the Canonical Ensemble, $P_\nu = \frac{e^{-\beta E_\nu}}{Q}$

$$\begin{aligned} S_{\text{Gibbs}} &= -k_B \sum_\nu P_\nu \overbrace{[-\beta E_\nu - \ln(Q)]}^{\ln(P_\nu)} \\ &= k_B \langle \beta E_\nu + \ln(Q) \rangle \\ &= k_B \beta \langle E_\nu \rangle + k_B \ln(Q) \end{aligned}$$

Going from line 1 to line 2, we are summing over all states multiplied by their associated probabilities which should scream ensemble average. Line 2 to line 3 is justified since $\langle a + b \rangle = \langle a \rangle + \langle b \rangle$. Further, β is a constant without ν dependence thus it can be removed from the $\langle \rangle$. At this point, Q is also a constant since you've already summed over all ν . Rearranging to isolate $\ln(Q)$:

$$\ln(Q) = \frac{S}{k_B} - \beta \langle E \rangle = -\beta [\langle E \rangle - TS] = -\beta \langle E - TS \rangle = -\beta \langle A \rangle = \ln(Q) \quad (1.8.1)$$

1.8.2 Grand Canonical

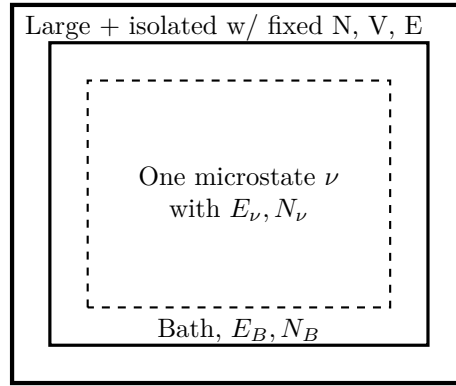


Figure 17: Visualization of a grandcanonical ensemble as a subsystem \mathcal{S} of an isolated system. Dashed lines surrounding \mathcal{S} indicate that matter can flow.

For \mathcal{S} , number of particles (N) and energy (E) can change there \mathcal{S} is characterized by $\{\mu, V, T\}$ or $\{\beta\mu, V, T\}$ since temperature is already specified. Once we fix ν , we fix E_B, N_B where $E_B = E - E_\nu$ and $N_B = N - N_\nu$.

Following the same procedure to find the partition function as we did for the Canonical Ensemble:

$$P_\nu \propto \Omega_B(V, N - N_\nu, E - E_\nu) \cdot \underbrace{\Omega_\nu}_1 \propto \exp[\ln\{\Omega_B(V, N - N_\nu, E - E_\nu)\}]$$

Performing a two-dimensional Taylor Expansion about $E_B = E, N_B = N$, we get:

$$\ln\{\Omega(V, N - N_\nu, E - E_\nu)\} = \ln\{\Omega(N, V, E)\} + (-E_\nu) \underbrace{\left(\frac{\partial \ln \Omega(E)}{\partial E}\right)}_{\beta} \Big|_{N, V} + (-N_\nu) \underbrace{\left(\frac{\partial \ln \Omega(E)}{\partial N}\right)}_{-\beta\mu} \Big|_{E, V} + \mathcal{O}(E_\nu, N_\nu)^2$$

Remark. Using the triple product rule, we evaluate the following:

$$\left(\frac{\partial \ln(\Omega)}{\partial N}\right)_{E, V} = - \underbrace{\left(\frac{\partial \ln(\Omega)}{\partial E}\right)}_{\beta} \Big|_{N, V} \underbrace{\left(\frac{\partial E}{\partial N}\right)}_{\mu} \Big|_{\ln(\Omega), V}$$

As another note to alleviate possible confusion, you use the **triple-product rule** when the variables we hold constant **differ** across each partial derivative. Here, we have constant N, V and $\ln(\Omega), V$ justifying the use of the triple-product rule.

Simplifying the results:

$$\ln\{\Omega(V, N - N_\nu, E - E_\nu)\} = \ln\{\Omega(N, V, E)\} - \beta E_\nu + \beta\mu N_\nu \quad (1.8.2)$$

Consequently we have

$$P_\nu \propto \exp[\ln\{\Omega(V, N - N_\nu, E - E_\nu)\}] = \exp[\ln\{\Omega(N, V, E)\} - \beta E_\nu + \beta\mu N_\nu] \propto e^{-\beta E_\nu + \beta\mu N_\nu}$$

This leaves us with

$$\Xi = \sum_{\nu} e^{-\beta E_\nu + \beta\mu N_\nu} \quad (1.8.3)$$

and

$$\ln \Xi = \beta PV \quad (1.8.4)$$

where Eqn. 1.8.4 is found following the same procedure as Eqn. 1.8.1.

In order to find a formula to produce a generalized ensemble, we return to the entropy differential:

$$dS = \underbrace{\left(\frac{\partial S}{\partial E}\right)_{\vec{X}}}_{1/T} dE + \underbrace{\left(\frac{\partial S}{\partial \vec{X}}\right)_E}_{-\vec{f}/T} d\vec{X} \implies \frac{dS}{k_B} = \beta dE + \underbrace{-\beta \vec{f}}_{\xi} d\vec{x}$$

Generalized Partition Function

$$P_\nu = \frac{e^{-\beta E_\nu - \xi \vec{x}_\nu}}{\Xi} \quad (1.8.5)$$

Here, $\xi = -\beta \vec{f}$. As some examples:

- $x = N \implies \xi = -\beta \mu \implies P_\nu = e^{-\beta E_\nu + \beta \mu N_\nu}$
- $x = V \implies \xi = \beta P \implies e^{-\beta E_\nu - \beta P V_\nu}$

Ξ is unfortunately also used to note a general partition function.

1.8.3 Energy Fluctuations

If we want $\langle E \rangle$ and $\langle (\delta E)^2 \rangle$ in the Canonical Ensemble (the latter being mean-square fluctuation in energy):

$$\langle E_\nu \rangle = \sum_\nu P_\nu E_\nu = \sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}} = -Q^{-1} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V}$$

Leveraging $\frac{d}{dx} [\ln(x)] = \frac{x'}{x}$

$$\langle E_\nu \rangle = - \left(\frac{\partial \ln(Q)}{\partial \beta} \right)_{N,V} \quad (1.8.6)$$

$$\langle (\delta E)^2 \rangle = \langle (E_\nu - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

Going from the second to third step is done as follows:

$$\begin{aligned} \langle (\delta E)^2 \rangle &= \langle (E_\nu - \langle E \rangle)^2 \rangle \\ &= \langle (E - \langle E_\nu \rangle)(E - \langle E_\nu \rangle) \rangle \\ &= \langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \rangle \\ &= \langle E^2 \rangle - 2 \langle E \rangle \langle E \rangle + \langle E \rangle^2 \\ &= \langle E^2 \rangle - \langle E \rangle^2 \end{aligned}$$

From here,

$$\begin{aligned} \langle E^2 \rangle - \langle E \rangle^2 &= \sum_\nu P_\nu E_\nu^2 - \left(\sum_\nu P_\nu E_\nu \right)^2 \\ &= Q^{-1} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} - \left(-Q^{-1} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} \right)^2 \\ &= \left(\frac{\partial^2 \ln(Q)}{\partial \beta^2} \right)_{N,V} \end{aligned}$$

Thus we have the following:

$$\langle (\delta E)^2 \rangle = - \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N,V} = \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} \quad (1.8.7)$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \implies \langle (\delta E)^2 \rangle = C_V k_B T^2$$

which tells us how heat capacity is related to fluctuations in energy. $C_V \sim N$ and $E \sim N$.

$$\frac{\sqrt{\langle(\delta E)^2\rangle}}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

thus we see as system size increases, energy fluctuations relative to $\langle E\rangle$ decreases.

Remark. *Per David Tong, once again:*

“The limit $N \rightarrow \infty$ is known as the thermodynamic limit. The energy becomes peaked closer and closer to the mean value $\langle E\rangle$ and can be treated as essentially fixed.” For the course we assume we have a very large N thus even in the canonical ensemble, we will often write E for the average energy rather than $\langle E\rangle$.

1.9 Unit I Review

1.9.1 A “Simple” Energy Calculation

Recall

Energy Definitions

$$\langle E\rangle = -\left(\frac{\partial \ln(Q)}{\partial \beta}\right)_{N,V}$$

and

$$\langle(\delta E)^2\rangle = -\left(\frac{\partial \langle E\rangle}{\partial \beta}\right)_{N,V} = \left(\frac{\partial^2 Q}{\partial \beta^2}\right)_{N,V}$$

In general, we have the following:

$$\langle x\rangle = -\left(\frac{\partial \ln(Q)}{\partial \xi}\right) \quad (1.9.1)$$

where $\xi = -\beta \times$ intensive and x is the extensive variable.

$$\langle(\delta x)^2\rangle = -\left(\frac{\partial \langle x\rangle}{\partial \xi}\right) \quad (1.9.2)$$

Example: N distinguishable particles each with energy 0 or ε . Microstate ν is specified $\nu = (n_1, n_2, \dots, n_N)$ where $n_j = \{0, 1\}$ and $E_\nu = \sum_j^N n_j \varepsilon$ where the argument in the sum is either 0 or ε . Calculate $\langle E\rangle$ using:

I. Canonical Ensemble

II. Microcanonical Ensemble

1.9.2 Canonical Approach

In thermodynamics, you start by writing your differential. In statistical mechanics, you begin with the partition function.

$$\ln(Q) = \ln\left(\sum_{\nu} e^{-\beta \sum_j^N n_j \varepsilon}\right)$$

$$Q(\beta, N) = \sum_{\substack{n_1, n_2, \dots, n_N \\ =0,1}} e^{-\beta \sum_j^N n_j \varepsilon}$$

If the states are uncorrelated, you can write them as follows:

$$Q(\beta, N) = \prod_{j=1}^N \left(\sum_{n_j=0,1} e^{-\beta \varepsilon n_j}\right)$$

Leveraging that $n_j = \{0, 1\}$:

$$Q(\beta, N) = \prod_{j=1}^N (1 + e^{-\beta\varepsilon})$$

Since there is no j -dependence, we can re-write this as:

$$Q(\beta, N) = (1 + e^{-\beta\varepsilon})^N$$

We now have

$$\ln(Q) = N \ln(1 + e^{-\beta\varepsilon}) \quad (1.9.3)$$

$$\langle E \rangle = - \left(\frac{\partial \ln(Q)}{\partial \beta} \right)_{N,V} = \frac{N\varepsilon e^{-\beta\varepsilon}}{(1 + e^{-\beta\varepsilon})} = \frac{N\varepsilon}{(1 + e^{\beta\varepsilon})}$$

Go from the second to third form by multiplying by $\frac{e^{\beta\varepsilon}}{e^{\beta\varepsilon}}$

1.9.3 Microcanonical Approach

Consider a **set** of microcanonical ensembles:

m th energy level is given as $E/\varepsilon = m$

$$\Omega(m, N) = \frac{N!}{(N-m)!m!}$$

where we choose m/N to be at ε . Using the chain rule (due to consistent, constant variables), we have:

$$\underbrace{\beta = \left(\frac{\partial \ln(\Omega)}{\partial E} \right)_N}_{\text{set of microcan. ens. here}} = \left(\frac{\partial \ln(\Omega)}{\partial m} \right)_N \left(\frac{\partial m}{\partial E} \right)_N = \left(\frac{\partial \ln(\Omega)}{\partial m} \right)_N \cdot \varepsilon^{-1}$$

Using Stirling's Approximation:

For large N , $\ln(N!) = N \ln(N) - N$:

$$\begin{aligned} \ln(\Omega) &= \ln(N!) - \ln([N-m]!) - \ln(m!) \\ &= [N \ln(N) - N] - [(N-m) \ln(N-m) - (N-m)] - [m \ln(m) - m] \end{aligned}$$

$$\left(\frac{\partial \ln(\Omega)}{\partial m} \right)_N = \ln\left(\frac{N-m}{m}\right) = \ln\left(\frac{N}{m} - 1\right)$$

We now have

$$\begin{aligned} \beta\varepsilon = \ln\left(\frac{N}{m} - 1\right) &\implies e^{\beta\varepsilon} = \frac{N}{m} - 1 \implies m = \frac{N}{1 + e^{\beta\varepsilon}} \\ \therefore E &= \frac{N\varepsilon}{(1 + e^{\beta\varepsilon})} \end{aligned}$$

which matches our answer using the canonical ensemble.