Systems in Thermal Contact with a Heat Reservoir

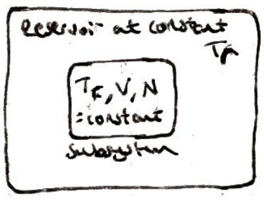
The Canonical Ensemble

Consider a microcanonical ensemble made up of macroscopic isolated systems, each system divided up into a large number of subsystems in mutual thermal contact with each other.

Assume all interactions among subsystems are negligible, i.e the subsystems are quasistatic, and can be considered statistically uncorrellated. So for two subsystems A and B with statistical distributions $\rho_A(q_A, p_A)$ and $\rho_B(q_B, p_B)$ have combined distribution:

$$\rho_{A+B} = \rho_A \rho_B$$

Let's consider a specific subsystem with volume V, number of particles N and Energy E. Hereafter, we refer to this subsystem as the "system" so don't get confused:



This small system is in thermal contact with a thermal reservoir. Since equilibrium is assumed, temperature of system is same as temperature of reservoir T_r.

The total energy remains constant and is conserved:

$$E_t = \underbrace{E_r}_{\text{energy reservoir}} + \underbrace{E}_{\text{energy system}} = \underbrace{E_0}_{\text{constant}}$$

The infinitesimal probability dP_t that the total system is in a phase space with volume $dp_t\, dq_t$ is:

$$dP_t = C_s\, \delta(E + E_r - E_0)\, dW_t$$

where dW_t is infinitesimal number of microstates in $dq_t\, dp_t$

$$dW_t = \frac{dp_t \, dq_t}{h^{3N} N!}$$

C_s is the scaled normalisation constant : $C_s = h^{3N} N! \, C$

We can write $dW_t = dW \, dW_r$ due to statistical independence.
where dW is infitesimal no. microstates of the system corresponding to $dp dq$, while dW_r is infinitesimal number of microstates of reservoir corresponding to $dp_r \, dq_r$.

$\therefore \quad dP_t = C_s \, \delta(E + E_r - E_0) \, dW \, dW_r$ integrate over all reservoir

$$\frac{dP(E)}{dW} = \omega(E) = C_s \int \delta(E + E_r - E_0) \, dW_r$$

where $dP(E)$ is probability of system to be in microstate with energy between E, $E + \delta E$

we get $dP(E)$ from :
$$\frac{dP_t}{dW} = \frac{dP \, dP_r}{dW} = \frac{dP}{dW} \underbrace{\int dP_r}_{=1}$$

$\omega(E)$ is the canonical distribution.
It is proportional to statistical distribution in phase space $\rho(E)$,
ie $\rho(E(p,q)) = \rho(p,q)$

The canonical distribution has explicit form

$$\boxed{\omega(E) = A e^{-E/\tau}}$$ This is also called Gibbs distribution.

If we define partition function: $\boxed{Z = \int e^{-E/\tau} \, dW}$

the canonical distribution can be written as:

$$\boxed{\omega(E) = \frac{e^{-E/\tau}}{Z}}$$

we can compute Z using $dW = \dfrac{d^{3N}p \, d^{3N}q}{h^{3N} N!}$ so $Z = \displaystyle\int e^{-E/\tau} \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!}$

We can compute the average value of energy:

$$\langle E \rangle = \int E\, w(E)\, dW = \int E \cdot \frac{1}{Z} e^{-E/\tau}\, dW \qquad \text{let } \beta = \frac{1}{\tau}$$

$$= \frac{1}{Z} \int E e^{-\beta E}\, dW \qquad \left[\text{but } Z = \int e^{-\beta E}\, dW \text{ and } \frac{\partial}{\partial \beta} Z = -E e^{-\beta E} \right]$$

$$= \underline{-\frac{\partial}{\partial \beta} \ln Z} \qquad = \underline{\tau^2 \frac{\partial}{\partial \tau} \ln Z}$$

Importance of the Free Energy F

The free energy F is given by:

$$\boxed{F = -\tau \ln Z = -k_B T \ln Z}$$

Recipe to calculate all other TD quantities:

1) Compute Partition function Z
2) Use $F = -k_B T \ln Z$ to obtain free energy
3) Recast $dF = -S\,dT - p\,dV$ from section 3 to:

$$dF = -\sigma\, d\tau - p\, dV$$

then:

$$\sigma = -\left.\frac{\partial F}{\partial \tau}\right|_V \qquad p = -\left.\frac{\partial F}{\partial V}\right|_\tau$$

Note:

$$\langle E \rangle = \tau^2 \frac{\partial}{\partial \tau} \ln Z = \tau^2 \frac{\partial}{\partial \tau}\left(-\frac{F}{\tau}\right)_V = -\tau^2 \frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)_V$$

$$= -\tau^2 \left\{ F \cdot -\tau^{-2} + \frac{1}{\tau}\frac{\partial F}{\partial \tau} \right\} = F - \tau \left.\frac{\partial F}{\partial \tau}\right|_V$$

$$= F + \tau\sigma = \underline{\underline{U}}$$

This is reassuring

Ideal Gas in the Canonical Ensemble

The equipartition function for an ideal gas is:

$$Z = \int e^{-E(p,q)/\tau} \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!}$$

For an ideal gas with N identical particles, total energy is sum of energy of each particle: $E(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2M}$

The integral thus gives:

$$Z = \frac{V^N}{h^{3N} N!} \left[\int_{-\infty}^{\infty} e^{-p_i^2/2m\tau} \, dp_i \right]^{3N}$$

where V^N is result of integral over the coordinates (q)

evaluating this:

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m \tau}{h^2} \right)^{3N/2}$$

If we define thermal de Broglie wavelength as: $\boxed{\lambda_{th} = \frac{h}{\sqrt{2\pi m \tau}}}$

the partition function is: $Z = \frac{1}{N!} \left(\frac{V}{\lambda_{th}^3} \right)^N$ showing it is a dimensionless quantity.

We can thus write free energy: $F = -\tau \ln Z$ use Stirling's approx

$$F = -N\tau \ln \left(\frac{eV}{N\lambda_{th}^3} \right)$$

Entropy is: $\sigma = N \ln \left(\frac{eV}{N\lambda_{th}^3} \right) + \frac{3N}{2}$ using $\sigma = -\left.\frac{\partial F}{\partial \tau}\right|_V$

using $n = N/V$: $\sigma = N \left[\frac{5}{2} - \ln(n\lambda_{th}^3) \right]$

The Boltzman Distribution

Recall $\frac{dP(E)}{dW} = \omega(E)$

For a particle with position vector $\underline{x}$ and momenta $\underline{p}$, the energy E can be written as $E(\underline{x}, \underline{p})$

so $$\frac{dP(\underline{x},\underline{p})}{dW} = \omega(\underline{x},\underline{p})$$

$$dP(\underline{x},\underline{p}) = \frac{e^{-\varepsilon(\underline{p})/\tau}}{Z} dW$$

For one particle, $Z = \frac{V}{\lambda_{th}^3}$ so $dP = \frac{\lambda_{th}^3}{V} e^{-\varepsilon(\underline{p})/\tau} dW$

Multiplying this by number of particles N, we obtain the infinitesimal no. particles dN in region of phase space $\underline{p} \to \underline{p} + d\underline{p}$ $\underline{x} \to \underline{x} + d\underline{x}$

$$dN = n \lambda_{th}^3 e^{-\varepsilon(\underline{p})/\tau} dW$$

$$\therefore \quad \frac{dN}{dW} = f_B(\underline{p}, \underline{x}) = \underline{\underline{n \lambda_{th}^3 e^{-\varepsilon(\underline{p})/\tau}}}$$

This is the Boltzman Distribution.

Maxwell Distribution of Velocities

Let's start from $dP = \frac{\lambda_{th}^3}{V} e^{-\frac{\varepsilon(\underline{p})}{\tau}} dW$ and integrate over the spacial coordinates $\underline{x}$. This gives us the infinitesimal distribution dP to find particle in $[\underline{p}, \underline{p}+d\underline{p}]$:

$$dP = f_M(\underline{p})\, dp_x\, dp_y\, dp_z$$

where $f_M(\underline{p}) = \frac{\lambda_{th}^3}{h^3} \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m\tau}\right)$ since $\varepsilon(\underline{p}) = \frac{p^2}{2m}$

is the maxwell distribution of momenta.

We obtain $f_M(\underline{v})$ from $f_M(\underline{p})$ since $p_{x,y,z} = m v_{x,y,z}$

$$f_M(\underline{p})\, dp_x\, dp_y\, dp_z = f_M(\underline{v})\, dv_x\, dv_y\, dv_z$$

but $dp_x dp_y dp_z = m^3 dv_x dv_y dv_z$

$$\Rightarrow \quad f_M(\underline{v}) = m^3 f_M(\underline{p})$$

$$\therefore \quad f_M(\underline{v}) = m^3 \frac{\lambda_{th}^3}{h^3} \exp\left(-\frac{m(v_x^2+v_y^2+v_z^2)}{2\tau}\right)$$

but $\lambda_{th} = \frac{h}{\sqrt{2\pi m\tau}}$ so :

$$f_M(\underline{v}) = \left(\frac{m}{2\pi\tau}\right)^{3/2} \exp\left(-\frac{m(v_x^2+v_y^2+v_z^2)}{2\tau}\right)$$

so for one particular component :

$$f_M(v_i) = \sqrt{\frac{m}{2\pi\tau}}\, e^{-mv_i^2/2\tau}$$

we can also work out distribution of energy $f_M(\varepsilon)$ from $f_M(|\underline{p}|)$:

$= f_M(p)$

$$f_M(p) = 4\pi \left(\frac{1}{2\pi m\tau}\right)^{3/2} p^2 e^{-p^2/2m\tau}$$

so $$f_M(\varepsilon) = 2\pi \left(\frac{1}{\pi\tau}\right)^{3/2} \sqrt{\varepsilon}\, e^{-\varepsilon/\tau}$$

and speed distribution is :

$$f_M(v) = 4\pi \left(\frac{m}{2\pi\tau}\right)^{3/2} v^2 e^{-mv^2/2\tau}$$

Theorem of Equipartition Energy

Consider energy of a system in a canonical ensemble being the sum of quadratic term in position and momenta, denoted generically with x_j, so that:

$$E = \sum_{j=1}^{f} a_j x_j^2$$ where a_j are positive constants for KE terms where x_j is a component of momentum

The number f is the number of quadratic terms in position (or number of components of momentum) in the expression for the energy. By number of quadratic terms, we mean x^2, p_x^2, y^2, p_y^2 etc but not xp_y or xy etc.

This gives:

$$\langle E \rangle = \frac{f\tau}{2}$$ a remarkable result!

So each quadratic term gives the same contribution $\frac{\tau}{2}$!

Energy is equally partitioned!

We extract heat capacity C_v:

$$C_v = \frac{\partial U}{\partial T} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_v = \frac{f}{2} k_B$$ remember, $\tau = k_B T$

Discrete Systems

So far we looked at the canonical ensemble only for classical systems, but what about discrete?

Here, the probabilities for the total system is just $P_i^t = \frac{1}{W_t}$ where W_t is the number of microstates accessible to the total system.

For subsystem the canonical distribution of probabilities is given by

$$P_i = \frac{e^{-E_i/\tau}}{Z}$$

where E_i is energy of subsystem in i^{th} microstate.

$$Z = \sum_i e^{-E_i/\tau}$$

The probability of a particular energy in the system is given by the P_i multiplied by the weighting $W(E_i)$ of macrostate E_i :

$$P(E_i) = W(E_i)\frac{e^{-E_i/\tau}}{Z}$$

Entropy in the Canonical Ensemble

The entropy can be expressed in terms of free energy $F = -\tau \ln Z$ and the internal energy $U = \langle E \rangle$ as:

$$\sigma = \frac{U-F}{\tau} \quad \text{from} \quad F + \tau\sigma = U$$

$$= \frac{1}{\tau}\left(\sum_i E_i P_i + \tau \ln Z\right) \quad \text{since } U = \langle E \rangle = \sum_i P_i E_i$$

$$\sigma = \sum_i \frac{E_i P_i}{\tau} + \underset{\substack{\uparrow \\ \text{outside} \\ \text{sum}}}{\ln Z} \qquad \sigma = \sum_i P_i\left(\frac{E_i}{\tau} + \ln Z\right) \text{ using } \sum_i P_i = 1 \text{ so } \sum_i P_i \ln Z = \ln Z$$

$$\sigma = \sum_i P_i \left(\frac{E_i}{\tau} + \ln Z \right)$$

Taking logarithm of $P_i = \frac{e^{-E_i/\tau}}{Z}$

$$\frac{E_i}{\tau} + \ln Z = -\ln P_i$$

so $\sigma = \sum_i P_i (-\ln P_i)$

$$\therefore \quad \boxed{\sigma = -\sum P_i \ln P_i = -\langle \ln P \rangle}$$

known as Gibbs Entropy. Note, the minus sign ensures $\sigma > 0$ since $\ln P_i < 0$ as $0 < P_i < 1$

Gibbs Entropy is a generalisation of Boltzman entropy.

In a microcanonical ensemble $E_i = E_0$ for all i so $P_i = \frac{1}{W(E_0)}$

$$\sigma(E_i = E_0) = -\sum_{j=1}^{W} \frac{1}{W} \ln\left(\frac{1}{W}\right) = \ln(W)$$

reproducing Boltzman entropy of the microcanonical ensemble.