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MPHYCC-8 Statistical Mechanics

Probability Theory.

Deviation from Most Probable Distribution:

Consider a system of $2N$ particles which distribute themselves in two identical boxes. If one box contains r particles, the other will have $2N-r$ particles.

The number of ways in which r particles can be chosen from $2N$ particles is

$$ {}^{2N}C_r = \frac{\lfloor 2N}{\lfloor r \, \lfloor 2N-r} .$$

The total number of possible distributions from $(2N, 0)$ to $(0, 2N)$ is

$$ \sum_{r=0}^{2N} {}^{2N}C_r = 2^{2N} .$$

Therefore the probability for the distribution in which r particles go to one box and $(2N-r)$ to the other is

$$P(r, 2N-r) = \frac{{}^{2N}C_r}{\sum {}^{2N}C_r} = \frac{\lfloor 2N}{\lfloor r \lfloor (2N-r)} \cdot \frac{1}{2^{2N}} \quad \text{---(i)}$$

The most probable distribution corresponds to equal number of particles in the two boxes, i.e., $r = N$.

$$\Rightarrow P(N, N) = \frac{\lfloor 2N}{\lfloor N \lfloor N} \cdot \frac{1}{2^{2N}} \quad \text{---(ii)}$$

Let us consider a distribution slightly deviated from the most probable distribution, having $N+r$ particles in one box and $N-r$ particles in the other where $r/N \ll 1$. According to eqn. (i), the probability of this distribution will be

$$P(N+r, N-r) = \frac{\lfloor 2N}{\lfloor (N+r) \lfloor (N-r)} \cdot \frac{1}{2^{2N}} \quad \text{---(iii)}$$

The ratio of this distribution to the most probable distribution is

$$Q = \frac{P(N+r, N-r)}{P(N, N)}$$

$$= \frac{\lfloor N \lfloor N}{\lfloor (N+r) \lfloor (N-r)}$$

$$= \frac{\lfloor N}{\lfloor (N+r)} \cdot \frac{\lfloor N}{\lfloor (N-r)}$$

$$= \frac{\lfloor N}{(N+r)(N+r-1)(N+r-2) \cdots (N+1)[\lfloor N]} \cdot \frac{N(N-1)(N-2) \cdots (N-r+1)[\lfloor (N-r)]}{\lfloor (N-r)}$$

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$$= \frac{N(N-1)(N-2)\cdots(N-r+1)}{(N+r)(N+r-1)(N+r-2)\cdots(N+1)}$$

$$= \frac{N}{(N+r)} \cdot \frac{N-1}{N+r-1} \cdots \frac{N-r+2}{N+2} \cdot \frac{N-r+1}{N+1}$$

$$= \left\{\frac{N}{N+r}\right\}\left\{\frac{N-1}{(N-1)+r}\right\}\cdots\left\{\frac{(N+2)-r}{N+2}\right\}\left\{\frac{(N+1)-r}{N+1}\right\}$$

$$= \left\{1-\frac{r}{N+r}\right\}\left\{1-\frac{r}{(N-1)+r}\right\}\cdots\left\{1-\frac{r}{N+2}\right\}\left\{1-\frac{r}{N+1}\right\}$$

For $\frac{r}{N} << 1$ or $r << N$ and $N >> 1$, this can be written as

$$R = \left(1-\frac{r}{N}\right)\left(1-\frac{r}{N}\right)\cdots\left(1-\frac{r}{N}\right)\left(1-\frac{r}{N}\right)$$

$$= \left(1-\frac{r}{N}\right)^r.$$

Taking Natural Logarithm both sides:

$$\log_e R = r \log_e\left(1-\frac{r}{N}\right)$$

$$= r\left(-\frac{r}{N}\right) = -\frac{r^2}{N} \quad \left(\text{Neglecting } \frac{r^2}{N^2} \text{ etc}\right)$$

$$\left[\because \log(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \cdots = -x; \text{ if } x<<1\right]$$

Putting $r/N = f$ (fractional deviation from the most probable distribution), we have

$$\log_e R = -f^2 N$$

or, $\boxed{R = e^{-f^2 N}}$, where $f = \frac{r}{N}$.

This is the relative probability of distribution corresponding to a fractional deviation δ from the most probable distribution.

This shows that the probability of distribution narrows down with increasing N.

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