Statistical Mechanics

Week 3

• Variables and constraints:

$$dE = TdS - pdV + \mu dN$$

Total 7 quantities, three intrinsic (T, p, μ) and four extrinsic (E, S, V, N)

Q: For the four extrinsic (E, S, V, N), how many are independent?

At most **three**, since the first law tell us $E = E(S, V, N)$
This is the "constraint" imposed by the first law.

The intrinsic (T, p, μ) be expressed as a function of (S, V, N) as well.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

$$T = T(S, V, N), p = p(S, V, N), \mu = \mu(S, V, N),$$

In principle, any three variables can be chosen. For example, from $T = T(S, V, N)$, we can solve $S = S(T, V, N)$, $p = p[S(T, V, N), V, N] = p(T, V, N)$.

The interrelationships are "equations of state" that can relate any set of variables. More often, **the equation of state is referred to $p = p(T, V, N)$** which involves easily measured quantities (T, p, V), such as $pV = NkT$.

• Variables and constraints:

- The internal energy E can also be expressed as $E = E(T, V, N)$.
- Internal energy $E = E(T, V, N)$ and the equation of state $p = p(T, V, N)$ are the basically two most important equations we need for understanding a system.
  Note: Many problems are about these two equations.
- Other physical quantity (C_V, C_p, κ, β) can be derived from these two equations.

$$C_V = \left(\frac{dE}{dT}\right)_V \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,$$

- Or reversely: (C_V, C_p, κ, β) can be measured first. $E = E(T, V, N)$ and $p = p(T, V, N)$ can be expressed by the experimental (C_V, C_p, κ, β).

- In addition to the constraint of first law, there are so called "imposed constraints" which can simplify our analysis further by reducing the number of independent variables

Table 9.1. *Common constraints on systems*

Type	constraint
adiabatic[a]	$dQ = 0$
isobaric	$dp = 0$
isochoric	$dV = 0$
isothermal	$dT = 0$
nondiffusive or closed	$dN = 0$

• Isothermal processes:

Isothermal non-diffusive processes operate under two constraints, $\mathrm{d}N = \mathrm{d}T = 0$.

Q1: How many independent variables?

Just one independent variable (3-2=1), which we are free to choose.

Q2: Which variables should we choose?

We choose our variables to be T, N, V because T and N are constants and we are measuring changes in V. The $E = E(V)$ is given by the first law:

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V = T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V - p\,\mathrm{d}V$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial S}{\partial p}\right)_{T,N}\left(\frac{\partial p}{\partial V}\right)_{T,N} \overset{Maxwell}{=} -\left(\frac{\partial V}{\partial T}\right)_{p,N}\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{\beta}{\kappa}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

We convert the partial derivative to measurable properties: $\mathrm{d}E = \left(\frac{T\beta}{\kappa} - p\right)\mathrm{d}V$

If we know how the properties p, κ, and β depend on V then we can integrate this equation to find the relationship for finite changes.

• Isobaric processes:

A considerable number of processes occur in closed systems at a constant pressure. (Why?)

The two constraints dp = 0 and dN = 0 ensure that all properties of the system depend on just one independent variable.

Q: How many independent variables? Which variables do you want to choose?

Only one independent. We choose (N, p, T) because N and p are constants and we are measuring changes in T. We want to know $E = E(T)$. The first law:

$$\mathrm{d}E = \mathrm{d}Q - p\,\mathrm{d}V = \left(\frac{dQ}{dT}\right)_p \mathrm{d}T - p\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

We can convert these partial derivatives to give

$$\mathrm{d}E = \left(C_p - pV\beta\right)\mathrm{d}T$$

If we know how the properties C_p, p, V, and β depend on T then we can integrate this equation to find the relationship for finite changes.

• Adiabatic processes:

A process during which there is no heat transfer is called adiabatic ($dQ = 0$).

Many processes occur sufficiently rapidly that there can be no significant heat transfer with the surroundings that the system itself remains in equilibrium. For these adiabatic processes, we can write: $dQ = TdS = 0$, i.e., $dS = 0$

Non-diffusive, the two constraints $dN = dS = 0$, so only one independent variable. For (T, V, p) , anyone can be expressed in terms of any one other.

$$dT = \left(\frac{\partial T}{\partial p}\right)_S dp, \quad dT = \left(\frac{\partial T}{\partial V}\right)_S dV, \quad dV = \left(\frac{\partial V}{\partial p}\right)_S dp$$

Convert the above partial derivatives to measurable properties :

$$\frac{dT}{T} = \frac{V\beta}{C_p} dp, \quad \frac{dT}{T} = -\frac{\beta}{\kappa C_V} dV, \quad \frac{dV}{V} = -\frac{\kappa C_V}{C_p} dp$$

The properties T, V, C_p, C_V, κ are always positive, and the coefficient of thermal expansion, β, is usually positive.

- Adiabatic processes:

$$\mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_S \mathrm{d}p = \left(\frac{\partial V}{\partial S}\right)_{p,N} dp = \left(\frac{\partial V}{\partial T}\right)_{p,N}\left(\frac{\partial T}{\partial S}\right)_{p,N} dp$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} \overset{\text{Maxwell}}{=} \left(\frac{\partial V}{\partial S}\right)_{p,N}$$

$$\frac{\mathrm{d}T}{T} = \frac{V\beta}{C_p}\mathrm{d}p,$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p, \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,$$

Your homework: $\frac{\mathrm{d}T}{T} = -\frac{\beta}{\kappa C_V}\mathrm{d}V, \quad \frac{\mathrm{d}V}{V} = -\frac{\kappa C_V}{C_p}\mathrm{d}p$

• Adiabatic process: Ideal gas

$$\frac{\mathrm{d}T}{T}=\frac{V\beta}{C_p}\mathrm{d}p,\qquad \frac{\mathrm{d}T}{T}=-\frac{\beta}{\kappa C_V}\mathrm{d}V,\qquad \frac{\mathrm{d}V}{V}=-\frac{\kappa C_V}{C_p}\mathrm{d}p$$

the values of the parameters C_p, C_V, β, κ for ideal gases (your homework):

$$C_{\mathrm{V}}=\frac{\nu}{2}R,\quad C_p=C_V+R,\quad \beta=\frac{1}{T},\quad \kappa=\frac{1}{p}$$

$$\frac{dT}{T}=\frac{V\beta}{C_p}dp=\frac{pV}{pTC_p}dp=\frac{RT}{pTC_p}dp=\frac{R}{C_p}\frac{dp}{p}=\left(\frac{C_p-C_V}{C_p}\right)\frac{dp}{p}=(1-\frac{1}{\gamma})\frac{dp}{p}$$

$$\frac{\mathrm{d}T}{T}=\left(1-\frac{1}{\gamma}\right)\frac{\mathrm{d}p}{p},$$

Define: $\gamma=\frac{C_p}{C_V}=\frac{\nu+2}{\nu}$

Integrating the equation, adiabatic processes in ideal gases: $Tp^{1/\gamma-1}=$ constant,

Your homework: $TV^{\gamma-1}=$ constant, $pV^{\gamma}=$ constant

• Discussion: Adiabatic Example

In an adiabatic (nondiffusive) process that takes an ideal gas from the state (p_1, V_1, T_1) to the state (p_2, V_2, T_2), the following relations hold:

$$pV^{\gamma} = \text{constant}, \quad \gamma = C_p/C_V,$$

For an ideal gas, $E = C_vT = vRT/2$, $pV = nRT$, $C_p = C_v + nR$.

Question: Find out the change in internal energy in this adiabatic process

In terms of the initial and the final temperature (T_1, T_2).

First law: $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$

Adiabatic nondiffusive processes : $\mathrm{d}Q = T\mathrm{d}S = 0$, $\mathrm{d}N = 0$

First law: $\mathrm{d}E = -p\mathrm{d}V = dW$

$$W = -\int_{V_1}^{V_2} pdV = -A\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = \frac{A}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right] = \frac{1}{1-\gamma}\left[p_2V_2 - p_1V_1\right]$$

• Reversibility

The second law demands that, during any process, the total entropy of all the interacting systems must either increase or remain constant:

$$\Delta S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3 + \cdots \geq 0$$

Q: If the total entropy increases then the process cannot be reversed, Why?
because the reversed process would require a decrease in entropy, in violation of the second law.

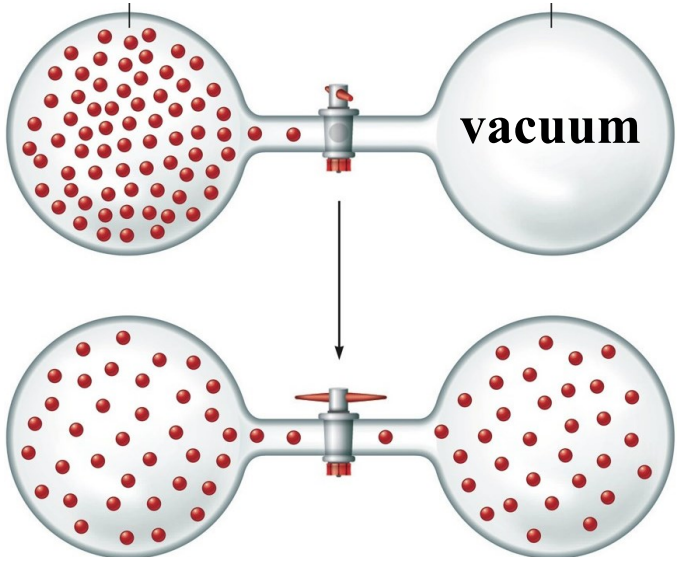
Q: When the process could be reversible?
For a process to be reversible, there must be no change in total entropy ($\Delta S_0 = 0$).

In previous cpt we found that when two systems are interacting thermally, mechanically, and/or diffusively, the change in entropy of the combined system is

$$\mathrm{d}S_0 = \mathrm{d}S_1 + \mathrm{d}S_2 = \frac{1}{T_2}\left[\left(\frac{T_2 - T_1}{T_1}\right)\mathrm{d}Q_1 + \left(p_1 - p_2\right)\mathrm{d}V_1 - \left(\mu_1 - \mu_2\right)\mathrm{d}N_1\right] \geq 0$$

We can see immediately that in order for a process to be reversible (i.e., $\mathrm{d}S_0 = 0$) then: [1] if heat is transferred, the temperatures must be equal; [2] if volume is transferred, the pressures must be equal; [3] if particles are transferred, the chemical potentials must be equal.

• Free expansion



In a "free expansion," a gas expands without doing any work at all, i.e., $dW = 0$

In the right figure, when the partition is removed and the gas rushes into the empty section, the molecules collide with stationary rigid walls. Walls don't move, gas does no work.

$dN = ?$ $dQ = ?$ $dE = ?$ $dV = ?$ $dT = ?$ $dp = ?$

$dN = 0$, $dQ = 0$, $dE = dQ + dW = 0$, $dV > 0$, no heat transfer, no work, no change in E

$dW = pdV = 0$ and $dE = TdS + dW = 0$, so $dS = 0$, correct?

Q1: Is the free expansion irreversible or reversible process?

Reversible: $dS = 0$. If V changes, p must be equal, so irreversible.

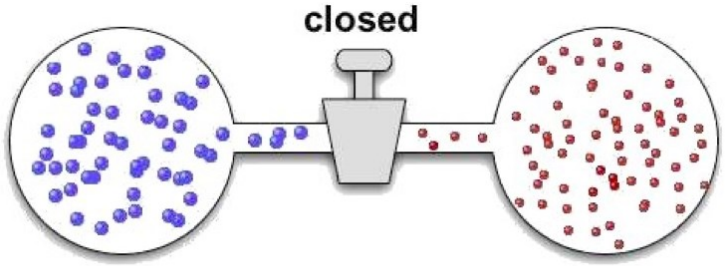
For each particle, the available microstates increase as V increases, so $dS > 0$.

Irreversible: $TdS > dQ$, and $dW = pdV$ is not well defined.

Q2: For ideal gas, $dT = ?$ $E = \frac{Nv}{2}kT$. $dE = 0$, so $dT = 0$ $pV = NkT$, p decreases.

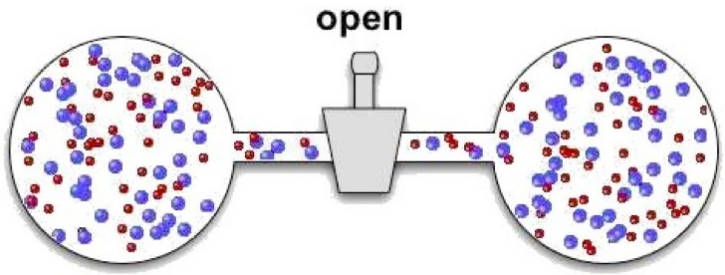
• Mixing

Gas mixing: Two gases of equal temperature and pressure are separated by a barrier. Two gases have different compositions.



Q: Irreversible or reversible?

The mixed state has higher entropy -- there is more volume in coordinate space for each molecule. No matter how long you wait, you will never see the two gases separate again. The entropy has increased and cannot go back.



Q: If the two gases have same initial composition, is it reversible?

When the partition is removed, nothing changes. The original state can be recovered simply by reinserting the partition. In this case, the removal of the barrier causes no change in entropy. The process is reversible.

• Discussion: interacting gas

The ideal gas model works well for low density gases. But it must be modified to describe gases at higher densities where mutual interactions cannot be ignored.

We begin this modification by rewriting the ideal gas law in terms of the **molar volume *v*** and the **gas constant *R***: $pv = RT$, where $R = N_A k$

This relation implies that we can make the volume arbitrarily small by applying a sufficiently large pressure. Q: Is this correct? Why?

In fact, once the electron clouds of neighbouring molecules begin to overlap it is almost impossible to compress the gas further. Q: What correction should we do?

Another deviation from the ideal gas model is the weak long-range forces among molecules, which cause them to condense to liquids at sufficiently low temperatures: **attractions**. Q: What correction should we do?

Start from $pv = NkT$, can you guess the equation of state for interacting gas? Why?

• Real gas: van der Waals equation of state

This attraction helps hold the molecules of the gas together, thus increases the pressure. So the factor of p in equation $pv = RT$ must be modified:

$$p \rightarrow p + \text{ mutual attraction}$$

This mutual attraction (van der Waals) is caused by charge polarizations. It is inversely proportional to $1/r^6 \approx 1/v^2$. Hence

$$p \rightarrow p + \frac{a}{v^2}$$

These two effects are incorporated into a modification of the ideal gas law $pv = RT$ called the "van der Waals equation of state" for a real gas:

$$\left(p + \frac{a}{v^2} \right)(v - b) = RT,$$

Q: Liquid? We do not yet have a good model for liquids…
The van der Waals equation can be useful in acquiring qualitative insight into the behaviour of liquids, particularly in studying gas--liquid phase transitions.

Summary

- Internal energy $E = E(T, V, N)$ and the equation of state $p = p(T, V, N)$ are the basically two most important equations we need for understanding a system.
- We can measure (C_V, C_p, κ, β). $E = E(T, V, N)$ and $p = p(T, V, N)$ can be expressed by the experimental (C_V, C_p, κ, β).
- From "microscopic" (statistics method), to get the internal energy (E-T) and equation of state, usually we need to find the entropy $S(N, V, E)$ first.

$$S = k \ln \Omega$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N},$$

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

$$\Omega = \omega_c^N \qquad \omega = C\left(\frac{V}{N}\right)\left(\frac{E_{\text{therm}}}{Nv}\right)^{v/2}$$

$$S = Nk \ln \omega_c = Nk \ln C\left(\frac{V}{N}\right)\left(\frac{E}{N}\right)^{v/2}$$

$$E = \frac{Nv}{2} kT, \quad pV = NkT,$$

More rigorous method?

Ensembles

$$S = k \ln \Omega$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

$$d\omega = \frac{dxdydzdp_x dp_y dp_z}{h^3}$$

Elemental volume in phase space

Consider all N particles

$$d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i$$

$$\omega = \int \frac{\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{h^3}$$

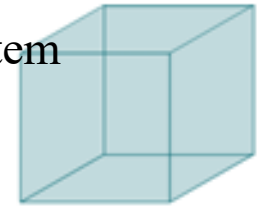
Microstates in N-particle phase space

$$\Omega = \omega_c^N$$

$$\Omega = \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p d^{3N}q$$

$6N$-dimensional Γ space

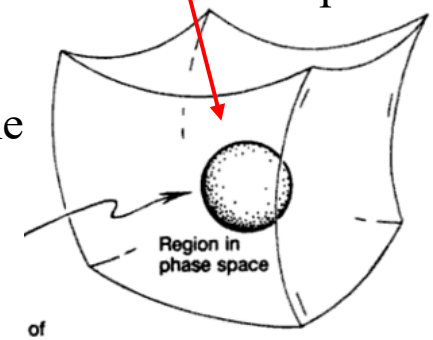
Consider the system as a whole, not single particle ω.



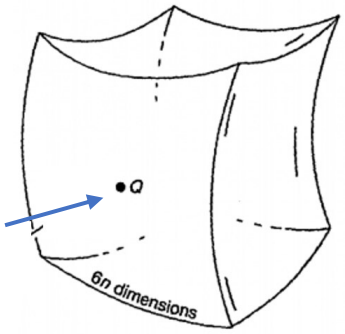
For a given macrostate: $E, V, N, T, p, \mu\ldots$
Many microstates, many-to-one mapping

Volume of a shell

Γ space



One microstate



Ensembles: Many copies of the same macrostate, each corresponding to a different representative microstate.

of

Microcanonical Ensemble

- **Fundamental postulate: Equal a priori equilibrium probability**
  - ✓ Our starting point is a mechanically and adiabatically **isolated** system. In the absence of heat or work input to the system, the **internal energy *E* is constant**.
  - ✓ An isolated system in equilibrium is equally likely to be in any of its accessible states, each of which is defined by a particular configuration of the system's elements.
  - ✓ The corresponding set of microstates form the *microcanonical ensemble*.
  - ✓ In the microcanonical ensemble every system has N molecules, a volume V, and an energy between E and $E+2\Delta$. All microstates are confined to the surface $\mathcal{H} = E$ in phase space, probability for microstate p

$$p = \frac{1}{\Omega} \cdot \begin{cases} 1 & \text{for } E - \Delta \le \mathcal{H} \le E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

  - ✓ Fundamental postulate: on the constant energy surface, p is constant, so does the normalization factor Ω.

Microcanonical Ensemble

- **Entropy:**
  - ✓ As p is probability and Ω is constant, the integral of p

$$\int_{E<\mathcal{H}(p,q)<E+\Delta} p d\Gamma = 1 = \frac{1}{\Omega}\int_{E<\mathcal{H}(p,q)<E+\Delta} d\Gamma$$

  - ✓ Ω is the area of the surface of constant energy E in phase space, and it counts the total number of accessible microstates.
  - ✓ Then entropy is given by $S = kln\Omega$.

Team Discussion

- ✓ Consider N impurity atoms trapped in a solid matrix. Each impurity can be in one of two states, with energies 0 and ϵ, respectively.
- ✓ There are $N_1 = E/\epsilon$ excited impurities, can you find out Ω**?**

Microcanonical Ensemble

- **Two-level system: discrete microstate**
  - ✓ As there are $N_1 = E/\epsilon$ excited impurities, the normalization Ω is the number of ways of choosing N_1 excited levels among the available N, and given by the binomial coefficient

$$\Omega(E,N) = \frac{N!}{N_1!(N-N_1)!}$$

  - ✓ The entropy $S(E,N) = k_B \ln \frac{N!}{N_1!(N-N_1)!}$

  - ✓ Stirling's formula and limit of $N_1, N \gg 1$,

$$\ln N! \approx N \ln N - N \qquad \ln N_1! \approx N_1 \ln N_1 - N_1$$

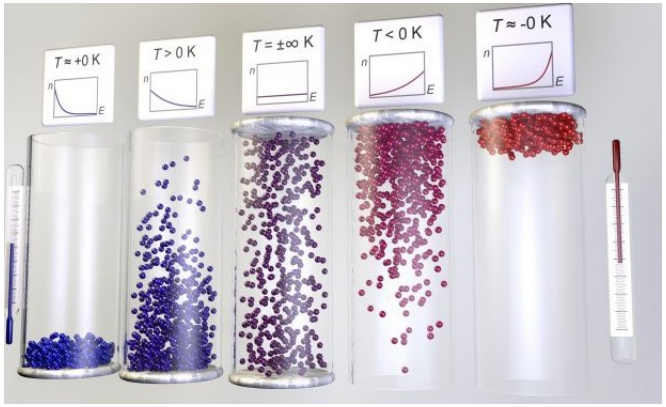
$$S(E,N) \approx -Nk_B\left[\frac{N_1}{N}\ln\frac{N_1}{N} + \frac{N-N_1}{N}\ln\frac{N-N_1}{N}\right]$$

$$S(E,N) = -Nk_B\left[\left(\frac{E}{N\epsilon}\right)\ln\left(\frac{E}{N\epsilon}\right) + \left(1-\frac{E}{N\epsilon}\right)\ln\left(1-\frac{E}{N\epsilon}\right)\right]$$

Microcanonical Ensemble

- **Two-level system:**

$$S(E,N) = -Nk_B\left[\left(\frac{E}{N\epsilon}\right)\ln\left(\frac{E}{N\epsilon}\right)+\left(1-\frac{E}{N\epsilon}\right)\ln\left(1-\frac{E}{N\epsilon}\right)\right]$$



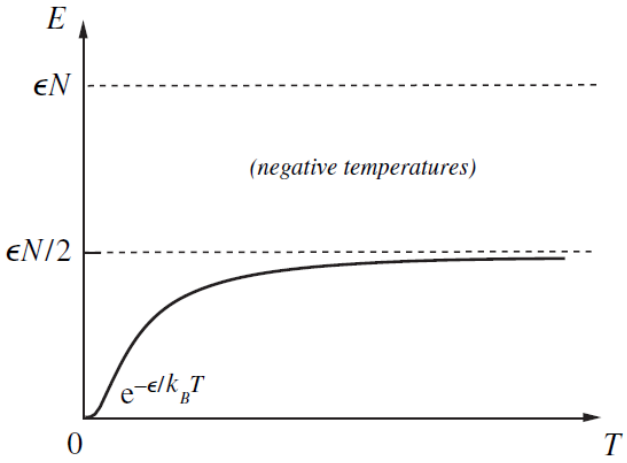
✓ The equilibrium temperature can be calculated

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = -\frac{k_B}{\epsilon}\ln\left(\frac{E}{N\epsilon - E}\right),$$

$$E(T) = \frac{N\epsilon}{\exp\left(\frac{\epsilon}{k_B T}\right)+1}$$

✓ $E > N\epsilon/2$, negative temperature?

$T = +0$ and -0, which is hotter?



✓ Heat capacity

$$C = \frac{dE}{dT} = Nk_B\left(\frac{\epsilon}{k_B T}\right)^2 \exp\left(\frac{\epsilon}{k_B T}\right)\left[\exp\left(\frac{\epsilon}{k_B T}\right)+1\right]^{-2}$$

Microcanonical Ensemble

- **Ideal gas:** continuous microstates
  - ✓ Hamiltonian is $\mathcal{H}(p,q) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$, and $E < \mathcal{H}(p,q) < E + \Delta$
  - ✓ Ideal gas, no 'q' term in $\mathcal{H}(p,q)$, so

$$\Omega(E) = \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p\,d^{3N}q = V^N \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p$$

  - ✓ We have identified the integral as the volume of a $3N$-dimensional spherical shell with radius $(2mE)^{1/2}$ and thickness Δ.
  - ✓ The calculation of the integral is complicated (not required), the final result is

$$\Omega(E) = V^N \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}(2mE)^{(3N-1)/2}$$

  - ✓ Using Stirling's formula, and neglecting terms of order of 1 or $lnE \sim lnN$ in the large N limit, results in

$$S(E,V,N) = k_B\left[N\ln V + \frac{3N}{2}\ln(2\pi mE) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\right] = Nk_B \ln\left[V\left(\frac{4\pi emE}{3N}\right)^{3/2}\right]$$

Microcanonical Ensemble

- **Equation of state:**

$$S(E,V,N) = Nk_B \ln\left[V\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right]$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{3}{2}\frac{Nk_B}{E}, \qquad E = 3Nk_BT/2, \quad C_V = 3Nk_B/2$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{Nk_B}{V}, \qquad \Rightarrow PV = Nk_BT.$$

- ✓ You may try to calculate other thermodynamic functions…

Microcanonical Ensemble

- **Strategy for solving problems using microcanonical ensemble:**
  - ✓ Consider an isolated system that occupied volume V and has an energy E within a small uncertainty $\Delta \ll E$. The Hamiltonian is presumed known.
  - ✓ To find the thermodynamic functions, proceed as follows:

[1] Calculate the microstate number $\Omega(E)$ of the system from the Hamiltonian.

$$\Omega = \begin{cases} \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p d^{3N}q\,, & \text{continuous microstates} \\ \text{Count } \Omega \text{ directly,} & \text{discrete microstates} \end{cases}$$

$d^{3N}q$ usually gives volume V in Ω (No interactions, no potential)

$d^{3N}p$ gives E in Ω. (such as free particle $\varepsilon = p^2/2m$ or $p = (2m\varepsilon)^{1/2}$)

[2] Find the entropy $S(E,V) = kln\Omega(E)$

[3] Solve for E in terms of S and V, the result is internal energy $E(S,V)$

Microcanonical Ensemble

- **Strategy for solving problems using microcanonical ensemble:**
  - ✓ Consider an isolated system that occupied volume V and has an energy E within a small uncertainty $\Delta \ll E$. The Hamiltonian is presumed known.
  - ✓ To find the thermodynamic functions, proceed as follows:

[4] Find other thermodynamic functions from the following formulas

$$\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{p}{T}=\left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T}=-\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Helmholtz free energy, $F \equiv E - TS$;

Enthalpy, $H \equiv E + pV$;

Gibbs free energy, $G \equiv E - TS + pV$.

$$C_p = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_p, \quad C_V = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_V$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Qualifying exam problem

Consider a lattice of N distinguishable non-interacting classical magnetic dipoles with two allowed directions - either ↑ or ↓. Under an external magnetic field $B > 0$ that is parallel with the ↑ direction, with the energy

$$\epsilon_{\uparrow} = -mB, \qquad \epsilon_{\downarrow} = mB,$$

where the m is the magnetic moment per dipole.

(a) The number of ↑ magnetic dipoles is $n_{\uparrow}$ and the number of ↓ magnetic dipoles is $n_{\downarrow}$, with $N = n_{\uparrow} + n_{\downarrow}$. Consider this system is a microcanonical ensemble, find out the total number of microstates $\Omega(n_{\uparrow})$ for a fixed number $n_{\uparrow}$, calculate the entropy using Stirling's approximation, and calculate the temperature.

Number of microstates $\Omega(n_{\uparrow}) = \frac{N!}{n_{\uparrow}!(N-n_{\uparrow})!}$,

entropy $S = k_B ln\Omega = k_B[NlnN - n_{\uparrow}lnn_{\uparrow} - (N - n_{\uparrow})\ln(N - n_{\uparrow})]$.

Temperature $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n_{\uparrow}}\frac{\partial n_{\uparrow}}{\partial E} = (\frac{-k_B}{2mB})ln\frac{N-n_{\uparrow}}{n_{\uparrow}}$.

Next week:

Canonical Ensemble
Partition function
Grand potential
Grand canonical Ensemble
Grand partition function