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Open System : Grand Canonical Ensemble

Grand Canonical Ensemble is useful in the study of open systems.

6.1 What is an Open System ?

An open system is one which exchanges energy and matter with its surroundings. The surroundings act as a heat bath as well as a particle (or material) bath.

- A heat bath transacts energy with the system. The temperature of the heat bath does not change because of the transaction.
- A material (or particle) bath transacts matter (or particles) with the system. The chemical potential of the material bath does not change because of the transaction.

The system is in thermal and diffusional equilibrium with the surroundings¹. The system can be described by its temperature, T , volume, V and chemical potential, μ . Notice that T , μ , and V are independent properties of an open system. Since the system is *not isolated*, its micro states are *not equi-probable*. Our aim is to calculate the probability of a micro state of the open system.

Let us take the open system, its boundary and surroundings and construct a universe, which constitutes an isolated system. *We are interested in constructing an isolated system because, we want to start with the only assumption we make in statistical mechanics : all the micro states of an isolated system are equally probable.* We have called this the *ergodic* hypothesis.

Let \mathcal{E} denote the total energy of the universe. $\mathcal{E} \gg E$, where E is the (average or typical) energy of the open system under study. Let \mathcal{N} denote the total number of particles in the universe. $\mathcal{N} \gg N$, where N is the (average or typical) number of particles in the open system.

We want to describe the open system in terms of its own micro states. Let C be a micro state of the open system. Let

- $E(C)$ be the energy of the open system when it is in its micro state C and
- let $N(C)$ be the number of particles in the open system when it is in its micro state C .

When the open system is in micro state C the universe can be in any one of its innumerable micro states² such that the energy of the surroundings is

¹equality of temperature signals thermal equilibrium; equality of chemical potential ensures diffusional or material equilibrium.

² The picture I have is the following. I am visualizing a micro state of the universe as consisting of two parts. One part holds the signature of the open system; the other holds the signature of the surroundings. For example a string of positions and momenta of all the particles in the universe defines a micro state. This string consists of two parts. The first

$\mathcal{E} - E(C)$ and the number of particles in the surroundings is $\mathcal{N} - N(C)$.

Let

$$\Omega_C = \Omega(\mathcal{E} - E(C), \mathcal{N} - N(C)),$$

denote the subset of micro states of the universe having common property described below.

When the universe is in a micro state belonging to Ω_C , then the system is in the chosen micro state C and the surroundings can be in any of its micro states having energy $\mathcal{E} - E(C)$ and the number of particles $\mathcal{N} - N(C)$.

Let $\hat{\Omega}_C$ denote the number of elements in the subset Ω_C . Following Boltzmann we define a statistical entropy associated with the event Ω_C as

$$\begin{aligned} S_C &= k_B \ln \hat{\Omega}_C \\ &= k_B \ln \hat{\Omega}(\mathcal{E} - E(C), \mathcal{N} - N(C)) \\ &= S(\mathcal{E} - E(C), \mathcal{N} - N(C)). \end{aligned} \tag{6.1}$$

Since $E(C) \ll \mathcal{E}$, and $N(C) \ll \mathcal{N}$, we can Taylor-expand S retaining only the first two terms. We have

$$S(\mathcal{E} - E(C), \mathcal{N} - N(C)) = S(\mathcal{E}, \mathcal{N}) - E(C) \frac{\partial S}{\partial E} - N(C) \frac{\partial S}{\partial N} \tag{6.2}$$

From the first law of thermodynamics we have, for a reversible process,

$$dE = TdS - PdV + \mu dN \tag{6.3}$$

part contains the positions and momenta of all the particle in the open system; the second part contains the positions and momenta of all the particles in the surroundings. Since the system is open, the length system-string is a fluctuating quantity and so is the length of bath-string. However the string of the universe is of fixed length.

from which it follows,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (6.4)$$

We have

$$S \equiv S(E, V, N) \quad (6.5)$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE + \left(\frac{\partial S}{\partial V} \right)_{E,N} dV + \left(\frac{\partial S}{\partial N} \right)_{E,V} dN \quad (6.6)$$

Comparing the coefficients of dE , dV and dN , in equations (6.4) and (6.6), we get,

$$\left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} ; \quad \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{P}{T} ; \quad \left(\frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T} \quad (6.7)$$

Therefore,

$$S\left(\mathcal{E} - E(C), \mathcal{N} - N(C)\right) = S\left(\mathcal{E}, \mathcal{N}\right) - \frac{1}{T}E(C) + \frac{\mu}{T}N(C) \quad (6.8)$$

The probability of the micro state C is given by

$$P(C) = \frac{\hat{\Omega}\left(\mathcal{E} - E(C), \mathcal{N} - N(C)\right)}{\hat{\Omega}_{\text{Total}}} \quad (6.9)$$

We are able to write the above because of the postulate of ergodicity : *All micro states of the universe - an isolated system, are equally probable.* We

have,

$$\begin{aligned}
 P(C) &= \frac{1}{\hat{\Omega}_{\text{Total}}} \exp \left[\frac{1}{k_B} S \left(\mathcal{E} - E(C), \mathcal{N} - N(C) \right) \right] \\
 &= \frac{1}{\hat{\Omega}_{\text{Total}}} \exp \left[\frac{S(\mathcal{E}, \mathcal{N})}{k_B} - \frac{E(C)}{k_B T} + \frac{\mu N(C)}{k_B T} \right] \\
 &= \alpha \exp(-\beta [E(C) - \mu N(C)]). \tag{6.10}
 \end{aligned}$$

In the above, the constant α can be determined by the normalization condition, $\sum_c P(C) = 1$, where the sum runs over all the micro states of the open system. We have,

$$P(C) = \frac{1}{Q} \exp(-\beta [E(C) - \mu N(C)]) \tag{6.11}$$

where the grand canonical partition function is given by

$$Q(T, V, \mu) = \sum_C \exp(-\beta [E(C) - \mu N(C)]) \tag{6.12}$$

The fugacity is given by $\lambda = \exp(\beta\mu)$; then we can write the grand canonical partition function as,

$$Q(T, V, \lambda) = \sum_C \lambda^{N(C)} \exp[-\beta E(C)] \tag{6.13}$$

- Collect those micro states of a grand canonical ensemble with a fixed value of N . Then these micro states constitute a canonical ensemble described by the canonical partition function, $Q(T, V, N)$.
- Collect all the micro states of a grand canonical ensemble with a fixed energy. and fixed number of particles. Then these micro states constitute a microcanonical ensemble.

Thus we can write the grand canonical partition function as,

$$\mathcal{Q}(T, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N Q(T, V, N) \quad (6.14)$$

Let $Q_1(T, V)$ denote single-particle canonical partition function. We have

$$Q(T, V, N) = Q_N(T, V) = \frac{Q_1^N}{N!}. \quad (6.15)$$

Therefore,

$$\mathcal{Q}(T, V, \mu) = \sum_{N=0}^{\infty} \frac{\lambda^N Q_1^N}{N!} = \exp(\lambda Q_1) \quad (6.16)$$

Grand canonical ensemble is an extremely useful ensemble. The reason is that the constraint of constant N required for calculating the canonical ensemble is often mathematically awkward³.

6.2 Micro-Macro Synthesis : \mathcal{Q} and \mathcal{G}

- Entropy is the thermodynamic counter part of the statistical mechanical micro canonical partition function - the density of states. We have $S(E, V, N) = k_B \ln \hat{\Omega}(E, V, N)$.
- Helmholtz free energy is the thermodynamic counter part of the statistical mechanical canonical partition function, $Q(T, V, N)$. We have $F(T, V, N) = -k_B T \ln Q(T, V, N)$.

³We shall experience this while trying to evaluate the canonical partition function for fermions and bosons. We will not be able to carry out the sum over occupation numbers because of the constraint that they add up to a constant N . Hence we shall multiply the restricted sum by λ^N and sum over all possible values of N . This would remove the restriction and we shall express the partition function as sum over (micro states) of product (over occupation numbers). We shall interpret λ as fugacity. The chemical potential and fugacity are related : $\lambda = \exp(\beta\mu)$. All these can be viewed as mathematical tricks. The language of grand canonical ensemble gives a physical meaning to these mathematical tricks.

What is the thermodynamic counter part of the grand canonical ensemble ? Let us call it, the "grand" potential; let the symbol \mathcal{G} denote the grand potential. \mathcal{G} is a function of T , V , and μ . The grand potential $\mathcal{G}(T, V, \mu)$, is obtained from $U(S, V, N)$ by Legendre transform of $S \rightarrow T$ and $N \rightarrow \mu$. We have,

$$\mathcal{G}(T, V, \mu) = U(S, V, N) - TS - \mu N \quad (6.17)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} : \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S, V} \quad (6.18)$$

Some authors *e.g.* Donald A McQuairrie, *Statistical Mechanics*, Harper and Row (1976) would like to identify PV as the thermodynamic counter part of the grand canonical ensemble. The correspondence is

$$\mathcal{G} = -PV = -k_B T \ln \mathcal{Q}.$$

Let us first establish the relation $\mathcal{G} = -k_B T \ln \mathcal{Q}$.

6.2.1 $\mathcal{G} = -k_B T \ln \mathcal{Q}$

Method-1

We follow the same method we employed for establishing the connection between Helmholtz free energy and canonical partition function. We have,

$$\mathcal{Q}(T, V, \lambda) = \sum_i \exp [-\beta (E_i - \mu N_i)] \quad (6.19)$$

where the sum runs over all the micro states i of the open system. E_i is the energy of the system when in micro state i , and N_i is the number of particles in the system when in its micro state i .

We replace the sum over micro states by sum over energy and number of particles. Let $g(E, N)$ denote the density of states. We have then,

$$\mathcal{Q}(T, V, \mu) = \int dE \int dN g(E, N) \exp[-\beta(E - \mu N)] \quad (6.20)$$

The contribution to the integrals come overwhelmingly from a single term at $E = \langle E \rangle$ and $N = \langle N \rangle$. We then get,

$$\mathcal{Q}(T, V, \mu) = g(\langle E \rangle, \langle N \rangle) \exp[-\beta(\langle E \rangle - \mu \langle N \rangle)] \quad (6.21)$$

Let us denote $\langle E \rangle$ by E and $\langle N \rangle$ by N . Taking logarithm on both sides,

$$\ln \mathcal{Q} = \ln g(E, N) - \beta(E - \mu N) \quad (6.22)$$

We then have,

$$\begin{aligned} -k_B T \ln \mathcal{Q} &= -T[k_B \ln g(E, N)] + E - \mu N \\ &= E - TS - \mu N = \mathcal{G} \end{aligned} \quad (6.23)$$

Method-2

Alternately, we start with $\mathcal{Q} = \sum_{N'} \lambda^{N'} Q(T, V, N')$. In principle, the number of particles in an equilibrium open system is not a fixed number. It fluctuates from one micro state to another. However the fluctuations are very small; it can be shown that the relative fluctuations are inversely proportional to the size of the system. In the above expression for \mathcal{Q} , only one term contributes overwhelmingly to the sum over N' . Let the value of N' for which the $\lambda^{N'} Q(T, V, N')$ is maximum be N . Hence the sum over N' can be replaced by a single entry with $N' = N$.

$$\mathcal{Q}(T, V, \mu) = \lambda^N Q(T, V, N) \quad (6.24)$$

$$\begin{aligned}
\ln \mathcal{Q}(T, V, \mu) &= \beta \mu N + \ln Q(T, V, N) \\
&= \frac{\mu N}{k_B T} + \ln Q(T, V, N)
\end{aligned} \tag{6.25}$$

$$k_B T \ln \mathcal{Q} = \mu N + k_B T \ln Q(T, V, N) \tag{6.26}$$

While studying Canonical ensembles we have shown that

$$F(T, V, N) = -k_B T \ln Q(T, V, N).$$

Therefore we can write the above equation as,

$$k_B T \ln \mathcal{Q} = \mu N - F(T, V, N) \tag{6.27}$$

$$-k_B T \ln \mathcal{Q} = F - \mu N = U - TS - \mu N = \mathcal{G} \tag{6.28}$$

Recall the discussions on Legendre Transform : We start with $U \equiv U(S, V, N)$. Transform S in favour of the "slope" T (partial derivative of U with respect to S). We get the "intercept" $F(T, V, N)$ as $U - TS$. Let us carry out one more transform : $N \rightarrow \mu$. *i.e.* transform N in favour of the slope μ (partial derivative of U with respect to N); μ is the chemical potential. We get the "intercept" $\mathcal{G}(T, V, \mu)$ - the grand potential. We have $\mathcal{G}(T, V, \mu) = U - TS - \mu N$. Thus we have, $\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}(T, V, \mu)$

6.3 Statistics of Number of Particles

The grand canonical partition function \mathcal{Q} of statistical mechanics (micro world) corresponds to the grand potential (\mathcal{G}) of thermodynamics (macro world). We have the micro-macro synthesis : $\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}$.

Some authors⁴ would like to identify PV as the thermodynamic counterpart of grand canonical partition function : $PV = k_B T \ln \mathcal{Q}$. Let us first derive this relation. To this end, let me tell you of a beautiful formula proposed by Euler, in the context of homogeneous function.

6.3.1 Euler and his Theorem

The internal energy U is a homogeneous function of S , V and N . U is an extensive property; so are S , V and N . Extensivity means that U is a first order homogeneous function of S , V , and N . Therefore $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$ where λ is a constant⁵. Euler's trick consists of differentiating both sides of the above equation with respect to λ . We get,

$$\frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = U(S, V, N) \quad (6.29)$$

$$S \frac{\partial U}{\partial(\lambda S)} + V \frac{\partial U}{\partial(\lambda V)} + N \frac{\partial U}{\partial(\lambda N)} = U(S, V, N) \quad (6.30)$$

The above is true for any value of λ . In particular it is true for $\lambda = 1$. Substitute in the above $\lambda = 1$ and get,

$$S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + N \frac{\partial U}{\partial N} = U(S, V, N) \quad (6.31)$$

$$TS - PV + \mu N = U \quad (6.32)$$

⁴Donald McQuairrie, *Statistical Mechanics*, Harper and Row (1976)

⁵do not confuse λ here with fugacity introduced earlier. Unfortunately I have used the same symbol. You should understand the meaning of λ in the context it is used.

6.3.2 \mathcal{Q} : Connection to Thermodynamics

We proceed as follows. From Euler relation : $U = TS - PV + \mu N$, we have $-PV = U - TS - \mu N$. The RHS of this equation is grand potential. Hence,

$$\begin{aligned} -PV = \mathcal{G}(T, V, \mu) &= -k_B T \ln \mathcal{Q}(T, V, \mu) \\ PV &= k_B T \ln \mathcal{Q}(T, V, \mu) \end{aligned} \quad (6.33)$$

6.3.3 Gibbs-Duhem Relation

Now that we are on the Euler's formula, let me digress a little bit and see if the equations we have derived, can be used to establish a relation amongst the intensive properties T , P and μ of the system.

Derivation from $U(S, V, N)$

We proceed as follows.

$$U = TS - PV + \mu N, \quad (6.34)$$

$$dU = TdS - PdV + \mu dN + SdT - VdP + Nd\mu \quad (6.35)$$

From the first law of thermodynamics, we have $dU = TdS - PdV + \mu dN$. Hence, $Nd\mu + SdT - VdP = 0$. It follows then,

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP \quad (6.36)$$

$$= -sdT + vdP \quad (6.37)$$

where s is the specific entropy - entropy per particle and v is specific volume - volume per particle. The important point is that Eq, (6.37) implies that $\mu \equiv \mu(s, v)$.

6.3.4 Average number of particles in an open system, $\langle N \rangle$

We start with, $\mathcal{Q}(T, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N Q_N(T, V)$. Take the partial derivative of \mathcal{Q} with respect to λ and get,

$$\begin{aligned} \left(\frac{\partial \mathcal{Q}}{\partial \lambda} \right)_{T,V} &= \sum_{N=0}^{\infty} N \lambda^{N-1} Q_N(T, V) = \frac{1}{\lambda} \sum_{N=0}^{\infty} N \lambda^N Q_N(T, V) \\ &= \frac{\mathcal{Q}}{\lambda} \left[\frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} N \lambda^N Q_N(T, V) \right] \\ &= \frac{\mathcal{Q}}{\lambda} \langle N \rangle \end{aligned} \quad (6.38)$$

Thus the average number of particles in an open system can be formally expressed as,

$$\langle N \rangle = \lambda \frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \lambda} = \lambda \frac{\partial \ln \mathcal{Q}}{\partial \lambda} \quad (6.39)$$

6.3.5 Probability distribution of N

We start with

$$\begin{aligned} \mathcal{Q}(T, V, \lambda) &= \sum_{N=0}^{\infty} \lambda^N Q_N(T, V) = \sum_{N=0}^{\infty} \lambda^N \frac{Q_1^N}{N!} \\ &= \exp(\lambda Q_1) \end{aligned} \quad (6.40)$$

The average of N can be formally expressed as,

$$\langle N \rangle = \frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} N \frac{(\lambda Q_1)^N}{N!} \quad (6.41)$$

We have already shown $\mathcal{Q} = \exp(\lambda Q_1)$. Therefore,

$$\langle N \rangle = \sum_{N=0}^{\infty} N \frac{(\lambda Q_1)^N \exp(-\lambda Q_1)}{N!} \quad (6.42)$$

We have earlier shown that $\langle N \rangle = \lambda Q_1 = \zeta$ say. Then,

$$\langle N \rangle = \sum_{N=1}^N N \frac{\zeta^N \exp(-\zeta)}{N!} = \sum_{N=1}^{\infty} N P(N) \quad (6.43)$$

$P(N)$ thus is a Poisson distribution : $P(N) = \frac{\zeta^N}{N!} \exp(-\zeta)$. For Poisson distribution, the mean equals variance. Therefore

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle = \zeta = \lambda Q_1. \quad (6.44)$$

6.3.6 Number Fluctuations

In an open system, the energy E and the number of molecules N are random variables. Energy fluctuates when the system goes from micro state to another. The number of molecules fluctuates from one micro state to the other. Let us now derive an expression for the variance of N :

$$\sigma^2 = \langle N^2 \rangle - \langle N \rangle^2.$$

To this end, we start with

$$\mathcal{Q}(T, V, \mu) = \sum_c \exp \left[-\beta \{E(C) - \mu N(C)\} \right] \quad (6.45)$$

In the above

C denotes a micro state of the open system

$E(C)$ denotes the energy of the open system when in micro state C

$N(C)$ denotes the number of particles of the open when in micro state C

Let us now take the partial derivative of all the terms in the above equation, with respect to the variable μ , keeping the temperature and volume constant. We have,

$$\begin{aligned} \left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} &= \sum_c \beta N(C) \exp \left[-\beta \{E(C) - \mu N(C)\} \right] \\ &= \beta \langle N \rangle \mathcal{Q}(T, V, \mu) \end{aligned} \quad (6.46)$$

$$\left(\frac{\partial^2 \mathcal{Q}}{\partial \mu^2} \right)_{T,V} = \beta \left[\langle N \rangle \left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} + \mathcal{Q} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \right] \quad (6.47)$$

The left hand side of the above equation equals ⁶ $\beta^2 \langle N^2 \rangle \mathcal{Q}$.

Substituting this in the above, we get,

$$\beta^2 \langle N^2 \rangle \mathcal{Q} = \beta^2 \langle N \rangle^2 \mathcal{Q} + \beta \mathcal{Q} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.48)$$

$$\sigma^2 = \langle N^2 \rangle - \langle N \rangle^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.49)$$

Since $\langle N \rangle = \lambda Q_1$, we have,

$$\frac{\partial \langle N \rangle}{\partial \mu} = Q_1 \frac{d\lambda}{d\mu} = \beta \lambda Q_1 \quad (6.50)$$

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$$\begin{aligned} \left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} &= \sum_C \beta N(C) \exp \left[-\beta \{E(C) - \mu N(C)\} \right] \\ \left(\frac{\partial^2 \mathcal{Q}}{\partial \mu^2} \right)_{T,V} &= \sum_C \beta^2 [N(C)]^2 \exp \left[-\beta \{E(C) - \mu N(C)\} \right] \\ &= \beta^2 \langle N^2 \rangle \mathcal{Q}. \end{aligned}$$

We have shown

$$\sigma_N^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.51)$$

Substituting in the above $\frac{\partial \langle N \rangle}{\partial \mu} = \lambda \beta Q_1$, we get,

$$\sigma_N^2 = k_B T Q_1 \beta \lambda \quad (6.52)$$

$$= \lambda Q_1 = \langle N \rangle \quad (6.53)$$

consistent with what we have shown earlier : *the distribution of N is Poissonian* with mean=variance= λQ_1

In what follows, we shall derive an expression for the fluctuations of N in terms of isothermal compressibility - a property measurable experimentally.

6.3.7 Number Fluctuations and Isothermal Compressibility

Let us express the number fluctuations in terms of experimentally measurable properties ⁷ of the open system. Let us define

$$v = \frac{V}{\langle N \rangle}.$$

⁷We shall show that,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{\langle N \rangle^2}{V} k_T \quad (6.54)$$

where k_T denotes isothermal compressibility - an experimentally measurable property. Isothermal compressibility is defined as

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (6.55)$$

It is called specific volume. It is the volume per particle. We have,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} \quad (6.56)$$

$$= -\frac{V}{v^2} \left(\frac{\partial v}{\partial \mu}\right)_{T,V} \quad (6.57)$$

$$= -\frac{\langle N \rangle^2}{V} \left(\frac{\partial v}{\partial \mu}\right)_{T,V} \quad (6.58)$$

In the above we can express,

$$\left(\frac{\partial v}{\partial \mu}\right)_{T,V} = \left(\frac{\partial v}{\partial P}\right)_{T,V} \left(\frac{\partial P}{\partial \mu}\right)_{T,V} \quad (6.59)$$

Employing Gibbs-Duhem relation, we find ⁸,

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{\langle N \rangle}{V} \quad (6.61)$$

Therefore,

$$\left(\frac{\partial v}{\partial \mu}\right)_{T,V} = \frac{\langle N \rangle}{V} \left(\frac{\partial v}{\partial P}\right)_{T,V} = \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_{T,V} = -k_T \quad (6.62)$$

⁸ Gibbs - Duhem relation reads as $\langle N \rangle d\mu = VdP - SdT$. At constant temperature, we have,
 $\langle N \rangle d\mu = VdP$,

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{\langle N \rangle}{V} \quad (6.60)$$

Finally we get,

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle^2}{V}k_T \quad (6.63)$$

$$\sigma^2 = k_B T \left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} \quad (6.64)$$

$$= k_B T \frac{\langle N\rangle^2}{V}k_T \quad (6.65)$$

$$\frac{\sigma^2}{\langle N\rangle^2} = \frac{k_B T}{V}k_T \quad (6.66)$$

Thus the fluctuations in the number of molecules of an open system is directly proportional to the isothermal compressibility. Hence we expect isothermal compressibility to be positive ⁹.

The number fluctuations are small in the thermodynamic limit; they are of the order of inverse of the square-root of the number of particles in the system.

Thus equilibrium fluctuations are related to an appropriate susceptibility which measures the response of the system to a small external perturbation. When heated, the system responds by raising its temperature. Energy absorbed by heat divided by the increase in temperature is called the heat capacity. The volume does not change during this process. We saw that the equilibrium energy fluctuations are proportional heat capacity.

Thus, the susceptibility is heat capacity for energy fluctuations; it is isothermal compressibility for the number fluctuations. These are special cases of a more general principle called *Fluctuation-Dissipation theorem* enunciated by Albert Einstein in the context of Brownian motion. If time permits, I shall

⁹The relative fluctuations of energy in a canonical ensemble is proportional to heat capacity at constant volume. Hence we expect heat capacity to be positive .

speak on Brownian motion in one of the extra classes.

However, close to first order phase transition, isothermal compressibility diverges. The fluctuations in the number of particles are large; they are of the order of the system size. The pressure-volume phase diagram has a flat region very near first order phase transition temperature, see discussions on van der Waal gas and Maxwell's construction.

Alternate Derivation of the Relation : $\sigma_N^2 / \langle N \rangle^2 = k_B T k_T / V$

In an earlier lecture I had derived a relation between the number fluctuation and isothermal compressibility. I had followed closely R K Pathria, *Statistical Mechanics*, Second Edition, Butterworth and Henemann (1996). I am giving below, an alternate derivation.

Start with a fluctuation-dissipation relation¹⁰ derived earlier,

$$\sigma^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} \quad (6.67)$$

We consider the reciprocal,

$$\left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} \quad (6.68)$$

We observe that μ is a function¹¹ of T and P . We are keeping T a constant. Hence μ can change only when P changes.

¹⁰relating number fluctuations to response to small changes in the chemical potential.

¹¹Gibbs and Duhem told us that the three intensive properties T , P , and μ are not all independent. Only two of them are independent. The third is automatically fixed by the other two.

Gibbs-Duhem relation tells us,

$$\langle N \rangle d\mu = V dP - S dT. \quad (6.69)$$

When T is a constant, we have $dT = 0$. This gives us

$$d\mu = \frac{V}{\langle N \rangle} dP \quad (6.70)$$

$$\left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{T,V} = \frac{V}{\langle N \rangle} \left(\frac{\partial P}{\partial \langle N \rangle} \right)_{T,V} \quad (6.71)$$

$$\left(\frac{\partial \mu}{\partial P} \right)_{T,V} = \frac{V}{\langle N \rangle} \quad (6.72)$$

Let us now define $\rho = \frac{\langle N \rangle}{V}$, which denotes the particle density : number of particles per unit volume. We have,

$$\left(\frac{\partial P}{\partial \langle N \rangle} \right)_{V,T} = \left(\frac{\partial P}{\partial (\rho V)} \right)_{V,T} = \frac{1}{V} \left(\frac{\partial P}{\partial \rho} \right)_{V,T} \quad (6.73)$$

The density can be changed either by changing $\langle N \rangle$ and/or V . Here we change ρ infinitesimally, keeping V constant. As a result the pressure changes infinitesimally. Let me repeat : both these changes happen at constant V and T .

As far as P is concerned, it does not care whether ρ has changed by change of $\langle N \rangle$ or of V . Hence it is legitimate to write

$$\left(\frac{\partial P}{\partial \rho} \right)_{V,T} = \left(\frac{\partial P}{\partial (\langle N \rangle / V)} \right)_{\langle N \rangle, T} \quad (6.74)$$

$$= - \frac{V^2}{\langle N \rangle} \left(\frac{\partial P}{\partial V} \right)_{\langle N \rangle, T} \quad (6.75)$$

Thus we get,

$$\begin{aligned}
 \left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} &= \frac{V}{\langle N \rangle} \left(\frac{\partial P}{\partial \langle N \rangle} \right)_{V,T} \\
 &= \frac{1}{\langle N \rangle} \left(\frac{\partial P}{\partial \rho} \right)_{V,T} \\
 &= -\frac{V^2}{\langle N \rangle^2} \left(\frac{\partial P}{\partial V} \right)_{\langle N \rangle, T}
 \end{aligned} \tag{6.76}$$

Take a reciprocal of the above and get,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = -\frac{\langle N \rangle^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_{\langle N \rangle, T} \tag{6.77}$$

Then we get,

$$\begin{aligned}
 \sigma_N^2 &= k_B T \left[-\frac{\langle N \rangle^2}{V^2} \right] \left(\frac{\partial V}{\partial P} \right)_{T, \langle N \rangle} \\
 &= k_B T \frac{\langle N \rangle^2}{V} k_T \\
 \frac{\sigma_N^2}{\langle N \rangle^2} &= \frac{k_B T}{V} k_T
 \end{aligned} \tag{6.78}$$

6.4 Energy Fluctuations

Let i label a micro state of an open system. Let E_i and N_i denote the energy and number of particles in the open system when it is in micro state i . Formally,

$$\mathcal{Q} = \sum_i \lambda^{N_i} \exp(-\beta E_i)$$

$$\left(\frac{\partial \mathcal{Q}}{\partial \beta} \right)_{\lambda, V} = - \sum_i \lambda^{N_i} E_i \exp(-\beta E_i)$$

$$\left(\frac{\partial^2 \mathcal{Q}}{\partial \beta^2} \right)_{\lambda, V} = \sum_i \lambda^{N_i} E_i^2 \exp(-\beta E_i)$$

The first and the second moment of E are given by,

$$\langle E \rangle = -\frac{1}{\mathcal{Q}} \left(\frac{\partial \mathcal{Q}}{\partial \beta} \right)_{\lambda, V}$$

$$\langle E^2 \rangle = \frac{1}{\mathcal{Q}} \left(\frac{\partial^2 \mathcal{Q}}{\partial \beta^2} \right)_{\lambda, V}$$

To derive an expression for the fluctuations of energy we proceed as follows.

$$\begin{aligned}
 \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{\lambda, V} &= - \left(\frac{\partial}{\partial \beta} \left[\frac{1}{\mathcal{Q}} \left(\frac{\partial \mathcal{Q}}{\partial \beta} \right)_{\lambda, V} \right] \right)_{\lambda, V} \\
 &= - \frac{1}{\mathcal{Q}} \left(\frac{\partial^2 \mathcal{Q}}{\partial \beta^2} \right)_{\lambda, V} + \left[\frac{1}{\mathcal{Q}} \left(\frac{\partial \mathcal{Q}}{\partial \beta} \right)_{\lambda, V} \right]^2 \\
 &= - \left(\langle E^2 \rangle - \langle E \rangle^2 \right) \\
 &= - \sigma_{E:\text{OPEN}}^2
 \end{aligned}$$

We can proceed in the same fashion and obtain a similar expression for the fluctuations of energy in a canonical ensemble¹²,

$$\left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N, V} = - \sigma_{E:\text{CLOSED}}^2$$

Note :

- For an open system, the partial derivative of energy with respect to β is taken at constant λ and V .
- For a closed system, the partial derivative of energy with respect to beta is taken at constant N and V

What is the relation between $\sigma_{E:\text{OPEN}}^2$ and $\sigma_{E:\text{CLOSED}}^2$?

The key to answering this question lies in the following entities :

$$\begin{aligned}
 {}^{12} \quad Q(T, V, N) &= \sum_i \exp(-\beta E_i); \quad \frac{\partial Q}{\partial \beta} = - \sum_i E_i \exp(-\beta E_i); \quad \frac{\partial^2 Q}{\partial \beta^2} = \sum_i E_i^2 \exp(-\beta E_i) \\
 \langle E \rangle &= - \frac{1}{Q} \frac{\partial Q}{\partial \beta}; \quad \frac{\partial \langle E \rangle}{\partial \beta} = - \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} + \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2; \quad \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N, V} = - \sigma_{E:\text{CLOSED}}^2
 \end{aligned}$$

- $U(T, V, N)$: Internal energy of a closed system described by canonical ensemble
- $U(T, V, \lambda) = U(T, V, N(T, V, \lambda))$: Internal energy of an open system described by a grand canonical ensemble

The central relation is,

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda, V} = \left(\frac{\partial U}{\partial T}\right)_{N, V} + \left(\frac{\partial U}{\partial N}\right)_{T, V} \times \left(\frac{\partial N}{\partial T}\right)_{\lambda, V}. \quad (6.79)$$

Equation (6.79) can be obtained from first principles¹³.

¹³ Formally, we have,

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda, V} = \lim_{\Delta T \rightarrow 0} \frac{U(T + \Delta T, V, N(T + \Delta T, V, \lambda)) - U(T, V, \lambda)}{\Delta T}$$

In the above, we express,

$$\begin{aligned} N(T + \Delta T, V, \lambda) &= N(T, V, \lambda) + \Delta T \left(\frac{\partial N}{\partial T}\right)_{\lambda, V} \\ &= N + (\Delta N)_{\lambda, V} \end{aligned}$$

We have used the short-hand notation

$$(\Delta N)_{\lambda, V} = \Delta T \left(\frac{\partial N}{\partial T}\right)_{\lambda, V}$$

Therefore,

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda, V} = \lim_{\Delta T \rightarrow 0} \frac{U(T + \Delta T, V, N + (\Delta N)_{\lambda, V}) - U(T, V, \lambda)}{\Delta T}$$

We can write,

$$\begin{aligned} U(T + \Delta T, V, N + (\Delta N)_{\lambda, V}) &= U(T, V, N) + \Delta T \left(\frac{\partial U}{\partial T}\right)_{V, N} \\ &\quad + (\Delta N)_{\lambda, V} \left(\frac{\partial U}{\partial N}\right)_{T, V} \end{aligned}$$

Evaluation of $\left(\frac{\partial N}{\partial T}\right)_{\lambda,V}$, the last term in Eq. (6.79)

Start with $N(T, V, \mu(T, \lambda))$, where $\mu = k_B T \ln \lambda$. We have,

$$\left(\frac{\partial N}{\partial T}\right)_{\lambda,V} = \left(\frac{\partial N}{\partial T}\right)_{\mu,V} + \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \times \left(\frac{\partial \mu}{\partial T}\right)_{\lambda,V} \quad (6.80)$$

The first term on the right hand side of Eq. (6.80) above can be evaluated, see below.

Consider $N(T, V, \mu)$. At constant V we can write,

$$dN = \left(\frac{\partial N}{\partial T}\right)_{\mu} dT + \left(\frac{\partial N}{\partial \mu}\right)_T d\mu$$

$dN = 0$ implies,

$$\begin{aligned} \left(\frac{\partial N}{\partial T}\right)_{\mu} dT &= - \left(\frac{\partial N}{\partial \mu}\right)_T d\mu \\ \left(\frac{\partial N}{\partial T}\right)_{\mu} &= - \left(\frac{\partial N}{\partial \mu}\right)_T \times \left(\frac{\partial \mu}{\partial T}\right)_N \end{aligned}$$

Therefore,

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_{\lambda,V} &= \left(\frac{\partial U}{\partial T}\right)_{V,N} + \frac{(\Delta N)_{\lambda,V}}{\Delta T} \left(\frac{\partial U}{\partial N}\right)_{T,V} \\ &= \left(\frac{\partial U}{\partial T}\right)_{V,N} + \left(\frac{\partial U}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{\lambda,V} \end{aligned}$$

Therefore Eq.(6.80) can be written as,

$$\begin{aligned}
 \left(\frac{\partial N}{\partial T}\right)_{\lambda,V} &= -\left(\frac{\partial N}{\partial \mu}\right)_{T,V} \times \left(\frac{\partial \mu}{\partial T}\right)_{N,V} + \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \times \left(\frac{\partial \mu}{\partial T}\right)_{\lambda,V} \\
 &= \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \left[\left(\frac{\partial \mu}{\partial T}\right)_{\lambda,V} - \left(\frac{\partial \mu}{\partial T}\right)_{N,V} \right] \\
 &= \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T}\right)_{N,V} \right] \tag{6.81}
 \end{aligned}$$

In the last step we have made use of the relation : $\left(\frac{\partial \mu}{\partial T}\right)_{\lambda,V} = \frac{\mu}{T}$, see box below.

$$\lambda = \exp(\beta\mu); \mu = k_B T \ln \lambda; \left(\frac{\partial \mu}{\partial T}\right)_{\lambda} = k_B \ln \lambda = \mu/T$$

Consider the second term on the right hand side of Eq. (6.81) - the term within the square brackets; we can show that

$$\left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T}\right)_{N,V} \right] = \frac{1}{T} \left(\frac{\partial U}{\partial N}\right)_{T,V},$$

see below.

At constant volume we have

$$dU = TdS + \mu dN.$$

Therefore,

$$\begin{aligned}
 \left(\frac{\partial U}{\partial N} \right)_{T,V} &= \mu + T \left(\frac{\partial S}{\partial N} \right)_{T,V} \\
 &= T \left[\frac{\mu}{T} + \left(\frac{\partial S}{\partial N} \right)_{T,V} \right] \\
 &= T \left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T} \right)_{N,V} \right]
 \end{aligned}$$

In the above, the last step follows from one of Maxwell's relations¹⁴ Therefore Eq. (6.81) can be written as, $\left(\frac{\partial N}{\partial T} \right)_{\lambda,V} = \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V}$.

Now we can go back to Eq. (6.79) and write it as

$$\left(\frac{\partial U}{\partial T} \right)_{\lambda,V} = \left(\frac{\partial U}{\partial T} \right)_{N,V} + \frac{1}{T} \times \left(\frac{\partial U}{\partial N} \right)_{T,V}^2 \times \left(\frac{\partial N}{\partial \mu} \right)_{T,V}$$

¹⁴ **Maxwell's Relation**

$$F = U - TS$$

$$\begin{aligned}
 dF &= -PdV + \mu dN - SdT \\
 &= \mu dN - SdT \quad (\text{at constant } V)
 \end{aligned}$$

We have

$$\begin{aligned}
 \left(\frac{\partial F}{\partial N} \right)_T &= \mu \quad ; \quad \left(\frac{\partial F}{\partial T} \right)_N = -S \\
 \frac{\partial^2 F}{\partial T \partial N} &= \left(\frac{\partial \mu}{\partial T} \right)_N \quad ; \quad \frac{\partial^2 F}{\partial N \partial T} = - \left(\frac{\partial S}{\partial N} \right)_T \\
 \frac{\partial^2 F}{\partial T \partial N} &= \frac{\partial^2 F}{\partial N \partial T} \Rightarrow \left(\frac{\partial \mu}{\partial T} \right)_N = - \left(\frac{\partial S}{\partial N} \right)_T
 \end{aligned}$$

Make use of the relation, $\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{\sigma_N^2}{k_B T}$ and re write the above as

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} + \frac{1}{k_B T^2} \sigma_N^2 \left(\frac{\partial U}{\partial N}\right)_{T,V}^2$$

$$k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{\lambda,V} = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{N,V} + \sigma_N^2 \left(\frac{\partial U}{\partial N}\right)_{T,V}^2$$

$$\sigma_{E:OPEN}^2 = \sigma_{E:CLOSED}^2 + \left(\frac{\partial \langle E \rangle}{\partial \langle N \rangle}\right)_{T,V}^2 \sigma_N^2$$