Statistical mechanics

Week 2

• Equilibrium state

The probability is proportional to the number of states ($P \propto \Omega_0$), and the, the distribution is the familiar Gaussian form:

$$P(E_1) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(E_1-\bar{E}_1)^2/2\sigma^2} \qquad \bar{E}_1 = \frac{n_1}{2}kT \qquad \text{and} \qquad \sigma = \sqrt{\frac{n_1 n_2}{2n_0}}kT \approx \sqrt{\frac{n_1}{2}}kT$$

If A_2 is a relatively large system, i.e., a "**reservoir**," so that $n_1 \ll n_2 \approx n_0$

$$n_1 = N_1\nu_1 \qquad \frac{\sigma}{E_1} \approx \sqrt{\frac{2}{n_1}} \approx 10^{-12} \quad \left(for\ 10\times10^{23}\ degrees\ of\ freedom\right).$$

Interacting macroscopic systems in ***equilibrium (?)*** will always be in a state with the one optimal distribution of energies between them. The chance of our seeing a different distribution of energies is infinitesimal.

Two interacting systems are in ***equilibrium (?)***: the distribution of energy must be such that the number of accessible states to the combined system is a ***maximum***.

An isolated system is said to be in **equilibrium** when the *probabilities* for the various possible configurations of its elements do not vary with time.

• Equilibrium: The fundamental postulate

The tools for the statistical analysis of the ***equilibrium*** behaviors of large systems are based on one single, very important fundamental postulate.

Fundamental postulate: 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.

This postulate seems quite reasonable, but itself does not justify its adoption. Rather, we must validate it by comparing its predictions with experiments.

This has been done for a huge number of systems and processes, and we find that the predictions are correct every time.

If the number of states accessible to the entire system is given, and all are equally probable, then the probability for the system to be in any one of them must be $P_{\text{any one state}} = 1/\Omega$, and if a subset has i states then the probability for the system to be in this subset is $P_{\text{subset } i} = \Omega_i / \Omega$.

• The meaning of Ω: the second law

Since the energies are functions of the ***system variables*** (*T, p, B* et al), we can say:

*When two interacting macroscopic systems are in equilibrium, the values of the various system **variables** will be such that the number of states Ω_0 available to the combined system is a maximum.*

There is a very important corollary to this result, which is called the "second law of thermodynamics."

There are many equivalent ways of stating it, but they all rely on the following:
For the number of states Ω_0 of two interacting systems, the Ω_0 must be increasing as they approach equilibrium.

Second law of thermodynamics

As two interacting macroscopic systems approach equilibrium, the changes in the system ***variable***s will be such that the number of states Ω_0 available to the combined system increases. More simply, in the **approach to equilibrium**,

$$\Delta\Omega_0 > 0.$$

• Entropy: measures the number of states Ω

The number of states for a macroscopic system is extremely large. The logarithm of a large number is smaller and more manageable, so we find it more convenient to work with the logarithm of Ω_0 rather than with itself.

A particular multiple of this logarithm is called the "entropy." It is given the symbol S and is defined as follows:

$$\text{entropy } S \equiv k \ln \Omega \, .$$

Boltzmann's constant k gives entropy the magnitude and units that are convenient for typical macroscopic systems.

If a number like $10^{10^{24}}$, then *ln* is a number like 10^{24}. If we multiply this by k, which is a number like 10^{-23}, the result is a number like 10. That is,

$$\Omega \approx 10^{10^{24}}$$

$$\ln \Omega \approx 10^{24}$$

$$k \ln \Omega \approx 10 \text{ J/K}$$

• Entropy: more convenient than Ω

Entropy has another convenient property:
Whereas the *number of states* accessible to the combined system is *multiplicative*, $\Omega_0 = \Omega_1\Omega_2$, the *entropy* of the combined system is **additive**:

$$k \ln\Omega_0 = k \ln\Omega_1 + k \ln\Omega_2 \quad \Rightarrow \quad S_0 = S_1 + S_2.$$

This makes it algebraically similar to some other system variables, such as internal energy, volume, or number of particles:

$$S_0 = S_1 + S_2,\ V_0 = V_1 + V_2,$$
$$E_0 = E_1 + E_2,\ N_0 = N_1 + N_2.$$

Also like the energy, volume, and number of particles, the entropy of a system can be determined at any time unambiguously, independently of what it was in the past or what it will be in the future.

Differential dS *is* exact (math), just like the differentials dE, dV, dT, dp and dN.

• Entropy and the second law

Because the entropy is the logarithm of the number of accessible states, when increases so does *S* and when is a maximum so is *S*. Consequently, an *alternative and equivalent* statement of the second law is as follows.

Second law of thermodynamics
For systems interacting in any way (whether or not they are yet in equilibrium) the entropy of the combined system cannot decrease:

$$\Delta S_0 \geq 0.$$

The second law applies to the combined entropy of all the interacting systems, not to the entropy of just one of them.

For example, our Sun loses entropy as it radiates energy out into space. But the entropy of the Universe as a whole increases as a result.

Valid for large system with large *N*! Small system may not work, one particle?

• Definition of temperature

Temperature measures the dependence of entropy on internal energy for *purely thermal interactions*. We can define temperature by

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

According to the first law ($\mathrm{d}E = \mathrm{d}Q - p\mathrm{d}V + \mu\mathrm{d}N$), the variation in E for purely thermal interactions (i.e., V, N constant) is precisely the heat transfer $\mathrm{d}Q$. Therefore, the above equation is equivalent to

$$\frac{1}{T} = \frac{\mathrm{d}S}{\mathrm{d}Q}, \qquad \mathrm{d}S = \frac{\mathrm{d}Q}{T}, \quad \text{or} \quad \mathrm{d}Q = T\,\mathrm{d}S.$$

This definition of temperature makes the change in entropy directly proportional to the heat transfer.

$\mathrm{d}Q$ and T can be measured by tools like thermometers and calorimeters!

Then $\mathrm{d}S$ can be calculated (Differential $\mathrm{d}S$ *is* exact).

• Variables: Intrinsic vs extrinsic

Let's look at the first law: $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$

There are three pairs of conjugate variables, (T, S), (p, V), and (μ, N), each term having the same mathematical form!

Each pair includes one "intrinsic" and one "extrinsic" variable.

If you divide a system in equilibrium into many pieces, the intrinsic variable for the entire system is *equal* to that of the individual parts, whereas the extrinsic variable for the entire system is the *sum* of the individual parts.

For two systems, intrinsic: $T = T_1 = T_2$, $p = p_1 = p_2$, $\mu = \mu_1 = \mu_2$;

extrinsic, $S = S_1 + S_2$, $V = V_1 + V_2$, $N = N_1 + N_2$.

• Definition of pressure and chemical potential

We want **d*S***, so rearrange the first law: $\mathrm{d}E = \mathrm{d}Q - p\mathrm{d}V + \mu\mathrm{d}N$, using $\mathrm{d}Q = TdS$

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$$

Looking at the coefficients of the three terms in equation, we see that

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

Definitions of pressure and chemical potential.

They tell us that p/T measures how the entropy varies with volume and that μ/T measures how the entropy varies with the number of particles.

• Team discussion: Entropy at $T = 0$ K

Entropy plays the central role in controlling the behaviors of systems. The entropy of any system at temperature T can be determined by integrating $dS = dQ/T$ from $T = 0$ to $T = T$:

$$\Delta S = S(T) - S(0) = \int_0^T \frac{dQ}{T'} \qquad S(T) = S(0) + \int_0^T \frac{dQ}{T'}$$

But to evaluate this, we must know the value of $S(0)$ and how to do the integral.

Q: What is the value of $S(0)$?

• The third law

As we remove energy from a system, we force it into states of ever decreasing total energy. Eventually, it will reach that one state of lowest energy, and that is as far as it can go. At this point $\Omega = 1$ and so its entropy is zero. This defines $T = 0$. Thus $S = k \ln \Omega = k \ln 1 = 0$ (at absolute zero, $T = 0$).

This observation provides us with the "third law of thermodynamics".

Third law of thermodynamics
The entropy of a system goes to zero as the temperature goes to zero,
$S(T = 0) = 0$,
no matter what the values of the external parameters are.

• Entropy at finite temperatures

Having solved the first problem, $S(0)$, we now face the second -- how to evaluate

$$S = S(0) + \int_0^T \frac{dQ}{T'}$$

From the definition of heat capacity, we can write the heat added as

$$dQ = C_y dT$$

so the value of the entropy for temperature T and other parameter values y is

$$S(T, y) = \int_0^T \frac{C_y dT'}{T'}$$

Heat capacity of an object to be a measure of how much heat energy must be added or removed in order to change its temperature by one degree.

If y is a parameter that remains constant as we add the heat, then we define the heat capacity at constant y as $C_y = \partial Q / \partial T_y$

For example, the symbol C_p indicates that the pressure is held constant and the symbol C_V indicates that the volume is held constant.

• Team Discussion: Heat capacities at T = 0

$$S(T,y) = \int_0^T \frac{C_y dT'}{T'}$$ Question: What will happen to C_y if T goes to zero?

Because the integrand in above equation has temperature in the denominator, the integral diverges at zero temperature unless the heat capacity is zero at that point.

Consequently, the heat capacities of all systems must go to zero as the temperature goes to zero, no matter what: $C_y \rightarrow 0$ as $T \rightarrow 0$.

• Qualifying exam problem

A system, maintained at constant volume, is brought in contact with a thermal reservoir at temperature T_f. If the initial temperature of the system is T_i, calculated ΔS, change in the **total entropy** of the system and reservoir.
Note: C_V, the specific heat of system and reservoir, independent of temperature.

The change in entropy of the system is

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{C_V dT}{T} = C_V ln \frac{T_f}{T_i}$$

The change in entropy of the heat source (thermal reservoir) is

$$\Delta S_2 = -\frac{|Q|}{T_f} = C_V \frac{T_i - T_f}{T_f},$$

The total change in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = C_V \left(ln \frac{T_f}{T_i} + \frac{T_i - T_f}{T_f} \right)$$

• Second law and equilibrium

The second law requires that when interacting systems are at equilibrium, their total entropy is a maximum.

1. As two interacting systems approach equilibrium,
(a) heat flows toward the system with the lower temperature,
(b) boundaries move toward the system with the lower pressure,
(c) particles flow toward the system with lower chemical potential.

2. After two interacting systems have reached equilibrium,
(a) their temperatures are equal,
(b) their pressures are equal,
(c) their chemical potentials are equal.

3. When heat, volume, or particles (Q,V,N) are transferred, one of these by itself with the other two held constant, the following must be true:
(a) $\Delta T \Delta Q > 0$ (if heat is added, the temperature must rise);
(b) $\Delta p \Delta V < 0$ (if the volume is increased, the pressure must fall);
(c) $\Delta \mu \Delta N > 0$ (if particles are added, the chemical potential must rise).

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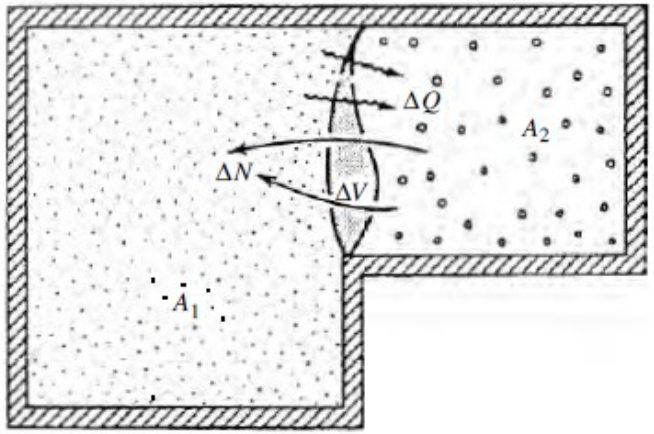
• Second law: approach equilibrium

To derive the above results, we consider the general interaction shown in the right figure: An isolated system, A_0, is composed of two interacting subsystems, A_1 and A_2.



We are interested in the change in entropy of the combined system,

$$dS_0 = dS_1 + dS_2 = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2}$$

and we express $\mathrm{d}Q_2$ in terms of the changes $\mathrm{d}Q_1$, $\mathrm{d}V_1$, $\mathrm{d}N_1$ in system 1. Any energy, volume, and/or particles gained by one subsystem come from the other:

$$\mathrm{d}E_2 = -\mathrm{d}E_1, \quad \mathrm{d}V_2 = -\mathrm{d}V_1, \quad \mathrm{d}N_2 = -\mathrm{d}N_1$$

The first of these relationships ($\mathrm{d}E_2 = -\mathrm{d}E_1$) can be rewritten using the first law:

$$\mathrm{d}Q_2 - p_2\,\mathrm{d}V_2 + \mu_2\,\mathrm{d}N_2 = -\left(\mathrm{d}Q_1 - p_1\,\mathrm{d}V_1 + \mu_1\,\mathrm{d}N_1\right)$$

We solve for $\mathrm{d}Q_2$, replacing $\mathrm{d}V_2$ and $\mathrm{d}N_2$ by $-\mathrm{d}V_1$ and $-\mathrm{d}N_1$, respectively:

$$\mathrm{d}Q_2 = -\mathrm{d}Q_1 + \left(p_1 - p_2\right)\mathrm{d}V_1 - \left(\mu_1 - \mu_2\right)\mathrm{d}N_1.$$

- Second law: approach equilibrium

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

First, imagine that the two interacting subsystems are not yet in equilibrium. The second law dictates that the entropy of the combined system must increase,

$$\mathrm{d}S_0 > 0 \quad \text{(approaching equilibrium)}$$

The three terms on the right-hand side of the above equation must each individually obey the inequality, because the changes dQ, dV, dN are independent;

(a) If the two are interacting thermally, then $[(T_2 - T_1)/T_1]\,\mathrm{d}Q_1 > 0$. That is, heat must flow toward the lower temperature (e.g., $\mathrm{d}Q_1 > 0$ if $T_2 > T_1$).
(b) If the two are interacting mechanically, then $(p_1 - p_2)\,\mathrm{d}V_1 > 0$. That is, boundaries must move toward the lower pressure (e.g., $\mathrm{d}V_1 > 0$ if $p_1 > p_2$).
(c) If the two are interacting diffusively, then $-(\mu_1 - \mu_2)\,\mathrm{d}N_1 > 0$. That is, particles must flow towards the lower chemical potential (e.g., $\mathrm{d}N_1 > 0$ if $\mu_1 < \mu_2$).

• More Definitions and differential forms

We name and define these special energy functions as follows:

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

Enthalpy, $H \equiv E + pV$;

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

Because $E = TS - pV + \mu N$

we have these alternative forms:

Helmholtz free energy, $F = -pV + \mu N$;

Enthalpy, $H = TS + \mu N$;

Gibbs free energy, $G = \mu N$.

• Definitions and differential forms

If we take the differential of the Helmholtz free energy $F \equiv E - TS$, we get

$$\mathrm{d}F = \mathrm{d}E - T\,\mathrm{d}S - S\mathrm{d}T.$$

Then, using the first law for $\mathrm{d}E$, we get the differential form

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N.$$

Doing the same for the enthalpy and the Gibbs free energy gives (your homework)

$$\mathrm{d}H = T\,\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}N,$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N.$$

Helmholtz free energy F	Enthalpy H	Gibbs free energy G
"work function"	"heat function"	"Gibbs function"
$F \equiv E - TS$	$H \equiv E + pV$	$G \equiv E - TS + pV$
$= -pV + \mu N$	$= TS + \mu N$	$= \mu N$
$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$	$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}N$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N$
if T constant, $F = \min$	if p constant, $H = \max$	if T, p constant, $G = \min$
if T, N constant, $\mathrm{d}F = -p\mathrm{d}V$	if p, N constant, $\mathrm{d}H = T\mathrm{d}S$	if T, p constant, $\mathrm{d}G = \mu\mathrm{d}N$

• Helmholtz free energy

The Helmholtz free energy is useful in the analysis of *isothermal* processes. Consider two systems ($A_0 = A_1 + A_2$) interacting mechanically and diffusively but held at constant temperature. For each, the change in Helmholtz free energy is given from equation $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$ by

$$\mathrm{d}F = -p\mathrm{d}V + \mu\mathrm{d}N \text{ (isothermal, } \mathrm{d}T = 0).$$

Since the volume and particles gained by one are lost by the other,

$$\mathrm{d}V_2 = -\mathrm{d}V_1,\ \mathrm{d}N_2 = -\mathrm{d}N_1,$$

we can write the total change in F as

$$\mathrm{d}F_0 = \mathrm{d}F_1 + \mathrm{d}F_2 = -(p_1 - p_2)\mathrm{d}V_1 + (\mu_1 - \mu_2)\mathrm{d}N_1.$$

V to be gained by the system with greater p, and particles to flow towards smaller μ.

$$-(p_1 - p_2)\mathrm{d}V_1 \le 0,\ (\mu_1 - \mu_2)\mathrm{d}N_1 \le 0 \Rightarrow \mathrm{d}F_0 \le 0.$$

For systems interacting isothermally, the second law demands that changes in their Helmholtz free energy must be negative, reaching a minimum at equilibrium.

If the process is both isothermal and nondiffusive ($\mathrm{d}T = \mathrm{d}N = 0$), the Helmholtz free energy measures the work done: $\mathrm{d}F = -p\mathrm{d}V$

For this reason, it is sometimes called the work function.

• Enthalpy

The enthalpy can be useful in the analysis of *isobaric* processes. Two systems interacting thermally and diffusively: held at constant pressure. For each, the change in enthalpy is given by: $dH = TdS + Vdp + \mu dN$ *and* $dE = TdS - pdV + \mu dN$

$$dH = dE + pdV \text{ (isobaric, } dp = 0)$$

Since the energy or volume gained by one comes from the other,

$$dE_2 = -dE_1,\ dV_2 = -dV_1,$$

the change in enthalpy for the combined system can be written as

$$dH_0 = 0 + (p_1 - p_2)dV_1$$

Second law: the right term is positive (V is gained by the system under higher p), so $dH_0 \geq 0$

Consequently, as systems approach equilibrium under isobaric conditions, changes in their enthalpy must be positive, reaching a maximum at equilibrium.

According to $dH = TdS + Vdp + \mu dN$, for processes that are nondiffusive as well as isobaric ($dp = dN = 0$), the enthalpy measures the heat transfer (heat function):

$$dH = TdS \qquad \text{(isobaric and nondiffusive, } dp = dN = 0)$$

• Gibbs free energy

Gibbs free energy is relevant in *diffusive* processes that reach equilibrium under *isothermal and isobaric* constraints ($dT = dp = 0$). Two systems interacting diffusively, because $dG = -SdT + Vdp + \mu dN$, the change in Gibbs free energy for either is $dG = \mu dN$ ($dT = dp = 0$)

Since particles gained by one are lost by the other ($dN_2 = -dN_1$), the change in Gibbs free energy for the combined system is

$$dG_0 = dG_1 + dG_2 = (\mu_1 - \mu_2)dN_1.$$

Second law: N is gained by the system with lower μ, so the term on the right must be negative, so $dG_0 \leq 0$

When a system is in diffusive equilibrium its Gibbs free energy is a minimum for that particular temperature and pressure.

Summary: for an equilibrium state,
Entropy S and Enthalpy H are at maximum,
Helmholtz free energy F and Gibbs free energy G are at minimum

• Maxwell's relations

The differentials dE, dF, dH, dG are exact.

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\mathrm{d}N \qquad \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\mathrm{d}N$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\mathrm{d}N \qquad \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\mathrm{d}N$$

Suppose that w is a function of (x, y, z) : $w = w(x, y, z)$. Its differential is given by

$$\mathrm{d}w = f\,\mathrm{d}x + g\,\mathrm{d}y + h\,\mathrm{d}z$$

$$f = \left(\frac{\partial w}{\partial x}\right)_{y,z}, \quad g = \left(\frac{\partial w}{\partial y}\right)_{x,z}, \quad h = \left(\frac{\partial w}{\partial z}\right)_{x,y}$$

Using the property that for exact differentials $\frac{\partial^2 w}{\partial y \partial x} = \frac{\partial^2 w}{\partial x \partial y}$, we get $\left(\frac{\partial f}{\partial y}\right)_{x,z} = \left(\frac{\partial g}{\partial x}\right)_{y,z}$

For the pair variables (x, z) and (y, z): $\left(\frac{\partial f}{\partial z}\right)_{x,y} = \left(\frac{\partial h}{\partial x}\right)_{y,z}$, and $\left(\frac{\partial g}{\partial z}\right)_{x,y} = \left(\frac{\partial h}{\partial y}\right)_{x,z}$

If $w = E$, $f = T$, $g = -p$, $h = \mu$, $\qquad x = S$, $y = V$, $z = N$,

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

• Maxwell's relations (Homework)

We now apply this to the following thermodynamic potentials:

Derived from internal energy, $E(S, V, N)$:

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

Derived from Helmholtz free energy, $F(T, V, N)$:

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

Derived from enthalpy, $H(S, p, N)$:

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

Derived from Gibb's free energy, $G(T, p, N)$:

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

Do more practice by yourself

• Heat capacity and compressibility

$$S(T,y)=\int_0^T \frac{C_y dT'}{T'}$$

Usually, we use *molar* heat capacities because we want our tests to depend only on the nature of the material and not on its size. The "*n*" is the molar number of a system:

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

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

and the coefficient of volume expansion, $\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Next let's calculate the heat capacities of ideal gas.

• Ideal Gas: Heat capacity

The first law ($dE = dQ - pdV$, with $N = N_A$), we get for one molar

$$dQ = dE + p\,dV = \frac{\nu}{2} R\,dT + p\,dV \qquad E_{\text{molar}} = N_A\left(\frac{\nu}{2}kT\right) = \frac{\nu}{2}RT$$

so that the molar heat capacities at constant y become

$$C_y = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_y = \frac{\nu}{2}R + p\left(\frac{\partial V}{\partial T}\right)_y$$

The molar heat capacities at constant volume $C_V \approx \frac{\nu}{2}R$

Constant pressure $C_p = \frac{\nu}{2}R + p\left(\frac{\partial V}{\partial T}\right)_p$

Equation of state: $pV = RT$,

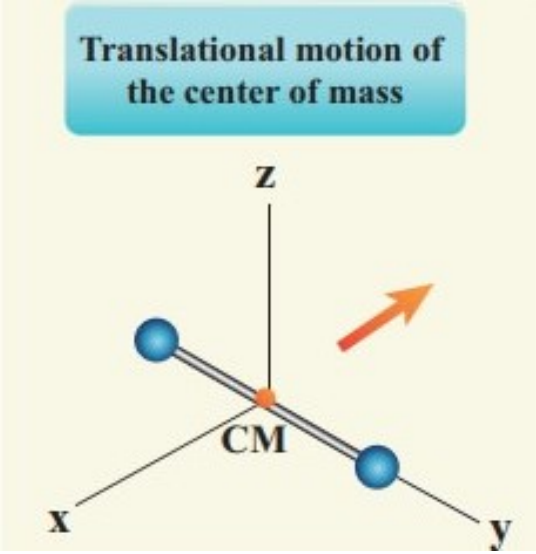
$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{Vp} = \frac{1}{T}$$

$$= \frac{\nu}{2}R + pV\beta = \frac{\nu}{2}R + R$$

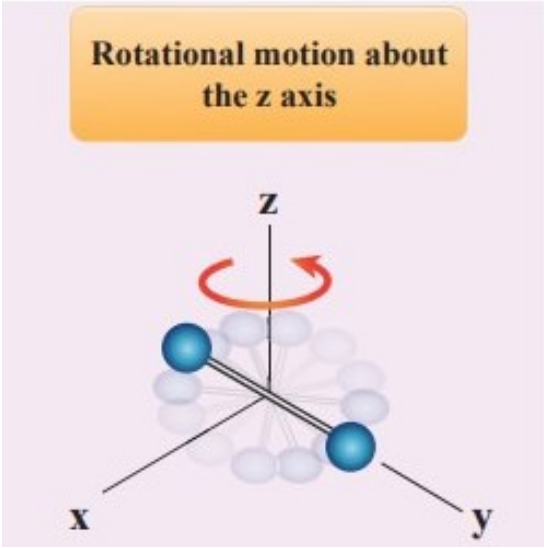
$$C_p - C_V \approx pV\beta = R$$

C_V and C_p for monoatomic gas?
Diatomic gas?

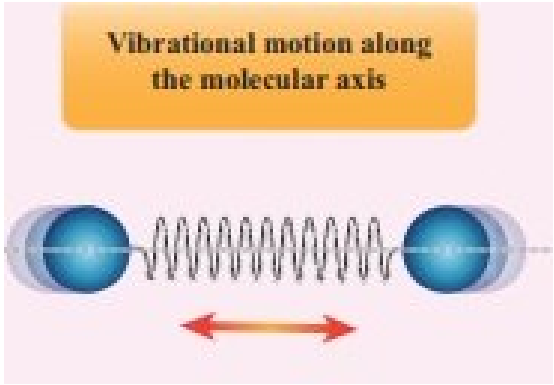
• Team Discussion: Diatomic gas



$$\frac{1}{2M_{mole}}p_x^2+\frac{1}{2M_{mole}}p_y^2+\frac{1}{2M_{mole}}p_z^2$$



$$\frac{1}{2I_y}L_y^2+\frac{1}{2I_x}L_x^2$$



$$\frac{1}{2\mu}p_{relative}^2+\frac{k}{2}x_{relative}^2$$

μ is reduced mass

Rigid bond mode: total 5 degrees of freedom, with 3 from translational motion and two from rotational motion.

Spring mode: total 7 degrees of freedom, with 3 from translational motion, two from rotational motion, and two from vibrational motion (active at high temperature).

• Strategy for solving equation of state (p, V, T)

(1) We start with the entropy of ideal gas:

$$S = k \ln \Omega = k \ln\left(\omega_{\mathrm{c}}^{N}\right) = Nk \ln \omega_{\mathrm{c}}, \qquad \omega_{\mathrm{c,gas}} \approx \left(C\frac{V}{N}\right)\left(\frac{E_{\mathrm{therm}}}{Nv}\right)^{v/2}$$

to find that the entropies are the following functions of E, V, N:

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

(2) Then we use the following equations with extrinsic variables S, E, V, N.

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

Apply to the entropy, these three equations give us for an ideal gas

$$E = \frac{Nv}{2}kT, \quad \text{equipartition} \qquad N\mu = NkT\left(\frac{v+2}{2} - \ln \omega_{\mathrm{c}}\right) \qquad S = k \ln\Omega = N k \ln\omega_{\mathrm{c}}$$

$$pV = NkT, \quad \textbf{Equation of state (ideal gas law)} \qquad = E + pV - NkT \ln \omega_{\mathrm{c}} \qquad E = TS - pV + \mu N$$

Next week:

Classical statistic,

Ensembles,