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Lecture 3: Other Ensembles and Fluctuations

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Other ensembles

Based on **canonical ensemble**:

$$Q(N,V,T) = \sum_i e^{-E_i/kT}$$ Partition function

$$F = -kT \ln Q(N,V,T)$$ Thermodynamic connection

Grand canonical ensemble can be represented:

(1) $$\Xi(V,T,\mu) = \sum_N Q(N,V,T) e^{\mu N/kT}$$

(2) $$pV = kT \ln \Xi$$

Isothermal-isobaric ensemble:

(3) $$\Delta(N,p,T) = \sum_V Q(N,V,T) e^{-pV/kT}$$

(4) $$G = -kt \ln \Delta$$ Gibbs free energy

Microcanonical ensemble:

(5) $$\Omega(N,V,E) = \text{ states accessible to system with energy E}$$

(6) $$S = k \ln \Omega$$

Ensembles contain equivalent Thermodynamic information:

Ex.

(7) Microcanonical entropy $\underline{S(N,V,E_0)}$ $\equiv$ canonical entropy $\underline{S(N,V,T_0)}$ when E_0 to be $E_0 = \bar{E}(T_0)$

And let's verify the equation above,

Ω : Microcanonical partition function

(8) $$Q(N,V,T) = \sum_{i \text{ states}} e^{-E_i/kT} = \sum_{j \text{ energy}} \Omega(N,V,E_j) e^{-E_j/kT}$$

We will show from energy fluctuation later,

(9) $$\sum_j \Omega(N,V,E_j) e^{-E_j/kT} \approx \Omega(N,V,\bar{E}\,) e^{-\frac{\bar{E}}{kT}}$$

$\Omega(N,V,E)$ Rapidly increasing function of E

$e^{-E/kT}$ Rapidly decreasing function of E

$\Omega(N,V,E)e^{-E/kT}$ Sharply peaked function

We trust the approximation (9) here, and we will later prove it.

Equivalent information

Now,

(10) $$S(N,V,E_0) = k\ln\Omega(N,V,E_0)$$

(11) $$S(N,V,T_0) = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

(12) $$F = -kT\ln\sum e^{\frac{-E_i}{kT}} = -kT\ln Q$$

From (11),

(13) $$\begin{aligned} S(N,V,T_0) &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} \\ &= k\ln Q + \frac{kT}{Q}\frac{\partial}{\partial T}\sum_i e^{\frac{-E_i}{kT}} \\ &= k\ln Q + \frac{kT}{kT^2Q}\sum_i E_i e^{\frac{-E_i}{kT}} \\ &= k\ln Q + \frac{\bar{E}}{T} \end{aligned}$$

From approximation (9),

(14) $$\begin{aligned} S(N,V,T_0) &= k\ln\Omega(N,V,\bar{E}\,)e^{-\frac{\bar{E}}{kT}} + \frac{\bar{E}}{T} \\ &= k\ln\Omega(N,V,\bar{E}\,) - \frac{\bar{E}}{T} + \frac{\bar{E}}{T} = S(N,V,E_0) \end{aligned}$$

Energy fluctuation in canonical ensemble and C_V:

Fluctuation are deviation of a variable from its mean value.
The mean value of a distribution of an ensemble and the fluctuations from the mean are determined by the probability distribution.

Variance is the mean square fluctuation from the average

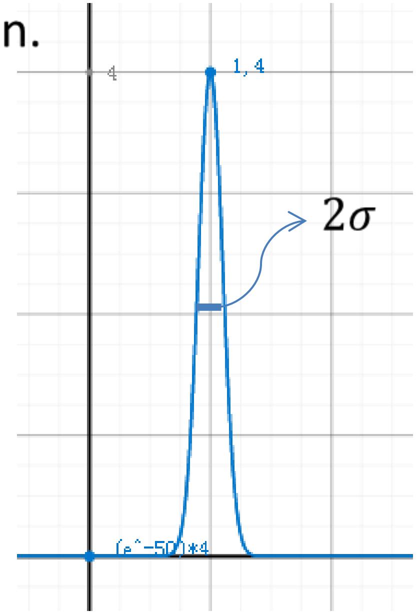
$$\sigma^2(x) = \langle (x - \langle x \rangle)^2 \rangle$$

Due to:

$$\langle x \rangle = \sum_i p(x_i) x_i \qquad \text{first moment}$$

$$\langle x^2 \rangle = \sum_i p(x_i) x_i \, x_i \qquad \text{second moment}$$

$$\sigma^2(x) = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$



For a normalized Gaussian distribution,

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\langle x \rangle)^2}{2\sigma^2}}$$

$$2\sigma = \text{full width at half height}$$

Ex. Gaussian distribution with $\mu = 1$ and $\sigma = 0.1$

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

Energy fluctuation in canonical ensemble and C_V:

Mean square energy fluctuation in canonical ensemble is proportional to the **heat capacity:**

(14) $$\sigma_E{}^2 = \langle E^2\rangle - \langle E\rangle^2 = \sum_j E_j{}^2 P_j - \left(\sum_j E_j P_j\right)^2$$

(15) $$\langle E^2\rangle = \sum_j E_j{}^2 P_j = \frac{1}{Q}\sum_j E_j{}^2 e^{-E_j\beta}$$

$$= -\frac{1}{Q}\frac{\partial}{\partial\beta}\sum_j E_j e^{-\beta E_j} = -\frac{1}{Q}\frac{\partial}{\partial\beta}[\langle E\rangle Q]$$

$$= -\frac{1}{Q}\left\{\langle E\rangle\frac{\partial Q}{\partial\beta} + Q\frac{\partial\langle E\rangle}{\partial\beta}\right\}$$

$$= -\langle E\rangle\frac{\partial \ln Q}{\partial\beta} - \frac{\partial\langle E\rangle}{\partial\beta}$$

$$= -\langle E\rangle \cdot -\langle E\rangle - \frac{\partial\langle E\rangle}{\partial\beta}$$

(16) $$\sigma_E{}^2 = \langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial\langle E\rangle}{\partial\beta} = kT^2\frac{\partial\langle E\rangle_{N,V}}{\partial T} = kT^2 C_v$$

Mean square energy fluctuation $\sigma_E{}^2$ Heat capacity C_v

The relative spread in energy:

For ideal monoatomic gas, the heat capacity and internal energy can be calculated, and we will prove it next lecture

(17) $$\langle E\rangle = \frac{3}{2}NkT$$

(18) $$C_v = \frac{3}{2}Nk$$

From(16), (17) and (18) we can calculate the relative spread of energy for ideal gas,

(19) $$\frac{\sigma_E}{\langle E\rangle} = \frac{(kT^2C_v)^{\frac{1}{2}}}{\langle E\rangle} = \frac{(kT^2\cdot 1.5Nk)^{\frac{1}{2}}}{1.5NkT} \propto \frac{N^{\frac{1}{2}}}{N} = \frac{1}{\sqrt{N}}$$

For a macroscopic system,

$$N \sim 10^{23}, \qquad \frac{\sigma_E}{\langle E\rangle} \sim 10^{-12}$$

The spread in internal energy about the mean is **EXTREMELY SMALL!**

Canonical distribution $P(E)$:

$$P(E) = \frac{\Omega(E)e^{-\beta E}}{Q}$$

The most probable distribution E^* is approximately the average energy because the spread $\frac{\sigma_E}{\langle E \rangle} \sim 10^{-12}$ is so small.

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

When most probable distribution, $P(E)$ or $\ln P(E)$ is at its maximum, its first derivative should be zero,

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

So,

The key to note is:
β is not a function of E
$\bar{E}$ is a function of β, so implicitly $\beta(\bar{E})$

(20) $$\left.\frac{\partial \ln \Omega}{\partial E}\right|_{E=E^*\approx\bar{E}} = \beta$$

And the second derivative,

(21) $$\left.\frac{\partial^2 \ln P(E)}{\partial E^2}\right|_{E=\bar{E}} = \left.\frac{\partial \beta}{\partial E}\right|_{E=\bar{E}} = -\frac{1}{kT^2}\left(\frac{\partial T}{\partial E}\right)_{E=\bar{E}} = -\frac{1}{kT^2 C_V}$$

Canonical distribution $P(E)$:

From Taylor expansion,

(22) $$\ln P(E)$$

$$= \ln P(\bar{E}) + \frac{\partial \ln P(E)}{\partial E}\bigg|_{E=\bar{E}} (E - \bar{E}) + \frac{1}{2}\frac{\partial^2 \ln P(E)}{\partial E^2}\bigg|_{E=\bar{E}} (E - \bar{E})^2 \cdots$$

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

So,

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

Compare to Gaussian distribution,

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

When $E = \bar{E} \pm \sigma_E$, $\frac{E-\bar{E}}{\sigma_E} = \pm 1$,

(24) $$P(\bar{E} \pm \sigma_E) = P(\bar{E})e^{-1/2} \sim 0.6P(\bar{E})$$

Canonical distribution $P(E)$:

The shape of P(E) is like a delta function

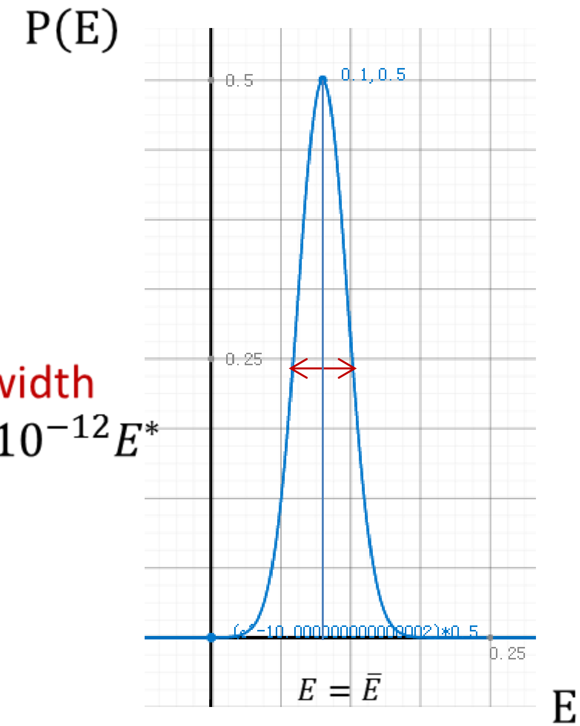
That's why:

$$Q(N,V,T) = \sum_j \Omega(N,V,E_j) e^{-E_j/kT}$$

$$\approx \Omega(N,V,\bar{E}) e^{\frac{-\bar{E}}{kT}}$$

Total width

$2\sigma_E \sim 10^{-12} E^*$



Thermodynamic relation between canonical ensemble and microcanonical ensemble:

In general, a canonical ensemble is a distribution over microcanonical ensembles, it "**degenerates**" to microcanonical ensemble.

In the microcanonical ensemble, the energy of the system is fixed, there are no energy fluctuation.

In canonical ensemble, only the average energy is fixed.

Grand canonical partition function:

The approximations of the partition functions in the different ensembles by a single term makes it easy to determine the characteristic function in any ensemble.

μ fixed, N vary

Let's represent grand canonical ensemble by canonical ensemble:

(25) $$\Xi(V,T,\mu) = \sum_N \sum_j e^{-E_{N,j}(V)} e^{\mu N/kT} \approx \sum_j e^{-E_j(\bar{N},V)} e^{\frac{\mu \bar{N}}{kT}}$$

N: # molecules; j: states

Approximation by a single term with $N = \bar{N}(\mu)$

$$= Q(\bar{N},V,T) \cdot e^{\frac{\mu \bar{N}}{kT}}$$

Characteristic function of Ξ,

(26) $$kT \ln \Xi \approx \underbrace{kT \ln Q}_{-F} + \underbrace{\mu \bar{N}}_{G}$$

$$= G - F = pV$$

So, the **characteristic function** of grand canonical partition function is

(27) $$kT \ln \Xi = pV$$