Notes on statistical Mechanics[1]

Arjun Mukhopadhyay

April 11, 2020

[1] E&OE

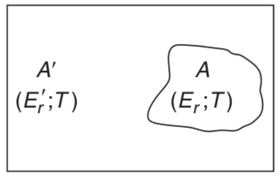

Figure 1

Canonical Ensemble

In microcanonical ensemble the system in its macrostate is defined by (N,V,E) where E is the fixed energy or enregy may vary in the range $E-\Delta$ to $E+\Delta$. The number of microstates $\Omega(N,V,E)$ compatible with the macrostate is the key to solve the thermodynamical problem and the determination of the number is quite a formidable task. Physically too, the concept of fixed enregy is not satisfactory because E can not be measured directly. in this situation, a system can be introduced that corresponds to an ensemble where all the elements are characterized by same temperature T. This can be done by taking a system in contact with a heat reservoir of infinite heat capacity. If the reservoir consists of an infinitely large number of replicas of the given system, then they together form another type of ensemble called canonical ensemble. In canonical ensemble the energy E is variable, it can take any values from 0 to ∞. The question is that what is the probability of a system in the ensemble found to be in any of the microstates characterized by the energy value E_r at any time t?

Equilibrium between a system and a heat reservoir

Consider **Figure 1**. The system $A(E_r;T)$ is immersed in a heat reservoir $A^{'}(E_r^{'};T)$, much larger than the system. The system and the reservoir would have a common temperature T but these energies vary from 0 to $E^{(0)}$where

$$E^{(0)} = E_r + E_r^{'} \tag{1}$$

and it is possible because the heat capacity of the reservoir is infinite.

Now

$$\frac{E_r}{E^{(0)}} = \left(1 - \frac{E_r^{'}}{E^{(0)}}\right) \ll 1. \tag{2}$$

The number of the states corresponding to $E_r^{'}$of the reservoir is denoted by $\Omega^{'}\left(E_r^{'}\right)$. This number depends upon the nature of the reservoir. The larger the number of states avilavle to energy $E_r^{'}$, the greater is the probability of the reservoir assuming $E_r^{'}$ (and the system of assuming E_r).

Thus

$$p_r \propto \Omega^{'}\left(E_r^{'}\right) \equiv \Omega^{'}\left(E^{(0)} - E_r\right) \tag{3}$$

which follows

$$\ln \Omega^{'} \left(E^{(0)} - E_r\right) = \ln \Omega^{'} \left(E^{(0)}\right) - E_r \frac{\partial \ln \Omega^{'}}{\partial E_r^{'}}. \tag{4}$$

Hence

$$\ln \Omega^{'} \left(E_r^{'}\right) \simeq C^{'} + \left(E_r^{'} - E^{(0)}\right) \frac{\partial \ln \Omega^{'}}{\partial E_r^{'}} = C^{'} - \beta^{'} E_r \tag{5}$$

where

$$C^{'} = \ln \Omega^{'} \left(E^{(0)}\right) \text{ and } \beta^{'} \equiv \frac{\partial \ln \Omega^{'}}{\partial E_r^{'}} \tag{6}$$

$\beta = \beta^{'} = \frac{1}{kT}$ in equilibrium.
So

$$p_r \simeq \exp\left(C^{'} - \beta E_r\right) = K e^{-\beta E_r}, K = \exp\left(C^{'}\right) \tag{7}$$

Normalizing we get $\sum p_r = 1$.

$$\begin{aligned} \sum P_r &= K \sum e^{-\beta E_r} \\ \implies k &= \frac{1}{e^{-\beta E_r}} \end{aligned}$$

So

$$P_r = \frac{\exp\left(-\beta E_r\right)}{\sum\limits_r \exp\left(-\beta E_r\right)} \tag{8}$$

Various statistical quantities in the canonical ensemble

Average energy

$$\begin{aligned} U &= \frac{\sum\limits_r E_r \exp\left(-\beta E_r\right)}{\sum\limits_r \exp\left(-\beta E_r\right)} \\ &= -\frac{\partial}{\partial \beta} \ln \left\{ \sum_r \exp\left(-\beta E_r\right) \right\} \end{aligned} \tag{9}$$

Helmholtz free energy

$$A = U - TS \tag{10}$$

whence follows

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}, P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}, \mu = -\left(\frac{\partial A}{\partial N}\right)_{V,T} \tag{11}$$

and

$$\begin{aligned} U &= A+TS \\ &= A-T\left(\frac{\partial A}{\partial T}\right)_{N,V} \\ &= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V} \\ &= \left[\frac{\partial\left(A/T\right)}{\partial\left(1/T\right)}\right]_{N,V} \\ &= \left[\frac{\partial\left(A/KT\right)}{\partial\left(1/KT\right)}\right]_{N,V} = \left[\frac{\partial\left(A/KT\right)}{\partial\beta}\right]_{N,V}. \end{aligned} \tag{12}$$

From eqns (9) and (12) we have

$$-\frac{A}{kT} = \ln\left\{\sum_r \exp\left(-\beta E_r\right)\right\} \tag{13}$$

The eqn (13) constitutes the most fundamental result of the canonical ensemble theory. Customarily we write this in the form

$$A\left(N,V,T\right) = -kT\ln Q_N\left(V,T\right) \tag{14}$$

where

$$Q_N\left(V,T\right) = \sum_r \exp\left(-\beta E_r\right) \tag{15}$$

$Q_N\left(V,T\right)$ is referred to the partition function of the system. It's considered as the sum over all states. The dependence of $Q_N\left(V,T\right)$ on $N$and V is through E_r. For the quantity $A(N,V,T)$ to be extensive, $\ln Q$ must be extensive. The other thermodynamic quantities can be expressed as follows,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V} \tag{16}$$

$$G = A+PV = A-V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu \tag{17}$$

Now

$$
\begin{aligned}
P &= -\left(\frac{\partial A}{\partial V}\right)_{N,T} \\
&= -\frac{\partial}{\partial V}\left[-kT\ln\left\{\sum_r \exp\left(-\beta E_r\right)\right\}\right] \\
&= \frac{1}{\beta}\frac{\partial}{\partial V}\left[\ln\left\{\sum_r \exp\left(-\beta E_r\right)\right\}\right] \\
&= -\frac{\sum_r \frac{\partial E_r}{\partial V}\exp\left(-\beta E_r\right)}{\sum_r \exp\left(-\beta E_r\right)}
\end{aligned}
$$

$$
\Longrightarrow PdV = -\sum_r P_r dE_r = -dU \tag{18}
$$

The quantity on the R.H.S of the eqn. (18) is clearly the change in the internal energy of the system (in the ensemble) during a process that alters the energy levels E_r, p_r unchanged. The left hand side then tells us that the volume change dV provides an example of such a process where the pressure P is the 'force' accompanying the process.

About entropy

$$
p_r = Q^{-1}\exp\left(-\beta E_r\right) \tag{19}
$$

$$
\begin{aligned}
\langle \ln p_r \rangle &= -\ln Q - \beta\left\langle E_r\right\rangle \\
&= \beta\left[A - \left\langle E_r\right\rangle\right] \\
&= \beta\left[A - U\right] = -\frac{S}{k}
\end{aligned} \tag{20}
$$

$$
\Longrightarrow S = -k\left\langle \ln p_r\right\rangle = -k\sum_r p_r \ln p_r \tag{21}
$$

The eqn. (21) is an interesting one from which one may conclude

- If $T = 0$, the system is in its ground state, p_r is 1 for this state. Essentially $S = 0$. This is **Nernst heat theorem** or the **Third law of Thermodynamics.**
- Vanishing entropy and perfect statistical order go together.
- Largeness of entropy and high degree of statistical disorder go together.

It may be pointed out that the formula (21) applies in the microcanonical ensemble as well. For each member system of the ensemble, we have a group of Ω no. of states, all occuring equally likely. Then $p_r = \frac{1}{\Omega}$,

$$S = -k\sum_{r=1}^{\Omega}\frac{1}{\Omega}\ln\left(\frac{1}{\Omega}\right) = k\ln\Omega \tag{22}$$

Alternative expression for the partition function

If g_i is the degenarcy of an energy state E_i, then

$$Q_N(V,T) = \sum_i g_i \exp\left(-\beta E_i\right). \tag{23}$$

Therefore

$$p_i = \frac{g_i \exp\left(-\beta E_i\right)}{\sum_i g_i \exp\left(-\beta E_i\right)} \tag{24}$$

If the difference in the energy levels are small enough so that E can be taken as continuous variable then $p(E)dE$ is the probability of the system in the ensemble having its energy lying between $E \text{and} E + dE$. Then

$$p(E)dE \propto \exp\left(-\beta E\right) g\left(E\right) dE. \tag{25}$$

Normalizing

$$p(E)dE = \frac{\exp\left(-\beta E\right) g\left(E\right) dE}{\int\limits_0^\infty \exp\left(-\beta E\right) g\left(E\right) dE} \tag{26}$$

clearly

$$Q_N(V,T) = \int\limits_0^\infty \exp\left(-\beta E\right) g\left(E\right) dE \tag{27}$$

and the expectation value of a physical quantity $f$is

$$\langle f\rangle = \frac{\sum\limits_i f\left(E_i\right) g\left(i\right) e^{-\beta E_i}}{\sum\limits_i f\left(E_i\right) g\left(i\right) e^{-\beta E_i}} \rightarrow \frac{\int\limits_0^\infty f\left(E\right) \exp\left(-\beta E\right) g\left(E\right) dE}{\int\limits_0^\infty \exp\left(-\beta E\right) g\left(E\right) dE} \tag{28}$$

From **eqn. (27)**, if $\beta > 0$, the partition function $Q\left(\beta\right)$ is just the lapcace transform of the density of states $g\left(E\right)$. We may therefore write inverse laplace transforms of $Q\left(\beta\right)$;

$$g\left(\beta\right) = \frac{1}{2\pi i}\int\limits_{\beta^{'}-i\infty}^{\beta^{'}+i\infty} e^{\beta E} Q\left(\beta\right) d\beta \quad \left(\beta^{'} > 0\right) \tag{29}$$

$$= \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} e^{\left(\beta^{'}+i\beta^{"}\right)E} Q\left(\beta^{'} + i\beta^{"}\right) d\beta^{"} \tag{30}$$

Bibliography

[1] Statistical Mechanics: R. K. Pathria