Temperature fixed but energy can fluctuate. What is energy is more likely? what is mean energy?

Canonical ensemble

Alternate method - Equilibrium between a system and a heat reservoir.

Temperature of system = Temperature of reservoir.
However their energies are variable, could be anywhere between 0 and E. If system is in state characterized by energy value E_r, then reservoir would have energy E_r' such that
Now $E_r + E_r' = E$ (constant)

Reservoir is much larger than given system
$\therefore E_r$ would be a small fraction of E

$$\frac{E_r}{E} = \left(1 - \frac{E_r'}{E}\right) \ll 1$$

With the state of system A having been specified, the reservoir A' can still be in any of a large number of states compatible with the energy value E_r'. Let the number of these states be denoted by $\Omega'(E_r')$.

functional form depends on nature of reservoir

Thus, the probability of finding system with energy value E_r (and reservoir with E_r') would be (as per principle of equal a priori probabilities). → ∵ system + bath = isolated ↓ microcanonical sys.

$$P_r \propto \Omega'(E_r') \equiv \Omega'(E - E_r)$$

We can expand Ω' about $E_r' = E$ (i.e. $E_r = 0$) ∵ E_r is small relatively very
For reasons of convergence, it is essential to expand the log of Ω', rather than Ω'. Remember Ω is $O(e^E)$

→ well-defined for a continuum.

$$\ln \Omega'(E_r') = \ln \Omega'(E) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E} (E_r' - E) + \dots$$

$$= \text{constant} - \beta' E_r \qquad \because \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \beta$$

β' is for reservoir. At equilibrium $\beta' = \beta = 1/kT$

$\therefore P_r \propto \exp(-\beta E_r)$

Normalizing

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}.$$

summation over all states accessible to system A.
Final result has no dependence on the nature of the reservoir.

We can get the same result from an ensemble treatment.

Canonical ensemble ⇒ Equilibrium thermally between a system and a heat reservoir. System can exchange energy with reservoir

Members of the ensemble can have any one of the possible eigenenergies E_r ($r=0,1,2,\ldots$) but they are all at the same temperature (and also same N and V).

We can specify state of entire ensemble by saying that $a_1, a_2, a_3, \ldots$ of the systems are in states $1,2,3,\ldots$ respectively with energies $E_1, E_2, E_3, \ldots$
↳ energy of whole system in given microstate

State No.	$1,2,3,\ldots,l,\ldots$	
Energy	$E_1, E_2, E_3, \ldots E_l, \ldots$	(Note each E_l is repeated according to it's degeneracy).
Occupation #	$a_1, a_2, a_3, \ldots a_l \ldots$	

↓
Number of systems of ensemble in that particular state
Set of occupation numbers is called a distribution $\{a_j\}$

Now $\sum_j a_j = A$ total no. of systems in ensemble

$\sum_j a_j E_j = \mathcal{E}$ total energy of ensemble.

→ This is equivalent to placing entire ensemble in a heat bath and surrounding it with thermal insulation thus making the entire ensemble itself an isolated system so we can apply principle of equal a priori probabilities. ie all possible $\{a_j\}$'s are likely provided they are consistent with total energy $\mathcal{E}$ of the entire ensemble.

Number of ways to distribute A objects into $\{a_j\}$ sets

$$W(a) = \frac{A!}{a_1!\, a_2!\, a_3! \ldots} = \frac{A!}{\prod_k a_k!}$$

Note we considered these systems as distinguishable which is a valid assumption since they are macroscopic.

There are many distributions $\{a_j\}$ consistent with the applied conditions. Each one of those distributions is equally likely ($\because$ super-system corresponding to the ensemble is an isolated system)

In any particular distribution, a_j/A is fraction of members of canonical ensemble in the j^{th} quantum state (with energy E_j). Overall probability P_j that a system is in j^{th} quantum state is obtained by averaging a_j/A over all the allowed distributions, giving equal weight to each one according to principle of equal a priori probabilities. Thus P_j is given by:

$$P_j = \frac{\bar{a}_j}{A} = \frac{1}{A} \frac{\sum_a W(a)\, a_j(a)}{\sum_a W(a)}$$

Mean-distribution method.

Note a denotes given distribution consistent with the constraints

Summation over distributions that satisfy constraints

Canonical ensemble average of any property M

$$\bar{M} = \sum_j M_j P_j \qquad M_j = \text{value of } M \text{ in } j^{th} \text{ quantum state.}$$

Now we can take $A \to \infty$ by making ensemble arbitrarily large. Then $\bar{a}_j \to \infty$. $\bar{a}_j/A$ will still be finite.

W(a)

Now we know a multinomial distribution is extremely peaked about it's maximum (most probable distribution) if all variables a_j are large.
Each one of the a_j's can be made arbitrarily large since A can be made arbitrarily large.

W(a) about it's maximum value can be made arbitrarily narrow as a_j's (i.e. A) to be arbitrarily large.
(Note $A \to \infty$, $W(a) \to$ delta function)
If set a^* represents most probable distribution (a^* maximizes W(a))
Thus the W(a) at any set other than a^* is completely negligible in value.

$$\therefore P_j = \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} = \frac{1}{A} \frac{W(a^*) \cdot a_j^*}{W(a^*)}$$

$$\therefore P_j = \frac{a_j^*}{A} \quad (\text{when } a_j, A \to \infty).$$

mean distribution = most probable distribution when large # of members in distribution.

$$P_j = \frac{\overline{a_j}}{A} = \frac{a_j^*}{A}$$

So, now we need to only determine a^* that maximizes W(a) under two constraints.

We use the Lagrange method of undetermined multipliers.
We can maximize $\ln W(a)$ instead.

$$\frac{\partial}{\partial a_j} \left\{ \ln W(a) - \alpha \sum_k a_k - \beta \sum_k a_k E_k \right\} = 0 \Rightarrow j = 1, 2, \ldots$$

Use Stirling's approximation for W(a) $\because$ $A \to \infty$, a_j's $\to \infty$

$$W(a) = \frac{(A/e)^A}{(a_1/e)^{a_1}(a_2/e)^{a_2}\cdots} = \frac{A^A}{a_1^{a_1} a_2^{a_2}\cdots}$$

for any j

$$\frac{\partial \ln W(a)}{\partial a_j} = -\frac{\partial\, a_j \ln a_j}{\partial a_j} = -(\ln a_j + 1).$$

$\therefore$ We have for each $j = 1, 2, \ldots$

$$-\ln a_j^* - 1 - \alpha - \beta E_j = 0 \qquad \text{(i.e. at most probable distribution)}$$

$$a_j^* = e^{-(1+\alpha)} \cdot e^{-\beta E_j}$$

Now $$\sum_j e^{-(1+\alpha)} e^{-\beta E_j} = A$$

$$\therefore e^{-(1+\alpha)} = \frac{A}{\sum_j e^{-\beta E_j}}$$

$$\therefore e^{(1+\alpha)} = \left(\sum_j e^{-\beta E_j}\right) \frac{}{A}$$

$$\therefore P_j = \frac{a_j^*}{A} = \frac{e^{-\beta E_j(N,V)}}{\sum e^{-\beta E_j(N,V)}}$$

$\therefore$ Average E is given as (at a given temperature).

$$\bar{E}(N,V,\beta) = \sum_j \frac{E_j(N,V)\, e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}}$$

As we showed, this average E must equal to the thermodynamic energy or the energy measured at equilibrium.

Now pressure is given as

$$P_j = -\left(\frac{\partial E_j}{\partial V}\right)_{N,T} \quad \text{in the } j^{th} \text{ state.}$$

definition from Helmholtz free energy (T,V,N) differential form

We can't use the fundamental energy eqⁿ form ∵ T is independent variable not S or E.

$$\therefore \bar{P} = \sum_j P_j P_j$$

$$= -\frac{\sum_j \left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

Let denominator $\sum_j e^{-\beta E_j}$ be denoted by $Q(N,V,\beta)$ → central function of the canonical ensemble. Known as a partition function, i.e. canonical partition function.

$$\therefore \bar{E} = \frac{-1\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}}{Q} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

Note E_j's are functions of N,V only. $\bar{E}$ is function of (N,V,β).

$$\bar{P} = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

Partition function serves as a bridge between quantum states of a system of a macroscopic system and its thermodynamic properties.

If we can get Q as a function of N,V,T we can calculate all other thermodynamic properties.

CANONICAL ENSEMBLE

Consider a function

$$f = \ln Q \quad \therefore f \text{ is a function of } \beta \text{ and all } \epsilon_j\text{'s (through } V)$$

$$\therefore \quad f = \ln\left(\sum_j e^{-\beta \epsilon_j}\right)$$

Total derivative of f

$$df = \left(\frac{\partial f}{\partial \beta}\right)_{\epsilon_j\text{'s}} d\beta + \sum_j \left(\frac{\partial f}{\partial \epsilon_j}\right)_{\beta, \text{other } \epsilon_j\text{'s}} d\epsilon_j$$

Now $$\left(\frac{\partial f}{\partial \beta}\right)_{\epsilon_j\text{'s}} = -\frac{1}{Q} \cdot \sum_j \epsilon_j e^{-\beta \epsilon_j} = -\bar{\epsilon}$$

$$\left(\frac{\partial f}{\partial \epsilon_j}\right)_{\beta, \text{other } \epsilon_j\text{'s}} = -\frac{\beta}{Q} e^{-\beta \epsilon_j} = -\beta p_j$$

Thus

$$df = -\bar{\epsilon}\, d\beta - \beta \sum_j p_j\, d\epsilon_j$$

$$df - \beta d\bar{\epsilon} = -\bar{\epsilon}\, d\beta - \beta d\bar{\epsilon} - \beta \sum_j p_j\, d\epsilon_j$$

$$d(f + \beta\bar{\epsilon}) = \beta d\bar{\epsilon} - \beta \sum_j p_j\, d\epsilon_j$$

$$d\left(\frac{S}{k}\right) = \beta\, d\bar{\epsilon} - \beta \sum_j p_j\, d\epsilon_j$$

$$dS = k\beta\, d\bar{\epsilon} - k\beta \sum_j p_j\, d\epsilon_j = k\beta d\bar{\epsilon} + k\beta\left(\sum_j p_j \frac{\partial \epsilon_j}{\partial V}\right) dV$$

$\Downarrow$

$\bar{p} \rightarrow$ mean pressure

Now $$\left(\frac{\partial S}{\partial \bar{\epsilon}}\right)_V = k\beta$$

$$\therefore \quad \frac{1}{T} = k\beta \quad \therefore \quad \beta = \frac{1}{kT}$$

$$\left(\frac{\partial S}{\partial V}\right)_{\bar{\epsilon}} = k\beta\bar{p} \quad \text{also consistent with } \beta = \frac{1}{kT}$$

$$S = -k \sum_j P_j \ln P_j$$

$$= -k \sum_j \left[\frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \cdot \ln \left(\frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \right) \right]$$

$$= \frac{-k}{\sum_j e^{-\beta E}} \left[\sum_j e^{-\beta E_j} \cdot \left(\ln e^{-\beta E_j} - \ln Q \right) \right]$$

$$S = \frac{-k}{Q} \left[\sum_j \left[-\beta E_j e^{-\beta E_j} - e^{-\beta E_j} \ln Q \right] \right]$$

$$S = -k \left[\sum_j -\beta E_j P_j - \ln Q \frac{\sum e^{-\beta E_j}}{Q} \right]$$

$$S = -k \left[-\beta \bar{E} - \ln Q \right]$$

$$S = k\beta \bar{E} + k \ln Q \quad \text{or} \quad \boxed{-k \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} + k \ln Q}$$

$$S = \frac{\bar{E}}{T} + k \ln Q$$

$$TS = \bar{E} + kT \ln Q$$

$$\therefore -kT \ln Q = \bar{E} - TS$$

$$\therefore A = -\frac{1}{\beta} \ln Q$$

ie. A is a natural function of N, V, β

Helmholtz free energy $A(N, V, \beta) = -\frac{\ln Q(N, V, \beta)}{\beta}$

natural variables are those of canonical ensemble.

$Q = \sum_{j \text{ states}} e^{-\beta E_j}$ → summation over all states → term associated with E_j will occur $\Omega(E_j)$ times where $\Omega(E_j)$ is degeneracy. Instead of listing it Ω times we could write $\Omega(E_j) \exp(-E_j/kT)$

$\therefore Q = \sum_{E \text{ levels}} \Omega(N, V, E) e^{-\beta E(N,V)}$

LEVELS ≠ STATES.

Second law

Spontaneous process ⇒ Removal of an internal constraint (from an isolated system) allows a greater number of quantum states to be accessible to the system, thus the "flow" of the system into these states is observed as a spontaneous process.

For System In a heat bath ⇒ we have to consider all possible energy levels of the system. When a restraint is removed, # of accessible states of each & every energy E usually increases since the original states are still available.

$$\therefore \Omega_2(N,V,E) \geq \Omega_1(N,V,E, \text{internal constraint})$$

$$Q_2 - Q_1 = \sum_E \{\Omega_2(N,V,E) - \Omega_1(N,V,E)\} e^{-E/kT} > 0$$

$$\therefore \Delta A = A_2 - A_1 = -kT \ln \frac{Q_2}{Q_1} < 0 \text{ for a spontaneous process}$$

Thus we have the 2nd law of thermodynamics.

Fluctuation ⇒ deviation in a variable from its mean value. Investigation of the probability of such fluctuations is called fluctuation theory.

↙

It tells us to what extent we expect to see observe deviations from mean values that we calculate. If fluctuations are large, experimentally we would measure a range of values who's mean value we have already learnt how to calculate.

Fluctuations also relate to driving forces that drive system to equilibrium.

Fluctuations in a canonical ensemble ⇒

N, V, T = fixed ; fluctuations in energy E, p & other properties

↙

vary from one system in ensemble to another ⇒ i.e. vary in time.

Fluctuations in energy ⇒

Variance in energy $\sigma_E^2 = \overline{(E-\bar{E})^2} = \bar{E}^2 - \bar{E}^2$

↙

Spread about mean value

$$= \sum_j E_j^2 P_j - \bar{E}^2$$

now $P_j = e^{-\beta E_j} / \sum_j e^{-\beta E_j}$

$$\sum_j E_j^2 P_j = \frac{1}{Q} \sum_j E_j^2 e^{-\beta E_j} = \frac{-1}{Q} \frac{\partial}{\partial \beta} \sum_j E_j e^{-\beta E_j}$$

$$= \frac{-1}{Q} \frac{\partial}{\partial \beta} (\bar{E} Q) = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E} \frac{\partial \ln Q}{\partial \beta}$$

$$= -\frac{\partial \bar{E}}{\partial T} \frac{1}{(\partial \beta / \partial T)} + \bar{E}^2 \quad \because \bar{E} = \frac{-\partial \ln Q}{\partial \beta}$$

$$= kT^2 \frac{\partial \bar{E}}{\partial T} + \bar{E}^2$$

$$\therefore \sigma_E^2 = kT^2 \left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} = kT^2 C_V$$

Fluctuation-Dissipation theorem.

$$\sigma_E^2 = kT^2 C_v$$

- σ_E^2: fluctuation in energy at given temperature
- C_v: rate at which energy changes in response to temperature

C_v = heat capacity.

Relative magnitude of this spread

$$\frac{\sigma_E}{\bar{E}} = \frac{(kT^2 C_v)^{1/2}}{\bar{E}}$$

$\bar{E}$ is of $O(NkT)$ and C_v is $O(Nk)$.

$$\frac{\sigma_E}{\bar{E}} \Rightarrow O\left(\frac{1}{\sqrt{N}}\right)$$

For large system, relative deviations from mean are extremely small. The probability distribution of the energy may, therefore, be regarded as a Gaussian function/distribution, which is practically a delta function for a large system.

Let's derive a Gaussian distribution approximation to $P(E)$, the probability of observing a particular value E in a canonical ensemble.

$$P(E) = C\,\Omega(E)\,e^{-E/kT}$$

C is normalization constant independent of E.
$\Omega(E)$ is increasing fun^{n} of E and $e^{-E/kT}$ is decreasing function of E, so their product $P(E)$ peaks at some value of E, say E^*. We have seen that the spread about maximum value is extremely small so E^* and $\bar{E}$ are essentially the same point.

Width of $P(E)$ is $O(N^{-1/2})$, so E^* & $\bar{E}$ differ by at most $O(N^{-1/2})$

Expand $P(E)$ in a Taylor's series about E^*, or $\bar{E}$.
It is more convenient to work with $\ln P(E)$.

$$\left(\frac{\partial \ln P}{\partial E}\right)_{E=E^*=\bar{E}} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{E=E^*=\bar{E}} - \beta = 0$$

$$\frac{\partial^2 \ln P}{\partial E^2} = \frac{\partial^2 \ln \Omega}{\partial E^2}$$

At $E = E^* = \bar{E}$

$$\left(\frac{\partial^2 \ln \Omega}{\partial E^2}\right)_{E=\bar{E}} = \frac{\partial^2 \ln \Omega(\bar{E})}{\partial \bar{E}^2} = \frac{\partial}{\partial \bar{E}}\left(\frac{\partial \ln \Omega(\bar{E})}{\partial \bar{E}}\right)_{E=\bar{E}}$$

$$= \frac{\partial \beta}{\partial \bar{E}} = \frac{-1}{kT^2 C_V}$$

∴ Taylor's series

$$\ln P(E) = \ln P(\bar{E}) - \frac{1}{kT^2 C_V}\frac{(E-\bar{E})^2}{2} + \dots$$

$$P(E) = P(\bar{E}) \exp\left\{\frac{-(E-\bar{E})^2}{2kT^2 C_V}\right\}$$

Thus $\sigma_E^2 = kT^2 C_V$ (by comparing to Gaussian function form)

↓ same result.

Probability of observing an energy that differs by 0.1% from the average value for 1 mole of an ideal gas is $O(e^{-10^{17}})$, an extremely small number.

Canonical ensemble of AB composite systems.

Consider two closed systems A and B, each having its own kind of particles and its own energy states, but in thermal contact with each other and immersed in a heat bath of temperature T. We now construct a canonical ensemble of composite AB systems representative of a composite thermodynamic AB system at temperature T.

Let's find the most probable distribution.

Let N_A, V_A be number of molecules and volume of system A
N_B, V_B " " " " " B

Let their energies be denoted by $\{E_{j_A}\}$ and $\{E_{j_B}\}$

Let a_j be number of systems with energy E_{j_A}
b_j " " " " E_{j_B}

Then the number of states of AB ensemble with compound distribution $\{a_j\}$ and $\{b_j\}$

$$W(a,b) = \frac{\mathcal{A}!}{\Pi_j a_j!} \frac{\mathcal{B}!}{\Pi_k b_k!}$$

$\mathcal{A}$ and $\mathcal{B}$ are number of A and B systems

$$\sum_j a_j = \mathcal{A}$$

$$\sum_j b_j = \mathcal{B} = \mathcal{A} \Rightarrow \text{same number of A and B systems.}$$

$$\sum_j (a_j E_{j_A} + b_j E_{j_B}) = \mathcal{E}$$

simultaneous probability that AB system has its A part in the i^{th} quantum state and its B part in j^{th} quantum state.

$$P_{ij} = \frac{e^{-\beta E_{j,A}}}{Q_A} \cdot \frac{e^{-\beta E_{j_B}}}{Q_B} = P_{i_A} P_{j_B}$$ (Can you show this?)

where $Q_A = \sum_k e^{-\beta E_{kA}}$ and $Q_B = \sum_k e^{-\beta E_{kB}}$

Two systems in thermal contact have the same β. We already know they have the same temperature. So the two systems must have the same value of k. Since the nature of the two systems is completely arbitrary, k must have the same value for all systems Thus k is a universal constant.