

Statistical Mechanics + Thermodynamics

Lecture 1 (8/30/23)

Thermodynamics is the macro perspective (top down)

Statistical Mechanics is the micro perspective (bottom up)

Roadmap

1. Thermodynamic basics
2. Statistical Mechanics; define entropy
3. Applications of Thermo
4. Further development; canonical ensemble
5. Applications of statistical Mechanics
6. Quantum Ideal Gases

Basic Concepts of Thermodynamics

Ancient Understanding

Heat makes things hotter!

How do we quantify this?

Art of Feel

Invention of thermometer

Mercury expands when it gets hotter

Hypothesis: Isolated systems reach a stationary state of "internal equilibrium" after a long time

Macrostate is a partial description of state in terms of macroscopic observables

Isolated means that no other external agency influences the system

State function is a macro property dependent on current state w/ no dependence on history

Thermometer

- Volume in internal equilibrium is our measure of temperature, Θ $\Theta \uparrow$, hotter
other conditions fixed
- To measure temperature of another 'Y', put the two in thermal contact and let the composite system reach equilibrium
Heat flows from hot to cold until equilibrium is reached
- Internal equilibrium requires the temp to be homogeneous

Zerth Law of Thermodynamics: Given Systems A, B, and C, if $\Theta_A = \Theta_B$ and $\Theta_B = \Theta_C$ then $\Theta_A = \Theta_C$

transitive property of temperature

Rules out cyclic heat flows

Thermal Equilibrium: Two systems are in thermal equilibrium if the objects have the same temperature

Independent of thermal contact

Relation between two systems whereas internal equilibrium is just one

If two objects are brought into thermal contact, then no heat would flow

The composite system would be in internal equilibrium

For a second thermometer $\tilde{\Theta}$ the Zerth law implies that there exists a function $f(\Theta) = \tilde{\Theta}$ which is invertible

Lecture 2 (9/1/23)

A composite system is composed of many parts

A simple system is one in which every part can exchange heat

Thermal Equilibrium: The condition when two simple systems, regardless of thermal contact, would not exchange heat if in thermal contact

Final equilibrium macrostate is equivalent to initial state given no other changes of conditions

Zerth law applies to simple systems

Zerth Law allows us to define a temperature scale

Establishes equivalence of state function transitivity to thermal equilibrium transitivity

Experiment shows that only one variable is required to establish thermal equilibrium

Therefore, if there are two scales then there is a function mapping the two

Function is monotonically increasing

Is injective the only necessary condition for the macrostate state function?

Heat



$$\Delta m = C \Delta \Theta$$

← Holds for different fuels and different systems

fuel constant for the system + fuel change in temp

Δm for a given fuel has the same amount of heat

we can quantify this power to change temp as heat

BTU is the amount of heat required to raise 1 lbs of water by 1°F

For each system C is the ratio of $\frac{\text{heat}}{\text{temp change}}$

← heat capacity

Two competing theories of heat:

i) Caloric Theory of Heat: Conserved quantity that is transferred as heat

ii) Molecular Motion Theory of Heat: Heat is just a form of energy

Ordinary form of mechanical energy

Count Rumford
or Baworia

→ Benjamin Thompson was an early proponent of molecular motion theory

Born in New Hampshire but fought on the British side of the war

Argued that heat was equivalent to work

Joule did this more thoroughly in the 1840's

First Law of Thermodynamics: Heat is a form of energy

Energy is conserved when heat is considered

Change in Internal energy is non-thermal and thermal energy

$$\Delta E = W + Q$$

non-thermal work on system heat into system

Holds for composite system as well

State Functions

Numerical macroscopic property defined for any internal equilibrium macrostate of a system

Ex. Internal energy, empirical temperature

no external forces

External Parameters: A state function we can control via Non-thermal parameters

- Provide coordinates to describe equilibrium macrostate of the system

$X_\alpha, \alpha=1,2,\dots$

Lecture 3 (9/6/23)

Processes: A change in the state of a system occurring in physical time

Should be specified in full macroscopic detail

ex. heat flow, volume expansion

Initial state is usually assumed to be an equilibrium macrostate, but the intermediate state is typically non-equilibrium

Independent Variables: A set of independent state functions s.t. the equilibrium state is uniquely determined by these parameters

external parameters will not be sufficient

For a simple system the set of external parameters and E uniquely determine the equilibrium state

Mathematical Methods for State Functions

Consider a space of dimension n (typically $n=2$; x, y)

A function of position is given by $f(x, y)$

Partial Derivative

$$\frac{\partial f}{\partial x} = \lim_{\delta x \rightarrow 0} \frac{\delta f}{\delta x} \equiv \left(\frac{\partial f}{\partial x} \right)_y$$

y is held constant

generally hold $n-1$ variables constant

For another function $z(x, y)$

1) $\left(\frac{\partial f}{\partial z} \right)_x$

2) $\left(\frac{\partial f}{\partial x} \right)_z \neq \left(\frac{\partial f}{\partial x} \right)_y$

Differential

df of a function that depends on position also depends on position

$$\delta f = df(\delta x, \delta y)$$

linear in $\delta x, \delta y$

Applying the chain rule

$$df = \left(\frac{\partial f}{\partial x} \right)_y \delta x + \left(\frac{\partial f}{\partial y} \right)_x \delta y$$

functions

$$\delta f = \left(\frac{\partial f}{\partial x} \right)_y \delta x + \left(\frac{\partial f}{\partial y} \right)_x \delta y \leftarrow \text{holds true for any small change}$$

Can recover partial derivative

A general position dependent linear combination is called differential

If there is a function f s.t.

$$df = a \delta x + b \delta y \quad \forall x, y$$

then $a \delta x + b \delta y$ is called an exact differential

If $a \delta x + b \delta y$ is not exact, but there exists a function g s.t. $g(a \delta x + b \delta y)$ is exact, then g is an integrating factor

Line Integral

Any differential can be integrated along a path C

$$\int_C (a \delta x + b \delta y) \leftarrow \text{line integral}$$

Path dependent!

If $a \delta x + b \delta y = df$ is exact, then

$$\int_C df = f(f_{\text{final}}) - f(f_{\text{initial}}) = \Delta f$$

Assume the domain is simply connected

No holes in the domain

$$a \delta x + b \delta y \text{ is exact} \Leftrightarrow \left(\frac{\partial a}{\partial y} \right)_x = \left(\frac{\partial b}{\partial x} \right)_y \quad \forall x, y \text{ is closed} \Leftrightarrow \int_C (a \delta x + b \delta y) \text{ is path independent} \Leftrightarrow \oint_{\text{closed path}} (a \delta x + b \delta y) = 0$$

green's/stokes thm

$$\sum a_i dx_i \text{ is exact} \Leftrightarrow \left(\frac{da_j}{dx_k} \right)_{x_k, k \neq j} = \left(\frac{da_k}{dx_j} \right)_{x_k, k \neq j}$$

multidimensional generalization

Differential version of 1st Law of Thermodynamics

In any infinitesimal process

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

Process dependent
infinitesimals

δQ and δW are not differentials since they are only defined for the particular points in use

Q and W are not state functions

transfers of energies

$$Q = \int \delta Q \leftarrow \text{path dependent}$$

General process may jump from initial to final equilibrium states without passing through intermediate equilibrium states

Quasistatic Processes

A process in which all state functions vary slowly and continuously s.t. the system is effectively in equilibrium at all times during the process

Path in the space of equilibrium states

Time derivatives approach 0 in the limit at all times
total time

Lecture 4 (9/11/23)

Assume that given a continuous path, $\exists$ a quasistatic process that corresponds

In general, with external parameters $\{X_\alpha\}$ then

$$\text{quasi-static} \Rightarrow \delta W = \sum_{\alpha} J_{\alpha} dX_{\alpha}$$

necessary but
not sufficient

generalized
forces

how external parameters can control a system (follows from definitions)

Releasing a constraint is never quasi-static

Work is only done by change in external parameters

Mechanical interaction

It follows from the 1st law of thermodynamics

$$\delta Q = dE - \sum_{\alpha} J_{\alpha} dX_{\alpha} \leftarrow \text{Simple system}$$

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

Adiabatic process is a quasistatic process with no heatflow (adiathermal)

We can view δW and δQ as inexact differentials in quasistatic processes

Since the above relations hold for all initial states, for all δX_{α} , δE

Implicit assumption that $E, \{X_{\alpha}\}$ uniquely determine the equilibrium state

In adiabatic processes,

$$J_{\alpha} = \lim_{\delta X_{\alpha} \rightarrow 0} \left(\frac{\delta E}{\delta X_{\alpha}} \right)_{X_{\beta} (\beta \neq \alpha)} \Big|_{\text{adiabatic}} \quad \delta E = \delta W$$

Reversible vs. Irreversible Processes

Reversible if you can retrace initial state by applying a process and then applying the reverse

Irreversible processes can still be quasi-static

Whole system can be irreversible even if each part of the process can be quasistatic

Second Law of Thermodynamics

Kelvin's 2nd Law: There does not exist any process in any system whose sole effect is to convert positive amount of heat entirely into work done by system

- sole effect means the system returns to its original state
- Can't have perfect heat engine

Consequences of 2nd Law

There exist state functions T, S s.t. $\leftarrow$ for simple systems

$$1) dE = T dS + \sum_{\alpha} J_{\alpha} dX_{\alpha}$$

$$T = \left(\frac{\partial E}{\partial S} \right)_{X_{\alpha}}, J_{\alpha} = \left(\frac{\partial E}{\partial X_{\alpha}} \right)_{S, X_{\beta} (\beta \neq \alpha)}$$

$\leftarrow$ Basic relation of
Thermodynamics

- 2) T is a temp scale called absolute temperature
 Sys w/ same absolute temp are in thermal equilibrium
- 3) S is entropy and for simple systems composed of parts,
 entropy of whole is sum of entropy of parts
- 4) Any process in any thermally isolated system (adiathermal)
 $\Delta S_{\text{tot}} > 0$ (Clausius Inequality)
 thermodynamic arrow of time

Lecture 5 (9/13/23)

Consequences of 2nd Law Continued

- 5) In infinitesimal process in simple system, not necessarily isolated

$$T dS \geq dQ$$

or by equivalence

$$\sum_{\alpha} J_{\alpha} dX_{\alpha} \leq dW$$

Equality holds if quasistatic

- 6) Quasistatic process $dQ = dE - \sum_{\alpha} J_{\alpha} dX_{\alpha}$ is inexact differential

now $\frac{1}{T}$ is an integrating factor

$$\frac{dQ}{T} = dS \text{ is an exact differential}$$

- 7) Equalities hold if quasistatic and if $\delta V = 0$, $\delta W = 0 \leftarrow$ only one direction

$$\delta E = dQ = T \delta S$$

Not for every small change

Some Derivations

- 5) In infinitesimal process in a simple system, then $T dS \geq dQ$

Simple system w/ arbitrary infinitesimal process, then dQ and dW in a path

By assumption for any path $\exists$ a quasistatic process



$$\text{Heat in} = -T \delta S$$

Change in entropy back to initial state

$$\text{Work in} = - \sum_{\alpha} J_{\alpha} dX_{\alpha}$$

$$\text{Net heat in: } dQ - T \delta S$$

Kelvin's formulation says that this must be ≤ 0

$$\Rightarrow T \delta S \geq dQ$$

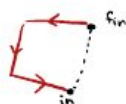
$$\Rightarrow -dW \leq - \sum_{\alpha} J_{\alpha} dX_{\alpha}$$

Can replace S w/ d since it holds for any process

- 6) Clausius' Inequality

Consider a thermally isolated (not necessarily simple) system

Three stage Quasistatic return Process



1st: Adiabatically change external parameters until temp reaches T_0 in all parts (fixed entropy)

2nd: Quasistatic heatflow at a fixed temperature T_0

3rd: Adiabatically change X_{α} to initial values (fixed entropy)

$$\text{Heat in: } -T_0 \Delta S_{\text{tot}}$$

2nd stage

Kelvin shows that this must be less than 0

$$\Delta S_{\text{tot}} \geq 0$$

(Assumes $T_0 > 0$)

Simple Examples

1) Heat Flow



• No external work

$$\delta Q_1 + \delta Q_2 = 0$$

$$\delta S_{\text{TOT}} = dS_1 + dS_2 \geq 0$$

↖ Clausius

$$\text{Quasi-static} \Rightarrow T_1 dS_1 + T_2 dS_2 = 0$$

$$dS_1 = -\frac{T_2}{T_1} dS_2$$

$$dS_2 \left(1 - \frac{T_2}{T_1}\right) > 0$$

$$(T_1 - T_2) dS_2 > 0$$

$$\text{if } T_1 > 0, T_2 > 0$$

$$\text{if } T_1 > T_2 \text{ then } dS_2 > 0, \delta Q_2 > 0$$

Heat flows from higher T to lower T (positive temperatures)

2) Free Expansion



Adiabatic container and no external work

$$\text{so } \delta Q = \delta W = 0 \text{ but } \delta V > 0$$

$$\delta E = T \delta S - P \delta V = 0 \quad (\text{1st Law})$$

$$\delta S = \frac{P \delta V}{T} > 0 \quad \text{if } \frac{P}{T} > 0$$

↖ Clausius!

In general for $\delta V > 0$ need $P > 0$ so in free expansion

$$\Rightarrow P \delta V > 0$$

Lecture 6 (9/18/23)

↖ side effect: returns to original state

Kelvin: No process takes in positive heat and does positive work

↖ new physics reinforcement
At any step in the process (including infinitesimal steps) into any path
Not net heat

Step 1: For a simple system, establish existence of "empirical entropy"

Write δQ_{eq} for heat in an infinitesimal quasistatic system

$$\delta Q_{\text{eq}} = dE - \sum_i J_i dX_i$$

↖ inexact differential

Solve $\delta Q_{\text{eq}} = 0$ corresponding process to find adiabatic paths (level sets of empirical entropy)

Want to show the existence of adiabatic hypersurfaces s.t. any adiabatic path lies in one and only one adiabatic
↖ n-1 dimensional

Proof: Construct σ

Pick a ref point in $n-1$ dimensional space of $\{X_i\}$ and call it $\{X_{\text{ref}}^{(0)}\}$

From any state, say $(X_1, \dots, X_{n-1}, E)$ can find adiabatic path to $\{X_{\text{ref}}^{(0)}\}$

Let $E^{(0)}$ be the energy of the resulting state

Initial point fixes n^{th} dimension in the reference point

$$\text{Let } \sigma = E^{(0)} + \sigma_0 \text{ where } \sigma_0 = \text{constant}$$

↖ empirical entropy

Still need to show that $E^{(0)}$ is uniquely determined by initial point

↖ Show path independence

Suppose there are two adiabatic paths to the reference point w/ $E_1^{(0)} \neq E_2^{(0)}$

Consider a quasi-static process from $E_1^{(0)}$ to $E_2^{(0)}$ ↖ monotonic heat flow

This produces a qs cycle w/ heat at $X_{\text{ref}}^{(0)}$ fixed

Can go in a cycle w/ heat in ≥ 0 for every step

Contradicts Kelvin so $E_1^{(2)} = E_2^{(2)}$

σ is a well-defined function of state

Path is adiabatic $\Leftrightarrow \sigma$ constant on a path

Proof:

$\Rightarrow$

Consider an adiabatic path $1 \rightarrow 2$

We can find $E^{(2)}$ from 2

Can also go from $1 \rightarrow 2 \rightarrow$ reference $E^{(2)}$

$$E_2^{(2)} = E_1^{(2)}$$

$\Leftarrow$ If σ is constant then the path is adiabatic

Take infinitesimal step

ref $\xleftarrow{\text{adiabatic}} 1 \xrightarrow{\text{adiabatic}} 2$ $\oint \sigma = 0$

$\exists$ adiabatic path 2 to 1 by going to ref

$$\sigma(2) = \sigma(1)$$

If $1 \rightarrow 2$ is non-adiabatic, then $\delta Q_{12} \neq 0$ so there is a positive heat direction

Contradiction w/ Kelvin!

$$\text{So } \delta Q_{12} = 0$$

σ 's are dependent on reference point but have same level sets

Step 2: Show $\delta Q_{qs} = \lambda d\sigma$
 $\leftarrow$ state function

- use σ as a coordinate

Step 3: Use 0th Law and 1st Law
Therm. Equilibrium Empirical Temp

Two simple systems 1,2 in thermal contact so composite 1,2 is simple

$$\delta Q_{qs} = \delta Q_{q1} + \delta Q_{q2}$$

$$\Rightarrow \lambda d\sigma = \lambda_1 d\sigma_1 + \lambda_2 d\sigma_2$$

Analyze dependence on variables

$$d\sigma = \frac{\lambda_1}{\lambda} d\sigma_1 + \frac{\lambda_2}{\lambda} d\sigma_2$$

σ is a function of σ_1 and σ_2

Must have

$$\lambda_1 = T(\theta) f_1(\sigma_1)$$

$$\lambda_2 = T(\theta) f_2(\sigma_2)$$

$$\lambda = T(\theta) f(\sigma_1, \sigma_2)$$

$\uparrow$
absolute temp!

Define $dS_1 = f_1 d\sigma_1$

$$S_1 = \int^{\sigma_1} f_1 d\sigma_1 + \text{constant}$$

$$f(\sigma_1, \sigma_2) d\sigma = dS_1 + dS_2 = d(S_1 + S_2)$$

$\rightarrow$
exact!

$$S = S_1 + S_2 + \text{constant}$$

Entropy S of a simple system is given by sum of two paths

Lecture 7 (9/20/23)

Ideal Gases

Boyle's Law: At fixed temp (not too low) P, V are inversely proportional

$PV = \text{const}$

We can use PV as "ideal gas temp"

$$PV = N k_B T \leftarrow \text{proportional to absolute temp}$$

$N = \# \text{ molecules}$

$k_B = \text{Boltzmann's constant}$

Joule's Law: Internal energy is independent of volume and for a monatomic ideal gas

$$E = \frac{3}{2} N \cdot k_B T$$

Def: For any system, the heat capacity at constant volume or at constant X_n

$$C_v \triangleq \left(\frac{\partial Q_{ex}}{\partial T} \right)_{X_n} = T \left(\frac{\partial S}{\partial T} \right)_{X_n} = \left(\frac{\partial E}{\partial T} \right)_{X_n}$$

Recall $dE = \underbrace{T dS}_{dQ_{ex}} + \underbrace{\sum_n J_n dX_n}_{dW_{ex}}$

If heat flow is fixed at X_n

$$\Delta S|_{fixed X_n} = \int_{in}^{fin} dS = \int_{in}^{fin} \frac{C_v}{T} dT = C_v \ln \frac{T_f}{T_i}$$

Expansion of a gas

Assume quasistatic expansion w/ heat flow s.t. T stays constant

For an ideal gas, $T = \text{constant} \iff dE = 0$

$$0 = dE = dQ + dW$$

$$dQ = T dS$$

$$dW = -P dV$$

Work done on a gas

$$W = \int_i^f dW = -N k_B T \int_i^f \frac{dV}{V} = -N k_B T \ln \frac{V_f}{V_i}$$

$$\Delta S|_{fixed T} = \int_{in}^{fin} dS = \int_{in}^{fin} \frac{P}{T} dV = N k_B \int_{in}^{fin} \frac{dV}{V} = N k_B \ln \frac{V_f}{V_i} = -\frac{W_{ex}}{T}$$

Free Expansion

$$\Delta V > 0, Q = W = 0$$

$$\text{Ideal gas: } \Delta E = Q + W$$

$$\Rightarrow T_{fin} = T_{in}$$

Since S is a state function it only depends on initial and final states

Select a path w/ constant temp and quasistatic

$$\Delta S|_{free expansion} = N k_B \ln \frac{V_{fin}}{V_{in}} \quad \leftarrow \text{apply above calculations}$$

respects Clausius Inequality

Entropy for ideal gas

$$S = N k_B \ln V + \frac{3}{2} N k_B \ln T + C(N)$$

$\uparrow$
constant depending on N

Heat Reservoirs

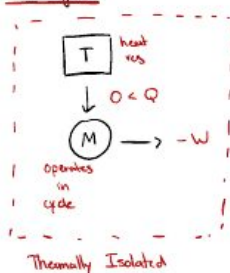
A system in internal equilibrium w/ external parameters fixed so $dX_n = 0, dW = 0$

$$\text{In any process } dE_{res} = dQ_{res} = T_{res} dS_{res}$$

True even if not quasi-static

$$Q_{res} = \int_{in}^{fin} T dS_{res} = T_{res} \Delta S_{res} \quad \text{if} \quad \frac{\Delta T_{res}}{T_{in}} \ll 1$$

Heat Engines



$$Res \Rightarrow \Delta S_{res} = -\frac{Q}{T} = \Delta S_{tot}$$

$\therefore M$ returns to original equilibrium macrostate

$$\text{Clausius} \Rightarrow \Delta S_{tot} \geq 0$$

$$\Rightarrow Q \leq 0, -W \leq 0$$

no perfect heat engine

Heat T_H $\rightarrow$ $Q_H > 0$

$\downarrow$

$(M) \rightarrow -W$

$\downarrow$ $Q_L < 0$

T_L $\leftarrow$

$$\Delta S_H = -\frac{Q_H}{T_H}, \Delta S_L = \frac{Q_L}{T_L}$$

$$Q_H - Q_L = -W \quad (1^{st} \text{ Law})$$

$$\Delta S_H + \Delta S_L \geq 0 \quad (\text{Clausius})$$

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0$$

$$\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H} \quad \text{if } \frac{Q_H}{T_H} > 0$$

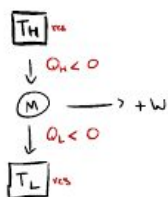
Def: Heat Efficiency

$$\eta = \frac{-W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H}$$

perfect for $\eta = 1$

Refrigerator

Heat engine running in reverse



Same conditions: $\frac{Q_L}{T_L} \geq \frac{Q_H}{T_H} \Rightarrow \frac{Q_L}{Q_H} \leq \frac{T_L}{T_H} \therefore \frac{Q_H}{T_H} < 0$

Def: Coefficient of refrigerator performance

$$\epsilon_r = \frac{-Q_L}{W} = \frac{-Q_L}{Q_L - Q_H} = \frac{1}{\frac{Q_H}{Q_L} - 1} \leq \frac{T_L}{T_H - T_L}$$

perfect if $\epsilon_r = \infty$

Lecture 8 (9/25/23)

Heat Pumps

Same as refrigerator

$$\epsilon_p = \frac{-Q_H}{W} > 0$$

$$\leq \frac{T_H}{T_H - T_L} \quad \leftarrow \text{Clausius}$$

Born fuel

$$\epsilon_{\text{born}} = \frac{-Q_H}{W} \leq 1$$

Heat Engine - Carnot Cycle

Machine is a simple system, temp T_m w/ 4 stages (quasistatic)

- 1) Extract heat at T_H by doing work till $T_m = T_H$
- 2) Decouple adiabatic work, $T_m \rightarrow T_L$
- 3) Dump heat at $T_m = T_L$ (work done on machine)
- 4) Decouple, adiabatic work on $T_m \nearrow T_H$

$$\text{Efficiency } \eta = 1 - \frac{T_L}{T_H}$$

Consider an ideal gas (Reif 5.1-5.3)

From $PV = nRT$, $E = E(T)$, ind of V

Def: Basic Relation $dE = TdS - PdV$

$$= \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV$$

$$= \frac{1}{T} dE + \frac{Nk_B}{V} dV$$

$$= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

rearranging things from basic relation

$$\text{so, } \left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_T + \frac{Nk_B}{T}$$

$$\left(\frac{\partial}{\partial V} \right)_T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial}{\partial T} \right)_V \left(\frac{\partial S}{\partial V} \right)_T$$

$\Rightarrow$ Maxwell Relation

$$\frac{1}{T} \left(\frac{\partial^2 E}{\partial V \partial T} \right) = -\frac{1}{T^2} \left(\frac{\partial E}{\partial V} \right)_T + \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial V} \right)$$

$$\Rightarrow T > 0 \quad \left(\frac{\partial E}{\partial V} \right)_T = 0$$

Heat Capacities

$\leftarrow$ if V is fixed not necessarily q.s.

$$C_V = \left(\frac{\partial Q_s}{\partial T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V \quad (\text{ind of } V \text{ for ideal gas})$$

Constant Pressure

$$C_P = \left(\frac{\partial Q_s}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P \neq \left(\frac{\partial E}{\partial T} \right)_V$$

$$TdS = \left(\frac{\partial E}{\partial T} \right)_V dT + PdV$$

$\uparrow$
 C_V

Change at fixed P

$$S(PV) = S(Nk_B T)$$

$$\delta P V + P \delta V = Nk_B \delta T$$

$$\delta P = 0$$

$$P \delta V = Nk_B \delta T$$

$$\Rightarrow T \delta S = C_V \delta T + Nk_B \delta T$$

$$= C_P \delta T$$

$$C_P = C_V + Nk_B \quad \leftarrow \text{Ideal Gas}$$

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{Nk_B}{C_V} \quad \leftarrow \text{Also Ideal Gas}$$

Def: Specific Heat

$$\left. \begin{aligned} C_V &= \frac{C_V}{N} = \frac{3}{2} k_B \\ C_P &= \frac{C_P}{N} = \frac{5}{2} k_B \end{aligned} \right\} \begin{array}{l} \text{Monatomic} \\ \text{Ideal Gas} \end{array}$$

$\leftarrow$ per mole, particle, mass

$$\gamma = \frac{C_P}{C_V} = 5/3$$

Adiabatic Expansion/Compression

Rem!! Adiabatic $\rightarrow$ adiabothermal and quasistatic

Adiabatic work done by expansion so E changes but what is change in P

Step 1: Basic Relation: $\left(\frac{\partial E}{\partial V} \right)_T > 0$ (ideal gas) and $T \delta S = 0$ (adiabatic)

$$\Rightarrow 0 = C_V \delta T + P \delta V$$

$$= \frac{C_V}{Nk_B} \cdot (P \delta V + V \delta P) + P \delta V$$

$$= \frac{\gamma}{V} \delta V + \frac{1}{P} \delta P = 0$$

Integrate assuming γ is constant (good approximation)

$$\Rightarrow \gamma \ln V + \ln P = \text{constant}$$

$$PV^\gamma = \text{constant}$$

Also, $V^{\gamma-1} T = \text{const}$

$$P^{1/\gamma-1} T = \text{const}$$

Lecture 9 (9/27/23)

Probability, mean, and variance

For a random variable x

$$\text{Prob}[a \leq x \leq b] = \int_a^b P(x) dx$$

$$\int_a^b P(x) dx = 1$$

In the discrete case

$$P(x) = \sum_{i=1} P_i \delta(x - x_i)$$

Def: Expectation of "any" function

$$\mathbb{E} f = \int_{-\infty}^{\infty} f(x) p(x) dx$$

Mean of x is given by $\int_{-\infty}^{\infty} x p(x) dx$

2nd Moment: $\int x^2 P(x) dx$

Variance: $\overline{x^2} - \bar{x}^2 = (x - \bar{x})^2$

Standard Deviation $\Delta x = \sqrt{\text{Var } x}$

Sums of RV.

Def: Statistical independence

$$P(x_1, x_2) = P_1(x_1) P_2(x_2)$$

For sums of RV.

$$\bar{X} = \bar{x}_1 + \bar{x}_2$$

$$\text{Var } X = \text{var } x_1 + \text{var } x_2$$

Large N limit of binomial distribution (Central Limit Theorem)



Consider $\ln P(n)$

$$\text{Max } \ln P(n) \text{ @ } \tilde{n} \text{ for } \left. \frac{d}{dn} \ln P(n) \right|_{n=\tilde{n}} = 0$$

In our Taylor series expansion

$$\ln P(n) \approx \ln P(\tilde{n}) + B_1 \eta + \frac{1}{2} B_2 \eta^2 + \dots$$

$$B_n = \left. \frac{d^n}{dn^n} \ln P(n) \right|_{n=\tilde{n}}$$

We know that $B_2 < 0$ since $\tilde{n}$ is max

$$P(n) \approx P(\tilde{n}) e^{-\frac{1}{2} |B_2| \eta^2} + \dots$$

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

$$\frac{d}{dn} \ln n! = \ln n$$

Stirling formula

$$\frac{d}{dn} \ln P = -\ln n + \ln(N-n) = \ln p - \ln q = 0 \text{ @ } \tilde{n}$$

$$(N - \tilde{n}) p = \tilde{n} q \Rightarrow N p = \tilde{n} (p+q) = \tilde{n}$$

$$\left. \frac{d}{dn} \ln P \right|_{n=\bar{n}} = -\frac{1}{\bar{n}} - \frac{1}{N-\bar{n}}$$

$$B_L = -\frac{1}{Np} - \frac{1}{N(1-p)} = -\frac{1}{Npq}$$

Higher order terms $B_k \sim \frac{\text{constant}}{N^{k-1}}$

$$\eta \sim \sqrt{N} \rightarrow B_k \eta^k = \frac{N^{k/2}}{N^{k-1}} \rightarrow 0$$

So we can approximate

$$P(n) \simeq P(\bar{n}) e^{\frac{-(n-\bar{n})^2}{2Npq}} \quad \text{for } N \gg 1$$

↑
gaussian distribution

Important Calculus Fact

$$I = \int_{-\infty}^{\infty} e^{-1/2 x^2} dx$$

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-1/2(x^2+y^2)} dx dy$$

$r^2 = x^2 + y^2$

$$= \int r dr d\theta e^{-1/2 r^2}$$

$$= 2\pi$$

$$I = \sqrt{2\pi}$$

$$\int e^{-x^2/2\sigma^2} dx = \sqrt{2\pi\sigma^2}$$

↑ use this to normalize gaussian distribution

Another Neat Trick

$$\int x^2 e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} dx = -2 \frac{d}{d(1/\sigma^2)} \int e^{-x^2/2\sigma^2} dx = \sqrt{2\pi\sigma^2} \cdot \sigma^2$$

$$\text{Var } x = \sigma^2$$

Central Limit Theorem

$$\text{Let } y = \frac{x - N\mu}{\sqrt{N}}, \text{ then prob. distribution of } y \text{ tends to } \frac{1}{\sqrt{2\pi\sigma^2}} e^{-y^2/2\sigma^2} \leftarrow \text{Gaussian!}$$

Lecture 10 (10/21/23)

Microscopic Description

Microstates w/ coordinates q_i , canonically conjugate momenta p_i

Ex. gas of N particles in 3D w/ $3N$ coordinates and $3N$ momenta

Space of (q_i, p_i) is called the phase space

Dynamics can be understood as microstate functions

$$\dot{q}_i = \frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i} \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

$$\mathcal{H}(q, p, t) = \frac{p^2}{2m} + V(q) \leftarrow \text{One dimension}$$

Microstates are represented by wavefunctions in QM

$$\hat{q}_i = \frac{1}{i\hbar} [q_i, \mathcal{H}] \quad \hat{p}_i = \frac{1}{i\hbar} [p_i, \mathcal{H}]$$

Consider a general observable $F = F(q, p, t)$

$$\frac{\partial F}{\partial t} = \frac{d}{dt} [F(q(t), p(t), t)]$$

$$= \left(\sum_i \frac{\partial F}{\partial q_i} \dot{q}_i + \frac{\partial F}{\partial p_i} \dot{p}_i \right) + \left(\frac{\partial F}{\partial t} \right)_{q,p}$$

$$= \{F, H\} + \left(\frac{\partial F}{\partial t} \right)_{q,p}$$

↑
poisson bracket

In QM $[q_i, p_j] = i\hbar \delta_{ij}$
 $\{q_i, p_j\} = \delta_{ij}$

Can think about the probability distribution on phase space

p evolves as prob carried along by v

Then prob current is $p \times v$

Conservation of Probability,

$$\frac{\partial p}{\partial t} + \nabla \cdot j = 0$$

Classic continuity equation

Hamiltonian Equations

$$\nabla \cdot j = \nabla \cdot (pv) = v \cdot \nabla p + p \nabla \cdot v$$

expansion of velocity field

$$\nabla \cdot v = \sum_i \frac{\partial}{\partial q_i} \left[\frac{\partial}{\partial p_i} \frac{\partial H}{\partial p_i} + \frac{\partial}{\partial p_i} \left(-\frac{\partial H}{\partial q_i} \right) \right]$$

$$= 0 \quad \text{divergenceless}$$

incompressible fluid

Liouville's Theorem

$$\frac{\partial p}{\partial t} + v \cdot \nabla p = 0 \quad \longrightarrow \quad \frac{\partial p}{\partial t} + \{p, H\} = 0$$

A macrostate is a probability distribution/density matrix on microstates

If H is time independent, then the system reaches a stationary macrostate
 internal statistical equilibrium macrostate

If $p(q,p)$ is dependent on q,p only through $H(q,p)$ then $\frac{\partial p}{\partial t} = 0$

pf: $v \cdot \nabla p(H) = g^i \cdot \sum \left[\frac{\partial H}{\partial p_i} \frac{\partial p}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial p}{\partial p_i} \right] = 0$

In many simple systems,

$p = g(H(q,p))$ are only stationary macrostates

can't partition H into decoupled system

Equivalent to ergodicity of dynamics on each energy surface

Microcanonical Ensemble/Distribution

Suppose $g \propto 1$ if $E \leq H \leq E + \delta H$
 0 otherwise } Classical Case

Discrete energy levels E_k w/ discrete probabilities p_k
 $p_r \propto \begin{cases} 1 & \text{if } E \leq E_r \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}$ } Quantum Case

Choose $\delta E \ll E$, but there are many r satisfying $E \leq E_r \leq E + \delta E$

$$p = \frac{1}{\Omega(E, \delta E)} \Theta(H - E) \Theta(E + \delta E - H) \quad QM$$

$$p_r = \frac{1}{\Omega(E, \delta E)} \Theta(E_r - E) \Theta(E + \delta E - E_r) \quad QM$$

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \geq 0 \end{cases}$$

$$\Omega(E, \delta E) = \int_{E \leq H \leq E + \delta E} \pi dq dp \quad QM$$

$$= \sum_{E \leq E_r \leq E + \delta E} 1 \quad QM$$

Def: Entropy of microstate

$$S = k_B \ln \Omega$$

$\nwarrow$ arbitrary constant

δE eventually drops out

Lecture 11 (10/4/23)

Microcanonical Distribution

$$p = \frac{1}{h_o^{3N} \Omega(E, \delta E)} \Theta(H - E) \Theta(E + \delta E - H)$$

$$p_r = \frac{1}{\Omega(E, \delta E)} \Theta(E_r - E) \Theta(E + \delta E - E_r)$$

$$\Omega = \begin{cases} \int_{E \leq H \leq E + \delta E} \pi dq dp \cdot \frac{1}{h_o^{3N}} \\ \sum_{r: E \leq E_r \leq E + \delta E} 1 \end{cases}$$

$$S = k_B \ln \Omega$$

Other quantities and Basic Relation

Suppose H depends on external params $(X_a)_a$ then $S = S(E, \delta E, (X_a)_a)$

All X_a fixed

$$\text{def: } \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_Y \Leftrightarrow T = \left(\frac{\partial E}{\partial S} \right)_X$$

$$\frac{J_a}{T} = - \left(\frac{\partial S}{\partial X_a} \right)_{E, X_B (B \neq a)}$$

Equivalent

$$\delta S = \frac{1}{T} \delta E - \frac{1}{T} \sum_a J_a \delta X_a$$

$$\delta E = T \delta S + \sum_a J_a \delta X_a \quad \leftarrow \text{Basic Relation}$$

Characterizations of T as a temp, S as additive

$$\Omega(E, \delta E) = \int_{E \leq H \leq E + \delta E} \frac{\pi dq dp}{h_o^{3N}} = \omega(E) \delta E$$

$$\omega(E) = \int \frac{\pi dq dp}{h_o^{3N}} \delta(H(q, p) - E) \quad \leftarrow \text{density of states in energy}$$

$$\Leftrightarrow \Omega = \int_E^{E + \delta E} \omega(E') dE'$$

$$S = k_B \ln \omega(E) + k_B \ln \delta E$$

Consider two systems w/ Hamiltonian $H = H_1 + H_2 + H_{12}$

Set $H_{12} \rightarrow 0$

$\nwarrow$ coupling

$$\begin{aligned}
 w(E) &\approx \int \frac{\pi d_1 d_2}{h_0^2} \delta(H_1 + H_2 - E) \\
 &= \int \frac{\pi d_1^{(1)} d_2^{(1)} \pi d_1^{(2)} d_2^{(2)}}{h_0^{2N_1 + 2N_2}} \\
 &= \int dE_1 \delta(H_1 - E_1) \delta(H_2 - (E - E_1)) \\
 &= \int dE_1 w_1(E_1) w_2(E - E_1)
 \end{aligned}$$

$$w(E_1) = e^{S_1(E_1)/k_B} \quad w_2(E_2) = e^{S_2(E_2)/k_B}$$

$$w(E) = \int dE_1 e^{(S_1(E_1) + S_2(E - E_1))/k_B}$$

$$\stackrel{!}{=} e^{S(E)/k_B}$$

Approximate integral by the value at the maximum of $e^{(S_1 + S_2)/k_B}$

$$\text{Max } S_1(E_1) + S_2(E - E_1) \text{ wrt } E_1$$

$$\frac{\partial}{\partial E_1} (S_1(E_1) + S_2(E - E_1)) = 0$$

$$\left. \frac{\partial S_1(E_1)}{\partial E_1} - \frac{\partial S_2(E_2)}{\partial E_2} \right|_{E_2 = E - E_1} = 0$$

$$\Rightarrow E_{\text{max}}, \quad \frac{1}{T_1} = \frac{1}{T_2}$$

$$\begin{aligned}
 \frac{\partial^2}{\partial E_1^2} (S_1(E_1) + S_2(E - E_1)) &= \frac{\partial}{\partial E_1} \left(\frac{1}{T_1} \right) + \left(\frac{\partial}{\partial E_2} \frac{1}{T_2} \right) \\
 &= -\frac{1}{T_1^2} \left(\frac{\partial T_1}{\partial E_1} \right) - \frac{1}{T_2^2} \left(\frac{\partial T_2}{\partial E_2} \right)
 \end{aligned}$$

Heat capacities need to be positive for stability of thermal equilibrium

Taylor expansion

$$S_1(E_1) + S_2(E - E_1) = S_1(E_{\text{max}}) + S_2(E - E_{\text{max}}) + \left(\frac{1}{T_1} - \frac{1}{T_2} \right) (E - E_{\text{max}}) - \frac{1}{2T_1^2} \left(\frac{1}{C_v^{(1)}} + \frac{1}{C_v^{(2)}} \right) (E - E_{\text{max}})^2 + \text{higher order}$$

$$1) T_1 = T_2$$

$$2) S = S_1 + S_2 + \text{small correction}$$

$$w(E) = e^{(S_1(E_{\text{max}}) + S_2(E - E_{\text{max}}))/k_B}$$

$$= \underbrace{\sqrt{2\pi T_1^2 \frac{1}{C_v^{(1)} + C_v^{(2)}}}}_{\substack{\ln \\ \text{is small correction}}}$$

Classical Ideal Gas

$$H = \sum_{i=1}^N \frac{p_i^2}{m} + \underbrace{\frac{1}{2} \sum_{i,j} V(x_i - x_j)}_{\substack{\text{Interactions Term} \\ \text{ensures equilibrium but it can be dropped}}} + \sum_i V_0(x_i)$$

$$\Omega(E, SE) = \int \frac{\prod_i d^3 p_i}{h_0^{3N}} \int_{\text{Vol}} \prod_i d^3 x_i$$

$E \leq H \leq E + SE \quad \text{Vol}$

$$= \frac{V^N}{h_0^{3N}} \int \prod_i d^3 p_i$$

$E \leq H \leq E + SE$

E is a sphere of radius $\sqrt{2mE}$

Volume of unit ball in 3N dimensions

$$C_{3N} = \frac{\pi^{3N/2}}{(3N/2)!} \leftarrow \text{Fact}$$

First Order in SE

$$\Omega(E, SE) = \frac{V^N}{h_0^{3N}} C_{3N} (2mE)^{3N/2} \times \frac{3N}{2E} SE$$

So,

$$S(E, V, SE) = N k_B \ln \left(\frac{V E^{3/2} (2\pi)^{3/2}}{h^3} \right) + k_B \ln \left(\frac{C_{3N} 3N SE}{2E} \right)$$

Lecture 12 (10/11/23)

$$S(E, V, SE) = N k_B \ln \left(\frac{V E^{3/2} (2\pi)^{3/2}}{h^3} \right) + k_B \ln \left(\frac{C_{3N} 3N SE}{2E} \right)$$

$$C_{3N} = \frac{\pi^{3N/2}}{(3N/2)!}$$

$$\ln C_{3N} = \frac{3N}{2} \ln \pi - \ln \left(\frac{3N}{2} \right)!$$

$$\ln n! = n \ln n - n$$

$$S(E, V) = N k_B \ln \left(\left[\frac{V}{N} \left(\frac{E}{N} \right)^{3/2} \right] \right) + \text{weakly } N, E \text{ - dependent terms}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V = \frac{3}{2} \frac{N k_B}{E}$$

$$E = \frac{3}{2} N k_B T \quad \leftarrow \text{Internal Energy}$$

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

$$PV = N k_B T$$

Entropy

$$S = N k_B \ln V + \frac{3}{2} N k_B \ln \frac{E}{N} + E, V \text{ independent terms}$$

$\frac{3}{2} k_B T$

Approach to Equilibrium

Consider Classical Mechanics

Initial density ρ in phase space (not microcanonical)

phase space



$$\rho = \begin{cases} \text{constant in region} \\ 0 \text{ otherwise} \end{cases}$$

$$\text{Liouville's Theorem: } \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = 0$$

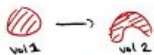
$$\nabla \cdot \mathbf{v} = 0$$

$\mathbf{v}$ is the set of time derivatives of p.q.

$$\mathbf{v} = (\dot{q}_1, \dot{q}_2, \dots, \dot{q}_{3N}, \dot{p}_1, \dots, \dot{p}_{3N})$$

$$\nabla = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial p_{3N}} \right)$$

Volume is preserved but the shape can change



If $S = k_B \ln \Omega$ then S is constant

We can deform ρ to ρ^* in the sense of weak* convergence

$$\int \prod_{i=1}^{3N} dq_i dp_i f(q_i, p_i) \rho \rightarrow \int \prod_{i=1}^{3N} dq_i dp_i f(q_i, p_i) \rho^*$$

Some continuous bounded function f

Then if ρ^* is uniform

$$S[\rho^*] > S[\rho_0]$$

unchanged for any finite time but increases in the limit

For many sys, balance mixing holds (approach stationary distribution)

Pro's Relating a Constant

Assume microcanonical model

Release: $\Omega_E > \Omega_L$

$$S_E > S_L$$

Processes

Suppose $X = \mathcal{H}(q, p, X)$

There are energy surfaces for each X

Consider $X_n = X_n(t)$ (independent of q, p)

$$\sum_{i=1}^n \mathcal{H}(q_i, p_i, X_i(t))$$

now $\mathcal{H}$ is not conserved

$$\left(\frac{\partial H}{\partial X_a}\right)_{q,p,X_B}$$

Suppose that the process occurs slowly

$$I \text{ from } X_a \rightarrow X_a + \delta X_a$$

System will travel around energy surface many times in time I

Change in energy E

$$\frac{\delta X_a}{I} \int_0^I \frac{\partial H}{\partial X_a} (q(t), p(t), X) dt$$

$H(X(t=0))$

$q(0), p(0)$ are given

$$\lim_{I \rightarrow 0} \frac{1}{I} \int_0^I \frac{\partial H}{\partial X_a} (q(t), p(t), X) dt = \overline{\frac{\partial H}{\partial X_a} (q, p, X)}$$

distribution average

Energy surfaces for X change to energy surfaces for $X + \delta X$

Lecture 13 (10/11/23)

Processes



Take $\delta E \rightarrow 0$ limit

$$P_E(q, p) = \frac{\delta (H(q, p) - E)}{\int_{H=E} \delta H}$$

larger when ∇H is smaller

$$\delta(f(x)) = \frac{\delta(x-x_0)}{|f'(x_0)|}$$

Given Liouville dynamics, we can say that a stationary distribution P_E is ergodic $\Leftrightarrow$ for any function of (q, p) time average = P_E average on energy surface E

initial point drawn from E

Birkhoff - Ergodic Theorem (1931) gives the equivalence

Let $X = X(t)$ Assume P_E is ergodic

Idea: $X(t)$ varies slowly so the system traverses the energy surface many times in the time it takes $X \rightarrow X + \delta X$

Change in H

$$\frac{dH}{dt} = \left(\frac{\partial H}{\partial t}\right)_{q,p}$$

by Liouville

$$\frac{\delta X_a}{I} \int_0^I \left(\frac{\partial H}{\partial X_a}\right) (q(t), p(t), X) dt$$

Ergodic Thm

$$\lim_{I \rightarrow \infty} \frac{1}{I} \int_0^I \frac{\partial H}{\partial X_a} (q(t), p(t), X) dt = \frac{\partial H}{\partial X_a} (q, p, X) \text{ w/ prob 1}$$

Independent of initial values

Adiabatic Theorem of Classical Mechanics

δE same for all points on the surface
each energy surface evolves to an energy surface

$$\delta E = \frac{\partial H}{\partial X_a} \delta X_a$$

No folding or mixing (Adiabatic guarantees no folding/mixing)

$\Rightarrow$ Phase space volume enclosed by energy surface doesn't change

so S is unchanged

Entropy doesn't change in adiabatic process

$$T_a = \left(\frac{\partial E}{\partial X_a}\right)_{q, X_B} = \overline{\left(\frac{\partial H}{\partial X_a}\right)_{q, p, X}} \leftarrow \text{microcanonical}$$

$$\delta W = \sum J_n dX_n$$

QM Adiabatic Theorem

$$\psi_{r,n}(t) \rightarrow \psi_{r,n} e^{i\phi} \quad \leftarrow \text{phase factor}$$

$\Rightarrow$ earlier result

$$J_n = \left(\frac{dE}{dX_n} \right)_{r,n} = \frac{\partial E_r}{\partial X_n} = \frac{dW}{dX_n}$$

Quasistatic Processes

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

$$= T dS + \sum_n J_n dX_n$$

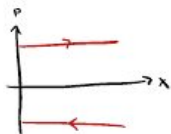
$$\text{so } \delta W = \sum_n J_n dX_n$$

$$\delta Q = T dS \quad \leftarrow \text{Carnot's Theorem}$$

Classical Adiabatic Process



Phase Space



Entropy

Suppose you have a prob. density in phase space
Partition the prob. density into cells of volume $(\epsilon h)^{3N}$

$$\text{Probabilities } p_r = \int_{\text{cell}} \pi dq dp \quad \text{for cell in } r$$

$$= \sum_r p_r = 1$$

Draw M samples from discrete distribution

If M is large, n_r , number of times got r

$$n_r \approx M p_r$$

seq of M cells $(r_1, \dots, r_M)$

$$\sum n_r = M$$

seqs with that set $n_1, n_2, \dots$

$$W = \frac{M!}{\prod_r n_r!} \quad \leftarrow \text{multinomial coefficient}$$

$$\ln W = M \log M - \sum_r [M p_r \ln M p_r - M p_r] \quad (\ln M + \ln p_r)$$

$$= M \left(- \sum_r p_r \ln p_r \right)$$

$$S[\{p_r\}]/k_B = - \sum_r p_r \ln p_r$$

$$\text{Classical: } - \sum_r (\epsilon h)^{3N} p(r, p) \ln [(\epsilon h)^{3N} p(r, p)]$$

$$\approx \int \frac{3N}{\pi} dq dp \cdot p(r, p) \ln [h^{3N} p(r, p)]$$

$$- 3N \ln \epsilon \quad \int \pi dq dp p = 1$$

$$- \ln \epsilon \rightarrow \infty \quad \text{as } \epsilon \rightarrow 0$$

throw away state independent constants

$$S[\{p_r\}]/k_B = \begin{cases} - \sum_r p_r \ln p_r & \text{discrete} \\ - \int \frac{3N}{\pi} dq dp p \ln p & \text{continuous} \end{cases}$$

Gibbs Entropy - Gibbs entropy

$$\frac{S[p_r \text{ or } p]}{k_B} = \begin{cases} -\sum_r p_r \ln p_r \geq 0 & (\text{each } \ln p_r \leq 0) \\ -\int \pi d\mathbf{q} d\mathbf{p} p \ln [h^{2N} p] \end{cases}$$

Also used in information theory

Some special cases

$$1) p_r = \begin{cases} \frac{1}{\Omega} & r \text{ in set} \\ 0 & \text{otherwise} \end{cases}$$

$$\frac{S}{k_B} = - \int_{\text{among shell}} \pi d\mathbf{q} d\mathbf{p} \frac{1}{h^{2N} \Omega} \ln \frac{1}{h^{2N} \Omega} = \ln \Omega$$

Entropy gives lower bound on information storage

$$\text{max } \frac{S}{k_B} \text{ is } p_r = \frac{1}{N_0} \text{ and } \frac{S}{k_B} = \ln N_0$$

Back to Stat Mech

$$\text{Liouville's theorem} \rightarrow \frac{\partial S}{\partial t} = 0$$

pf: For any function $f(x)$, x real

$$\begin{aligned} \frac{\partial}{\partial t} f(p(\mathbf{q}, \mathbf{p})) &= \left. \frac{\partial f}{\partial x} \right|_{x=p} \left(\frac{\partial p}{\partial t} \right) && \text{Chain Rule} \\ &= - \left. \frac{df}{dx} \right|_{x=p} \mathbf{v} \cdot \nabla p \\ &= - \mathbf{v} \cdot \nabla f(p) \\ &= - \nabla \cdot (\mathbf{v} f(p)) \\ &&& \nabla \cdot \mathbf{v} = 0 \end{aligned}$$

Let $f = -x \ln x$

$$f(x) = \lim_{x \rightarrow 0} f(x) = 0$$

$$\begin{aligned} \frac{d}{dt} \left(S(p)/k_B \right) &= \int \pi d\mathbf{q} d\mathbf{p} \frac{d}{dt} (-p \ln p) \\ &= - \int \pi d\mathbf{q} d\mathbf{p} \nabla \cdot (\mathbf{v} (-p \ln p)) \\ &&& \text{Apply Green's theorem} \\ &= - \int d^{2N-1} a \cdot \mathbf{v} (-p \ln p) \\ &= \text{flux of } -p \ln p \text{ through surface at } \infty \end{aligned}$$

Flux should be 0

$$\Rightarrow \frac{dS}{dt} = 0$$

Gibbs Mixing Phenomena

Thm: S/k_B is "upper semicontinuous" wrt weak star convergence

If $p_k \rightarrow p^*$ in weak*, then

$$\lim_{k \rightarrow \infty} S[p_k]/k_B \leq S[p^*]/k_B$$

assuming the limit exists

Does equilibration take an infinite amount of time?

In practice,

- 1) may be interested in limit of P/L
- 2) Systems are usually homogeneous

Apply CLT

- 3) Traditional approximations (Boltzmann's H theorem or master eq) have entropy increase in time & p tends to max S

Thermal Interaction of two isolated systems

$$E = E_1 + E_2$$

$$\Omega(E) = \int dE_1 \omega_1(E_1) \omega_2(E-E_1)$$

$$e^{S(E)/k_B} = \int dE_1 e^{(S(E_1) + S_2(E-E_1))/k_B}$$

neglecting in SE in exponent

$$\max_{E_1} S_1(E_1) + S_2(E-E_1) \text{ at } E \text{ fixed} \iff T_1(E_{\max}) = T_2(E-E_{\max})$$

Taylor Expand $\hookrightarrow$

$$S_1 + S_2 = (S_1 + S_2)|_{E_{\max}} - \frac{1}{2T_1^2} \left(\frac{1}{C_1^{(1)}} + \frac{1}{C_2^{(1)}} \right) (E_1 - E_{\max})^2 + \text{higher order}$$

Prob dist of E_1 in microcanonical

$$P_1(E_1) \delta E_1 = \frac{\# \text{ states w/ } E_1 \text{ in range } E_1 \text{ to } E_1 + \delta E_1}{\text{Total \# of states } \Omega(E)}$$

$$= \frac{\omega_1(E_1) \omega_2(E-E_1) \delta E_1}{\Omega(E)} \quad \delta E \text{ cancelled}$$

$$\approx \frac{e^{-\frac{1}{2} \lambda (E_1 - E_{\max})^2}}{\int dE_1 e^{-\frac{1}{2} \lambda (E_1 - E_{\max})^2}}$$

$$\lambda = \frac{1}{k_B T_1^2} \left(\frac{1}{C_1^{(1)}} + \frac{1}{C_2^{(1)}} \right)$$

$$\Rightarrow \bar{E}_1 = E_{\max}$$

$$\text{Var } E_1 = (\overline{E_1^2} - \bar{E}_1^2) = \frac{1}{\lambda} = k_B T^2 \left(\frac{1}{C_1^{(1)}} + \frac{1}{C_2^{(1)}} \right)^{-1}$$

Let size of sys 2 $\rightarrow \infty$ (heat reservoir)

$$C_2^{(1)} \rightarrow \infty$$

$$\overline{\Delta E_1^2} = k_B T^2 C_1^{(1)}$$

$$\sim \sqrt{\text{system size}}$$

$$\frac{\overline{\Delta E_1^2}}{\bar{E}_1} \approx \frac{1}{\sqrt{\text{sys. size}}}$$

In microcanonical E_1 is fixed between $E_1 \pm \delta E_1$ w $\overline{\Delta E_1^2} \ll \bar{E}_1^2$

Pressure Reservoir



$$\text{Total Energy} = E + P_0 A X$$

Claim: height of mass will be max entropy with X in a given E_{tot}

Entropy Maximum Principle

Value of unconstrained macro parameter in isolated sys is st. S is maximized at fixed Energy and external parameters

Probabilistic Argument

$$\Omega(E_{\text{tot}}) = \int \frac{dX dP_0}{h_0} e^{(S(E_{\text{tot}} - P_0 A X, V))/k_B}$$

Neglect KE of mass

$$P_1(X) dX = \frac{e^{(S(E_{\text{tot}} - P_0 A X, V))/k_B}}{\Omega(E_{\text{tot}})} dX$$

Find maximum $S(E_{\text{tot}} - P_0 A X, V)$ at fixed E_{tot}

$$\left(\frac{\partial S}{\partial X} \right)_{E_{\text{tot}}} = 0 \text{ at equilibrium}$$

$$\left(\frac{\partial S}{\partial X} \right)_{E_{\text{tot}}} = \left(\frac{\partial S}{\partial X} \right)_E + \left(\frac{\partial S}{\partial E} \right)_V \left(\frac{\partial E}{\partial X} \right)_{E_{\text{tot}}}$$

$$= \frac{P}{T} - \frac{P_0}{T} = 0 \Rightarrow P = P_0$$

determines X_{max} and V_{max}

$$P_V(V) = \frac{e^{-\frac{1}{2} \left(\frac{\partial^2 S}{\partial V^2} \right)_{E_{\text{int}}} (V - \bar{V})^2}}{\int dV e^{-\frac{1}{2} \left(\frac{\partial^2 S}{\partial V^2} \right)_{E_{\text{int}}} (V - \bar{V})^2}}$$

Requires $\left(\frac{\partial^2 S}{\partial V^2} \right)_{E_{\text{int}}} \Big|_{E_{\text{int}}}$ has to be negative for stability

$$\Rightarrow \overline{\Delta V^2} = -\frac{1}{\left(\frac{\partial^2 S}{\partial V^2} \right)_{E_{\text{int}}}}$$

General Probabilistic Argument

Consider any continuous function of microstate

$$P(y) \propto \frac{\Omega(E, y)}{\Omega(E)}$$

$\Omega(E, y) \propto E = \# \text{ states/phase space volume at } y \in [y_1, y_1 + \delta y_1] \text{ and } E \in [E, E + \delta E]$

Homogeneous Systems (Intensive + Extensive Quantities) (Ref 4.7)

Some sys. are homogeneous

Energy and Entropy are additive

Formally, for a fluid if N, V, S are increased by λ , then $E(\lambda N, \lambda V, \lambda S) = \lambda E(N, V, S)$

for homogeneous systems

Def: Any state function that obeys $\gamma(\lambda N, \lambda V, \lambda S) = \lambda \gamma(N, V, S)$ is called extensive

Any state function is intensive if $\gamma(\lambda N, \lambda V, \lambda S) = \gamma(N, V, S)$

Any ratio of extensive quantities

Basic Relation

$$dE = T dS - P dV + \mu dN \quad \text{View } N \text{ as external parameter}$$

$\mu = \left(\frac{\partial E}{\partial N} \right)_{S, V}$ Chemical potential

Take $\frac{d}{d\lambda}$, set $\lambda = 1$

$$E = \left(\frac{\partial E}{\partial N} \right)_{V, S} N + \left(\frac{\partial E}{\partial V} \right)_{N, S} V + \left(\frac{\partial E}{\partial S} \right)_{N, V} S$$

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

Euler Relation

Take dE subtract Basic Relation

$$\Rightarrow -S dT + V dP - N d\mu = 0$$

Gibbs-Duhem relation

Lecture 17 (11/123)

Legendre Transformations

$$dE = TdS - PdV \leftarrow \text{is fixed}$$

$$F = E - TS$$

$$dF = dE - TdS - SdT$$

$$= TdS - PdV$$

$$= -SdT - PdV$$

$$dF = -SdT + \sum_i J_i dX_i$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \text{ or } -\left(\frac{\partial F}{\partial T}\right)_{X_i}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \text{ or } J_i = \left(\frac{\partial F}{\partial X_i}\right)_T, X_j$$

$$E = E(S, V)$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V$$

$$\Rightarrow F = E - TS \leftarrow \text{Legendre Transform}$$

$$\text{Entropy: } dH = TdS + VdP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P, V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$\text{Gibbs Free Energy: } dG = -SdT + VdP$$

$$\Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P, V = \left(\frac{\partial G}{\partial P}\right)_T$$

Maxwell Relations

$$dE = TdS - PdV$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V, P = -\left(\frac{\partial E}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

For other Legendre transforms

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \text{ (from } dF)$$

$$\left(\frac{\partial S}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \text{ (from } dH)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \text{ (from } dG)$$

Some applications

1) Heat Capacity at constant volume

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Constant pressure

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P \neq \left(\frac{\partial E}{\partial T}\right)_P$$

$$= \left(\frac{\partial H}{\partial T}\right)_P \leftarrow \text{Enthalpy}$$

2) Consider T, P independent

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

Substitute dP

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$TdS = \left[C_P + T \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \right] dT + T \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\Rightarrow T \left(\frac{\partial S}{\partial T}\right)_V = C_V = C_P + T \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

Apply the Maxwell relation

$$\text{Def: } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \text{ is the thermal expansion coefficient}$$

(intensive)

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -V \alpha$$

Also

$$\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$\text{Def: } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \text{ is the isothermal compressibility}$$

$\kappa_T > 0$

$$C_P - C_V = \frac{VT\alpha^2}{\kappa_T} \geq 0$$

Note on heat, work w/ reservoirs

$$\text{Temp Res: } -P = \left(\frac{\partial E}{\partial V}\right)_{T,W} \text{ (fixed)}$$

QS process w/ no heat

$$dW = -PdV$$

$$dE = dW + dQ = dW + TdS$$

A.S.

$$\begin{aligned} \delta W &= \delta E - T \delta S \\ &= \delta(E - TS) \\ &= \delta F \leftarrow \text{Fixed } T \end{aligned}$$

If not q.s.
 $-\delta W \leq -\delta F$ max work done by system

Heat flow into Sys at fixed T , X_n

then $\delta F = 0$ (not necessarily q.s.)
 energy + entropy goes to reservoir

Prob Distributions

Microcanonical: $P(\gamma) = \frac{\Omega(E, \gamma)}{\Omega(E)}$

Extend to Reservoir

$y = y(q, p)$ and all X_n fixed

$$P(\gamma) = \frac{\int dE \omega(E, \gamma) w(E_{\text{tot}} - E)}{\int dy \int dE \omega(E, \gamma) w(E_{\text{tot}} - E)}$$

$$\frac{S_{\text{tot}}}{k_B} = \ln(w_{\text{tot}} \Omega E)$$

Lecture 18 (11/6/25)

System in contact w/ heat reservoir

As a function of E for fixed E_{tot}

$$w_{\text{tot}}(E_{\text{tot}} - E) \propto e^{-\beta E} \quad \beta = \frac{1}{k_B T}$$

$$P(\gamma) = \frac{\int dE \omega(E, \gamma) e^{-\beta E}}{\int dE \int dy \omega(E, \gamma) e^{-\beta E}}$$

If E integral is strongly peaked for a given γ , we can replace integral value by max

$$P(\gamma) \approx \frac{e^{-\beta F(\gamma)}}{\int dy e^{-\beta F(y)}}$$

where for all γ ,

$$F(\gamma) = \min_E (E - TS(E, \gamma))$$

$$S(E, \gamma) = k_B \ln(\omega(E, \gamma) \Omega E)$$

If γ macroscopic, $P(\gamma)$ sharply peaked

$$\gamma_{\text{max}} = \arg \min_{\gamma} F(\gamma)$$

$$= \gamma \text{ s.t. } F(\gamma) \text{ is min at } \gamma$$

Free Energy min principle recovered from probabilistic argument

$$w(E, \gamma) = \int \frac{\pi dq dp}{h_0^{2N}} \delta(E - \mathcal{H}(q, p)) \delta(\gamma - y(q, p))$$

Analogous for quantum case

Plug the above expression into $P(\gamma)$ expression to recover canonical distribution

Canonical Distributions

Can replace $y \rightarrow \underline{y}$

$\leftarrow$ vector function of $\underline{q}, \underline{p}$

$$\underline{y} = (q, p)$$

$$\text{Then } p(\underline{q}, \underline{p}) = \frac{e^{-\beta \mathcal{H}(\underline{q}, \underline{p})}}{h_0^{2N} Z}$$

$$Z = \int \frac{\pi d\underline{q} d\underline{p}}{h_0^{2N}} e^{-\beta \mathcal{H}(\underline{q}, \underline{p})} \quad (CM)$$

$$= \sum_r e^{-\beta E_r} \quad (QM)$$

Partition Function

Helmholtz Free Energy

$$Z = e^{-\beta F}$$

$$\beta = \frac{1}{k_B T}$$

$$F = -k_B T \ln Z$$

$$F = F(X_\alpha, T)$$

$$dF = \left(\frac{\partial F}{\partial T} \right)_{X_\alpha} dT + \sum_\alpha \left(\frac{\partial F}{\partial X_\alpha} \right)_{T, X_{\alpha'}} dX_\alpha$$

$$= -S dT + \sum_\alpha J_\alpha dX_\alpha$$

From before,

$$S = - \left(\frac{\partial F}{\partial T} \right)_{X_\alpha}, \quad J_\alpha = \left(\frac{\partial F}{\partial X_\alpha} \right)_{T, X_{\alpha'}}$$

Then define

$$E = F + TS$$

$$dE = T dS + \sum_\alpha J_\alpha dX_\alpha$$

$$J_\alpha = -k_B T \left(\frac{\partial}{\partial X_\alpha} \ln Z \right) = -k_B T \sum_r \left(\frac{1}{k_B T} \left(\frac{\partial E_r}{\partial X_\alpha} \right)_{X_{\alpha'}} \right) \frac{e^{-\beta E_r}}{Z}$$

$$= \sum_r \left(\frac{\partial E_r}{\partial X_\alpha} \right)_{X_{\alpha'}} p_r = \left(\frac{\partial E}{\partial X_\alpha} \right)_{X_{\alpha'}}$$

$$S = - \left(\frac{\partial}{\partial T} (-k_B T \ln Z) \right)_{X_\alpha}$$

$$= k_B \ln Z + k_B T \sum_r \frac{(-E_r) e^{-\beta E_r}}{Z} \left(-\frac{1}{k_B T^2} \right)$$

$$= \frac{-F}{T} + \sum_r \frac{E_r p_r}{T}$$

$$= \frac{-F + \bar{E}}{T} \quad \bar{E} = \sum_r E_r p_r$$

Internal Energy is expected value of microscopic energy

$$S = k_B \ln Z + k_B \sum_r p_r (-\ln e^{-\beta E_r})$$

$$= -k_B \sum_r p_r \ln p_r \quad (QM)$$

Boltzmann-Gibbs-Shannon Entropy

$$S = -k_B \int \pi d\mathbf{q} d\mathbf{p} \rho(\mathbf{q}, \mathbf{p}) \ln(h^3 \rho) \quad (CM)$$

For two independent systems 1,2

$$p_{12} = p_1 p_2$$

$$\ln(p_{12}) = \ln(p_1) + \ln(p_2) \Rightarrow S_{12} = S_1 + S_2$$

Fluctuations

$$\left(\frac{\partial}{\partial \beta} \ln Z \right)_{X_\alpha} = - \sum_r E_r \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\bar{E}$$

$$-\frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} = \sum_r E_r e^{-\beta E_r}$$

$$\left(-\frac{\partial}{\partial \beta} \right)^2 \sum_r e^{-\beta E_r} = \sum_r E_r^2 e^{-\beta E_r}$$

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} - \left(\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \right)^2$$

$$= \overline{\Delta E^2} = \text{Var } E$$

$$\begin{aligned}\frac{\partial}{\partial \beta} \ln Z &= \frac{\partial}{\partial \beta} (-\beta F) \\ &= -k_B T^2 \frac{d}{dT} \left(\frac{-F}{k_B T} \right) \\ &= -F - TS = -E\end{aligned}$$

$$\begin{aligned}\frac{\partial^2}{\partial \beta^2} \ln Z &= -\frac{\partial \bar{E}}{\partial \beta} = k_B T^2 \frac{\partial \bar{E}}{\partial T} \\ &= k_B T^2 C_V \\ &= \Delta E^2\end{aligned}$$

$$\Rightarrow \overline{\Delta E^2} = k_B T^2 C_V$$

Canonical and microcanonical distributions agree in the limit for thermodynamic properties, but disagree in fluctuations

Griffin Connection

$$Z' = \frac{Z}{N!} \quad \text{classical particles}$$

$$= \frac{1}{N!} \int \frac{\pi d\mathbf{q} d\mathbf{p}}{h^{3N}} e^{-\beta \mathcal{H}}$$

$$= e^{-\beta F'}$$

$$dF' = -S dT + \sum_{\alpha} J_{\alpha} dX_{\alpha} + \mu dN$$

$$\mu = \left(\frac{\partial F'}{\partial N} \right)_{T, X_{\alpha}}$$

In the non-interacting (ideal) gas

$$Z'_N = \frac{Z_1^N}{N!}$$

Equipartition Theorem

$$\text{if } Z = \int dx e^{-\frac{1}{2} \alpha x^2}$$

$$\text{then } \bar{E} = \overline{\frac{1}{2} \alpha x^2} = \frac{1}{2} k_B T$$

$$-\frac{\partial}{\partial \beta} \ln Z$$

$$F = -k_B T \ln \left(\frac{2\pi k_B T}{h \omega} \right)$$

$$S = \frac{\bar{E} - F}{T} = k_B \left(1 + \ln \frac{2\pi k_B T}{h \omega} \right) \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Simple Harmonic Oscillator}$$

Consider the Hamiltonian

$$\mathcal{H} = \frac{1}{2} \sum_{i=1}^N a_i p_i^2 + \frac{1}{2} \sum_{j=1}^N b_j q_j^2$$

mean of each term is $\frac{1}{2} k_B T$

Classical Ideal Gas

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad E = \bar{E} = \frac{3}{2} N k_B T$$

No contribution from q variables

Classical Solid

Ball + springs

$$3N q, 3N p$$

Use normal modes to find $3N$ Simple Harmonic Oscillators

$$\left. \begin{array}{l} E = 3N k_B T \\ C_v = 3N k_B \end{array} \right\} \text{Dulong-Petit Law}$$

Real solids agree at high temperatures $300 < T < 500 \text{ K}$
(insulators)

Classical Ideal Gas in Canonical Distribution

$$Z_N = \frac{V^N (2\pi k_B T)^{\frac{3N}{2}}}{h^{3N}} = Z_1^N \quad \leftarrow \text{No Gibbs correction}$$

$$\Rightarrow F = -N k_B T \ln \left(\frac{V (2\pi m k_B T)^{\frac{3}{2}}}{h^3} \right)$$

$$\Rightarrow P = \left(-\frac{\partial F}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \quad \text{ideal gas law!}$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = N k_B \ln \frac{V (2\pi m k_B T)^{\frac{3}{2}}}{h^3} + \frac{3}{2} N k_B$$

$$= N k_B \left[\ln V + \frac{3}{2} \ln T + \sigma \right]$$

$$\sigma = \frac{3}{2} \ln \frac{2\pi m k_B}{h^3} + \frac{3}{2}$$

$$\bar{E} = F + TS = \frac{3}{2} N k_B T$$

Chemical Potential:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \ln \left(V \left(\frac{2\pi m k_B T}{h^3} \right)^{\frac{3}{2}} \right)$$

Gibbs Correction

$$Z'_N = \frac{Z_N}{N!}, \quad F' = F + k_B T (N \ln N - N)$$

$$\mu' = -k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^3} \right)^{\frac{3}{2}} \right]$$

$$S' = N k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma' \right]$$

$$\sigma' = \sigma + 1$$

Kinetic Theory of Gases

$$\text{Canonical Distribution: } p(x,p) = e^{-\beta \mathcal{H}_1(x,p)} + \beta F \quad \leftarrow \text{No Gibbs correction}$$

$$\text{For any } i, \quad p(x_i, p_i) = \frac{e^{-\beta \mathcal{H}_1(x_i, p_i)}}{(2\pi m k_B T)^{3/2} V}$$

$$P_p(p) = \frac{e^{-\beta p^2/2m}}{(2\pi m k_B T)^{1/2}} V$$

For velocity $v_i = \frac{p_i}{m}$

$$P_v(v_i) = e^{-\frac{1}{2} \beta m v_i^2} \left(\frac{m}{2\pi k_B T} \right)^{3/2} \quad \left. \vphantom{P_v(v_i)} \right\} \text{Maxwell probability distribution of velocities}$$

Distribution of Speeds

$$P_v(v_i) = \int d\Omega_v v^4 P_v(v_i) = 4\pi v^4 e^{-\frac{1}{2} \beta m v^2} \times \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

↑
solid angle integrated

Pressure



If they all have the same velocity

$\bar{n} v_x$ hit unit area in unit time

↑
avg. density

Impulse on wall is $2m v_x$, so pressure = impulse $\times$ flux

$$P = 2m v_x \cdot \bar{n} v_x$$

Accounting for distribution of velocities

$$P = \bar{n} \int d^3v P_v(v) 2m v_x^2$$

$$= \frac{4}{2} \bar{n} \int d^3v P_v(v) \frac{1}{2} m v_x^2$$

$$= 2\bar{n} \cdot \frac{1}{2} k_B T \quad \leftarrow \text{Equipartition Theorem}$$

$$= \bar{n} k_B T$$

Finite # of quantum or discrete energy levels

$$m = -J, \dots, J \quad (2J+1 \text{ values})$$

$$J = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

Consider $J = \frac{1}{2}$

In magnetic field H

$$\mathcal{H} = -g\mu_B H_m = E_m$$

← Bohr magneton

$$\text{Set } g\mu_B = 1$$

$$Z = e^{-\frac{1}{2} H/k_B T} + e^{\frac{1}{2} H/k_B T}$$

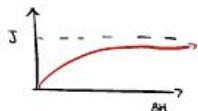
$$= 2 \cosh \frac{H}{2k_B T}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -H \bar{x}$$

$$\bar{x} = \frac{1}{2} \tanh \frac{BH}{2} \quad -\frac{1}{2} \leq \bar{x} \leq \frac{1}{2}$$

Expected number w. $m = \frac{1}{2}$

$$= \frac{e^{BH}}{1 + e^{BH}} = \frac{1}{1 + e^{-BH}} \quad \leftarrow \text{Fermi distribution function}$$



$$\bar{E} = \frac{H}{2} \tanh \frac{BH}{2}$$

$$\text{As } T \rightarrow 0, B \rightarrow \infty$$

$$\tanh \rightarrow 1$$

$$\bar{E} = H/2$$

$$\text{As } T \rightarrow \infty, B \rightarrow 0$$

$$\text{prob} \rightarrow 1/2$$

$$\bar{E} = 0$$

Infinitely many quantum energy levels

$$E_n = (n + \frac{1}{2}) \hbar \omega$$

$$Z = e^{-\frac{1}{2} \beta \hbar \omega} + e^{-\frac{3}{2} \beta \hbar \omega} + \dots$$

$$= \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad \leftarrow \text{quantum simple harmonic oscillator}$$

Diverges as $\beta \hbar \omega \rightarrow 0$ ($T \rightarrow \infty$)

$$F = \frac{1}{2} \hbar \omega + k_B T \ln(1 - e^{-\beta \hbar \omega})$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{2} \hbar \omega - \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$= \left(\bar{n} + \frac{1}{2}\right) \hbar \omega$$

$$\bar{n} = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Bose-Einstein Distribution

$$\bar{n} \rightarrow \infty \text{ as } T \rightarrow \infty$$

$$1) \text{ As } T \rightarrow 0, \bar{E} = \frac{1}{2} \hbar \omega [1 + 2e^{-\beta \hbar \omega} + \dots]$$

↑
exponentially small

$$2) \text{ As } T \rightarrow \infty,$$

$$\bar{E}_{osc} \sim \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\beta \hbar \omega + \frac{1}{2}(\beta \hbar \omega)^2 + \dots}$$

$$= \frac{1}{2} \hbar \omega + k_B T \left(1 - \frac{1}{2} \beta \hbar \omega + \dots\right)$$

$$= k_B T$$

← equipartition result

Correspondence Principle

Lecture (11/15/23)

Q1. Simple Harmonic Oscillator

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

$$\bar{E}_{osc} = \frac{1}{2} \hbar \omega + \hbar \omega \bar{n}$$

$$\bar{n} = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Einstein model of a solid (Ref 7.7)

$3N$ q.v. SHO with equal ω

$$C_v = 3N \frac{\partial \bar{E}_{osc}}{\partial T}$$

$$\frac{C_v}{3N} = -\frac{1}{k_B T^2} \left(\frac{\partial \bar{E}_{osc}}{\partial \beta} \right)$$

$$= k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

Resonance Dulong-Petit law

Polyatomic Molecules

$$\bar{E} = \frac{3}{2} N k_B T + N \epsilon(T)$$

↑
translational motion

↑
internal

→ constant as $T \rightarrow 0$

Application to Field Theories (Ref 9.13-9.15)

Maxwell's equations → wave equation

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} = c^2 \nabla^2 \mathbf{E}$$

Some solutions are $\mathbf{E} \sim \hat{\mathbf{e}} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$

$$\omega = \omega_{\mathbf{k}} = c|\mathbf{k}| = ck > 0$$

and $\nabla \cdot \mathbf{E} = 0$ implies $\mathbf{k} \cdot \hat{\mathbf{e}} = 0 \Rightarrow$ two linearly indep. possibilities of $\hat{\mathbf{e}}$ for each $\mathbf{k}$

Each mode $\mathbf{k}, \hat{\mathbf{e}}$ is an oscillator w/ freq. $\omega_{\mathbf{k}}$

$$\text{energy density} \propto \frac{1}{2} (\dot{\mathbf{E}}^2 + \mathbf{B}^2)$$

Periodic Boundary Conditions

$$\mathbf{E}(\mathbf{r} + L_x \hat{\mathbf{x}}) = \mathbf{E}(\mathbf{r} + L_y \hat{\mathbf{y}}) = \mathbf{E}(\mathbf{r} + L_z \hat{\mathbf{z}}) = \mathbf{E}(\mathbf{r})$$

$$\text{Impose } \mathbf{k} = 2\pi \left(\frac{m_x}{L_x}, \frac{m_y}{L_y}, \frac{m_z}{L_z} \right) \quad m_x, m_y, m_z = \text{integers}$$

Each allowed $\mathbf{k}, \hat{\mathbf{e}}$ have one SHO

Discrete microstates: $(n_{k,z} = 0, 1, 2, \dots)_{k,z}$

$$E_{k,z} = \sum_{k,z} (n_{k,z} + \frac{1}{2}) \hbar \omega_k$$

↑
zero-point energy

subtract off infinite contribution from zero-point energy

Statistical Mechanics

Equipartition

$$\bar{E} = \sum_{k,z} k_B T = \infty$$

Ultraviolet catastrophe!

Energy density

$$\sum_k \approx V \int \frac{d^3k}{(2\pi)^3}$$

$$\Rightarrow \frac{\bar{E}}{V} \rightarrow 2 \int \frac{d^3k}{(2\pi)^3} k_B T = \infty$$

In Quantum Mechanics

$$\bar{n}_{k,z} = \frac{1}{e^{\beta \hbar \omega_k} - 1} \rightarrow \begin{cases} 0 & \hbar \omega_k \gg k_B T \\ \frac{k_B T}{\hbar \omega_k} & \hbar \omega_k \ll k_B T \end{cases}$$

Energy per unit volume as $V \rightarrow \infty$ is $(n_{k,z} + \frac{1}{2}) \hbar \omega_k$

Thermal Avg.

$$\frac{2 \hbar \omega_k}{e^{\beta \hbar \omega_k} - 1} \cdot \frac{d^3k}{(2\pi)^3}$$

$$d^3k = 4\pi k^2 dk$$

$$\bar{u}(\omega, T) = \frac{1}{\pi^2 c^3} \frac{\hbar \omega d\omega}{e^{\beta \hbar \omega} - 1}$$

UV cutoff $\Rightarrow \hbar \omega \sim k_B T$

Scaling:

$$\text{def } \eta = \beta \hbar \omega$$

$$\bar{u}(\omega, T) = \frac{(k_B T)^4}{\pi^2 c^3 \hbar^3} \frac{\eta^3 d\eta}{e^\eta - 1}$$

Total Energy density

$$\bar{u}(T) \equiv \frac{\bar{E}}{V} \propto T^4$$

$$\int_0^\infty \frac{\eta^3 d\eta}{e^\eta - 1} = \frac{\pi^4}{15}$$

$$\bar{u}(T) = \frac{\pi^2}{15} \frac{k_B T^4}{15 (\hbar c)^3}$$

Radiation Pressure

EM waves carry momentum

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

$$F = -k_B T \ln Z$$

$$P = \frac{\partial}{\partial V} k_B T \sum_{k,z} \ln (1 - e^{-\beta \hbar \omega_k})^{-1}$$

$$= k_B T \sum_k \frac{\partial}{\partial V} \frac{\partial}{\partial \omega_k} \ln (1 - e^{-\beta \hbar \omega_k})^{-1}$$

$$= \sum_{k,z} \left(- \frac{\partial \hbar \omega_k}{\partial V} \right) \frac{1}{e^{\beta \hbar \omega_k} - 1}$$

$$= \sum_{k,z} \left(- \frac{\partial \hbar \omega_k}{\partial V} \right) \bar{n}_{k,z}$$

$$\hbar = \frac{2\pi}{L} (m_x, m_y, m_z)$$

$$\hbar \omega_k = \hbar c k$$

$$\Rightarrow - \frac{\partial \hbar \omega_k}{\partial V} = - \frac{1}{\partial L} \frac{\partial \hbar \omega_k}{\partial L}$$

$$= \frac{\hbar \omega_k}{\partial V}$$

$$P = \frac{1}{3} \bar{u}(T)$$

Photon P.D.V

Photons are particles travelling at c

$$E = c|p|$$

$$= \hbar \omega$$

$$= \hbar c |k|$$

$$p = \hbar k \leftarrow \text{de Broglie}$$

$n_{k,\epsilon}$ = # photons in mode k, ϵ

$$v = \frac{c \hbar}{|h|} \Rightarrow \text{pressure (using plank dist.)}$$

Lecture (11/27/23)

Black Bodies

Object that absorbs all incident EM radiation

Power radiated per unit area per unit frequency ^{Stefan}

$P_e(\omega)$ of ideal black body

$$P_e(\omega) d\omega = 2 \int \frac{d^3k}{(2\pi)^3} \hbar \omega \frac{c \hbar k}{\hbar} n_k$$

cut off $\rightarrow$ $k_x > 0$
 $\frac{\omega}{c} < k < \frac{\omega + d\omega}{c}$
 $\uparrow$
frequency range

$$= 2 \cdot \frac{2\pi}{(2\pi)^3} \frac{\hbar \omega^2 d\omega}{c^2} \cdot \frac{1}{e^{\beta \hbar \omega} - 1} \int_0^{\pi/2} d\theta \sin \theta \cos \theta$$

$$= \frac{\hbar \omega^2 d\omega}{4\pi^2 c^2 (e^{\beta \hbar \omega} - 1)} = \frac{1}{4} c \bar{u}(\omega, T) d\omega$$

Total power radiated per unit area

$$P_e = \int_0^\infty \dots d\omega$$

$$= \frac{1}{4} c \bar{u}(T)$$

$$= \frac{\pi^2}{60} \frac{(k_B T)^4}{\hbar^3 c^2} = \sigma T^4 \quad \text{Stefan-Boltzmann Law}$$

Realistic Body

Absorbs fraction $a(\omega)$ of incident radiation

T dependent and ignore polarization dependence

Principle of Detailed Balance $\leftarrow$ related to time reversal symmetry of microscopic dynamics

$$\text{implies } P_e(\omega, T) = a(\omega) \frac{\hbar \omega^2 d\omega}{4\pi^2 c^2 (e^{\beta \hbar \omega} - 1)}$$

$a(\omega) = 1$ for all black body

$P_e(T) = a \sigma T^4$ if a is ind. of ω over relevant frequencies

Debye Model of a Solid

Vibrations of solid 3N degrees of freedom for N atoms

Periodic Boundary Conditions

Small k sound waves (long & transverse)

3 polarizations, speed c_s

Debye: $\omega_{k,c} = c_s |k|$

Impose cutoff $k = k_D$

$$\sum_k 1 \equiv V \int \frac{d^3k}{(2\pi)^3} = N \quad \checkmark \text{ } k_D \text{ determined by density}$$

$$\frac{4\pi}{3} \frac{k_D^3}{(2\pi)^3} = \frac{k_D^3}{6\pi^2} = \frac{N}{V}$$

$$\Rightarrow k_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} \sim \text{spacing of atoms}$$

$$\omega_D = c_s k_D \quad \Theta_D = \frac{\hbar c_s k_D}{k_B}$$

When $T \ll \Theta_D$

$$\frac{\bar{E}}{V} = \frac{\pi^4}{15} \frac{(k_B T)^4}{(h c)^3} \text{ zero point energy}$$

$$\frac{E_V}{V} \sim \frac{2\pi^2}{5} \frac{k_B^4 T^4}{(h c)^3}$$

$$C_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3 \text{ Debye Law}$$

For $T \gg \Theta_D$, get classical result

$$C_V \approx 3N k_B \text{ Dulong-Rohrbaugh Law}$$

Grand Canonical Distribution

Classical indistinguishable particles

$$\bar{Z} = \sum_{N=0}^{\infty} e^{-\alpha N} \cdot \frac{1}{N!} \int \prod_{i=1}^N \frac{d^3 p_i d^3 q_i}{h^3} e^{-\beta \sum_{i=1}^N \epsilon_{p_i}}$$

Canonical Partition Function

$$\epsilon_p = \frac{p^2}{2m}, \quad \beta = \frac{1}{k_B T}, \quad \alpha = \frac{-\mu}{k_B T}$$

$$Z_N = Z_1^N$$

$$Z_1 = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

$$\bar{Z} = \exp(e^{-\alpha} Z_1)$$

Define grand thermodynamic potential Φ

$$\bar{Z} = e^{-\beta \Phi}$$

$$\Phi = -k_B T \ln \bar{Z} /$$

$$= -\frac{V k_B T}{h^3} (2\pi m k_B T)^{3/2} e^{\mu/k_B T}$$

$$d\Phi = -S dT - P dV - \bar{N} d\mu$$

Legendre Transformation

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

$$\bar{E} = \Phi + TS + \mu \bar{N} =$$

Prob dist: $p_N(q, p) = \frac{e^{-\beta \sum \epsilon_{p_i} - \alpha N}}{N! h^3 \bar{Z}} \text{ (Normalized)}$

$$\beta \epsilon_p + \alpha N = \beta (\epsilon_p - \mu)$$

common

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, V}$$

$$= \sum_{N=0}^{\infty} N \frac{e^{-\alpha N}}{N! \bar{Z}} \left(\int \frac{d^3 p_i d^3 q_i}{h^3} e^{-\beta \epsilon_{p_i}} \right)^N$$

$$= \sum_{N=0}^{\infty} N \frac{\lambda^N e^{-\lambda}}{N!}, \quad \lambda = e^{-\alpha} Z_1$$

Poisson

$$\lambda = \bar{N} = e^{-\alpha} Z_1$$

$$P = -\Phi/V = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{\mu/k_B T} \cdot k_B T$$

$$PV = \bar{N} k_B T$$

Ideal Gas Law!

Lecture (11/24/22)

Indistinguishable particles in QM

N identical particles

general microstate: $\psi(x_1, \dots, x_N)$

Assume Hamiltonian: $\mathcal{H}_N = \sum_{i=1}^N \mathcal{H}_1(x_i, p_i)$

$$\psi(x_1, \dots, x_N) = \psi_{x_1}(x_1) \psi_{x_2}(x_2) \dots \psi_{x_N}(x_N)$$

orthonormal basis

with eigen value $\sum_{i=1}^N \epsilon_{k_i}$
 $\chi_i(x,p) \psi_{k_i}(x) = \epsilon_{k_i} \psi_{k_i}(x)$ *eigenfunctions*

k labels the single particle microstates (orbitals)

Count states

Ex. $N=2$ 3 orbitals

$k =$	1	2	3
	AB-BA	AB	AB
	A	B	B
	A		

occupation number $n_k = \#$ identical particles in orbital k

$$n_k = \begin{cases} 2 & \text{if } n_1=1, n_2=1 \\ 1 & \text{if } n_1=2 \end{cases}$$

General: N particles over $\#$ distinct states

$$= \frac{N!}{\prod_k n_k!}$$
 multinomial coefficient

Maxwell-Boltzmann Statistics

Indistinguishable particles

In QM, any n particle wavefunction

$$\Psi(x_1, x_2, \dots, x_n) = \pm \Psi(x_2, x_1, \dots, x_n)$$

Any exchange between x_i, x_j $i \neq j$

Bose-Einstein or Fermi-Dirac Statistics
bosons *fermions*

For two particles and two orbitals

$$\frac{1}{\sqrt{2}} (\psi_{k_1}(x_1) \psi_{k_2}(x_2) \pm \psi_{k_2}(x_1) \psi_{k_1}(x_2))$$

$k_1 \neq k_2$

For $k_1 = k_2$

$\psi_{k_1}(x_1) \psi_{k_1}(x_2)$ is symmetric

Anti-symmetric gives 0 $\leftarrow$ Pauli exclusion principle

	1	2	3
Bose-Einstein Case	AA	AA	AA
	A	A	A
	A	A	A
Fermi-Dirac Case	A	A	
		A	A
	A		A

Grand Canonical Distribution

$$\text{energy } E_r = \sum_{i=1}^N \epsilon_{k_i} = \sum_k \epsilon_k n_k$$

Grand Partition Function

$$\mathcal{Z} = \sum_{\substack{n_k=0,1,\dots \text{ BE} \\ \text{or } 0,1 \text{ FD} \\ n=1/2,\dots \text{ }}}$$

$$= \prod_k \left(\sum_{\substack{n_k=0,1,2,\dots \text{ BE} \\ \text{or } 0,1 \text{ FD}}} e^{-\beta n_k (\epsilon_k - \mu)} \right)$$

$\epsilon_k - \mu > 0$ for BE

BE is simple Harmonic Oscillator $\hbar \omega \rightarrow \epsilon_k - \mu$

FD is spin $1/2$ $\hbar \rightarrow \epsilon_k - \mu$

Reuse earlier results

$$\text{BE: } \bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}$$
 BE distribution

$$\text{FD: } \bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$
 Fermi Dirac Distribution

$$P_{B,F}(n_k) = \begin{cases} \frac{1}{\pi} e^{-\beta n_k (\epsilon_k - \mu)} (1 - e^{-\beta(\epsilon_k - \mu)}) & \text{Bose-Einstein} \\ \frac{e^{-\beta n_k (\epsilon_k - \mu)}}{1 + e^{-\beta(\epsilon_k - \mu)}} & \text{Fermi-Dirac} \end{cases}$$

Number Fluctuations

$$\text{Var}(N) = \overline{(N - \bar{N})^2} = \sum_k \text{var } n_k$$

$$\text{Var}(n_k) = \overline{n_k^2} - \bar{n}_k^2$$

$$\bar{Z}_k = (1 \mp e^{-\beta(\epsilon_k - \mu)})^{\pm 1} = \sum_{n_k} e^{-\beta n_k (\epsilon_k - \mu)}$$

$$\bar{n}_k = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \bar{Z}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}$$

$$\overline{(An_k)^2} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \bar{n}_k = \frac{e^{\beta(\epsilon_k - \mu)}}{(e^{\beta(\epsilon_k - \mu)} \pm 1)^2}$$

$$= \bar{n}_k (1 \pm \bar{n}_k)$$

Classical Limit

$\bar{n}_k \ll 1 \quad \forall k$ then both FD and BE yield the same results

recover indistinguishable or Gibbs corrected Maxwell-Boltzmann statistics

$$\bar{n}_k \ll 1 \quad \text{if} \quad e^{\beta(\epsilon_k - \mu)} \gg 1$$

$$\text{require } \epsilon_k - \mu \gg kT \quad \forall k$$

$$\text{lowest } \epsilon_k \text{ is } \epsilon_0 = 0$$

$$\alpha = -\frac{\mu}{kT} \gg 1$$

Partition Function

$$\bar{Z}_{\text{BE/FD}} = \prod_k (1 \mp e^{-\beta(\epsilon_k - \mu)})^{\pm 1}$$

$$= \prod_k (1 + e^{-\beta(\epsilon_k - \mu)} + \dots)$$

$$= \prod_k e^{-\beta(\epsilon_k - \mu)}$$

$$1 + x \approx e^x \text{ if } |x| \ll 1$$

$$= \exp\left(\sum_k -\beta(\epsilon_k - \mu)\right)$$

$$\sum_k e^{-\beta \epsilon_k} = Z_1, \text{ canonical partition for one particle}$$

$$= e^{Z_1 e^{-\alpha}} = \bar{Z}_{\text{MB}}$$

Lecture (12/14/23)

Quantum Ideal Gas in a box w/ periodic boundary conditions

$$\mathcal{H}_1 = \frac{p^2}{2m}$$

$$\text{P.b.c's: } \psi_k = \frac{e^{ikx}}{\sqrt{L_x L_y L_z}}, \quad k = 2\pi \left(\frac{m_x}{L_x}, \frac{m_y}{L_y}, \frac{m_z}{L_z} \right) \quad m_{x,y,z} \in \mathbb{Z}$$

$$\text{Grand Canonical Distribution: } \bar{Z}_{\text{BE/FD}} = -k_B T \sum_k \ln \left[(1 \mp e^{-\frac{\beta \hbar^2 k^2}{2m}} - \alpha)^{\pm 1} \right]$$

$$\approx -k_B T V \int \frac{d^3 k}{(2\pi)^3} \ln(\dots)$$

For a large system,

$\bar{N}$ fixed as T, V vary

$$\bar{N} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1} = V \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1}$$

Classical Limit: $\epsilon_{\mathbf{k}}$ is $\epsilon_0 = 0 \rightarrow$ larger $\bar{n}_0 = \frac{1}{e^{-\beta\mu} + 1}$

Large when $T \rightarrow \infty$ and μ fixed

to keep $\bar{n}$ fixed as $T \rightarrow \infty$, need $\mu \rightarrow -\infty$

$$\bar{n}_{\mathbf{k}} = e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} \ll 1$$

$$\begin{aligned} \text{Then } Z_1 &= \sum_{\mathbf{k}} e^{-\beta \epsilon_{\mathbf{k}}} \simeq V \int \frac{d^3k}{(2\pi)^3} e^{-\beta \epsilon_{\mathbf{k}}} \\ &= \int_V d^3x \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta \epsilon_{\mathbf{p}}} = P/k \end{aligned}$$

Classical partition function!

$$h_0 = 2\pi\hbar = h \text{ planck's constant}$$

Quantum Effects set in when $\frac{\hbar^2}{m k_B T} \simeq 1$

$$\bar{n} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \simeq 1$$

$$\bar{n}^{2/3} \left(\frac{\hbar^2}{m k_B T} \right) \simeq 1$$

$$\bar{n} = \frac{1}{a^3}$$

$\nearrow$ typical spacing
between particles

a is $\sqrt[3]{V}$ of volume of each particle

$$\text{Given } \bar{n} \text{ at } T \lesssim T_{\text{deg}} = \frac{\hbar^2 \bar{n}^{2/3}}{2\pi m k_B}$$

$$\bar{n} \geq \bar{n}_{\text{deg}} \left(\frac{2\pi m k_B T}{\hbar^2} \right)^{3/2}$$

Typical KE at temp $\sim k_B T$

$$\text{where } \frac{1}{a_{\text{deg}}} = \frac{1}{\lambda_{\text{deg}}} = n_{\text{deg}} \sim \left(\frac{2\pi m k_B T}{\hbar^2} \right)^{3/2}$$

Classical Mechanics good when $\lambda_{\text{deg}} = a_{\text{deg}} \ll a$

geometric/ray optics is valid when λ small compared to other scales

Summary

Classical Limit Fixed $\bar{n}$ breaks down below

$$T \lesssim T_{\text{deg}} = \frac{\hbar^2 \bar{n}^{2/3}}{2\pi m k_B}$$

Empirical Results

Classical is good except for helium and atomic gases

Element liquefies before classical limit

Electromagnetic Radiation + Debye Solid

Photons + phonons are not conserved

$$\mu = 0 \quad \epsilon_{\mathbf{k}} = \hbar \omega_{\mathbf{k}}$$

get back planck's formula

Field particle duality

Pressure in quantum ideal gas

$$\text{Non-relativistic } \epsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}$$

$$V = L^3 \quad \leftarrow \text{phases}$$

Then,

$$-\frac{\partial \epsilon_n}{\partial V} = \frac{2}{3} \frac{\epsilon_n}{L^3} \quad (\text{similar to radiation})$$

$$P = \frac{2}{3} \frac{\bar{E}}{V}$$

Conduction in metal

Spin-Statistics Thm: particles w/ spin $0, 1/2, 3/2, \dots$ bosons
 $1/2, 3/2, \dots$ fermions

Model electrons in metal as a gas of free fermions

$$\bar{N} = 2V \int \frac{d^3p}{h^3} \overline{n_{\mathbf{p}/h}} = V \bar{n}$$

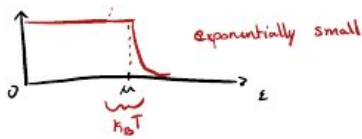
spin ↑

$$\bar{E} = 2V \int \frac{d^3p}{h^3} \frac{p^2}{2m} \overline{n_{\mathbf{p}/h}}$$

$\bar{N}$ fixed, solve for μ as a function of T

Focus on low T $k_B T \ll \mu$

$$f(\epsilon, \mu) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad \leftarrow \text{Fermi function}$$



$T=0$: Define $\mu(T=0) = \epsilon_F$ Fermi Energy

$$= \frac{p_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m}$$

$$\bar{n} = \frac{\bar{N}}{V} = 2 \frac{p_F^3}{h^3} \frac{4\pi}{3}$$

$$= \frac{p_F^3}{3} \left(\frac{2m \epsilon_F}{\hbar^2} \right)^{3/2} \quad \text{at } T=0$$

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{8\pi} \right)^{2/3} = k_B T_F$$