PHYS7721 Homework 4

Ryan Carelli

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Exercise 1. A vessel of volume $V^{(0)}$ contains $N^{(0)}$ molecules. Assuming that there is no correlation whatsoever between the locations of the various molecules, calculate the probability, $P(N, V)$, that a region of volume V (located anywhere in the vessel) contains exactly N molecules.

(a) Show that $\bar{N} = N^{(0)}p$ and $(\Delta N)_{r.m.s.} = \{N^{(0)}p(1-p)\}^{\frac{1}{2}}$, where $p = \frac{V}{V^{(0)}}$.

(b) SHow that if both $N^{(0)}p$ and $N^{(0)}(1-p)$ are large numbers, the function $P(N, V)$ assumes a Gaussian form.

(c) Further, if $p << 1$ and $N << N^{(0)}$, show that the function $P(N, V)$ assumes the form of a Poisson distribution:

$$P(N) = e^{-\bar{N}}\frac{(\bar{N})^N}{N!}$$

Solution. We have a probability distribution with a binary choice and fixed probability that a particular particle is in a volume (for each particle). So we use the binomial distribution,

$$P(N, V) = \binom{N^{(0)}}{N} p^N q^{N^{(0)}-N}$$

where $p = \frac{V}{V^{(0)}}$ is the probability in question and $q = 1 - p$.

(a)

$$\bar{N} = \sum_{N=0}^{N^{(0)}} NP(N, V) = N^{(0)}p(q+p)^{N^{(0)}} = N^{(0)}p$$

Now to find $(\Delta N)_{r.m.s.}$, we need to find $\overline{N^2}$.

$$\overline{N^2} = \overline{N(N-1)} + \overline{N} = (N^{(0)}p)^2 - N^{(0)}p^2 + N^{(0)}p$$

which implies

$$\overline{(\Delta N)^2} = \overline{N^2} - \overline{N}^2 = N^{(0)}p(1-p)$$

(b) Consider centering at $N = N^{(0)}p$ and

$$N = N^{(0)}p + x$$

$$N^{(0)} - N = N^{(0)}q - x$$

We want to expand the probability in these terms,

$$\ln P(x) = \ln N^{(0)}! - \ln(N^{(0)}p + x)! - \ln(N^{(0)}q - x)! + (N^{(0)}p + x)\ln p + (N^{(0)}q - x)\ln q$$

and apply Stirling,

$$\ln P(x) \approx -(x + N^{(0)}p)\ln\left[1 + \frac{x}{N^{(0)}p}\right] - (N^{(0)}q - x)\ln\left[1 - \frac{x}{xN^{(0)}q}\right]$$

At $x << N^{(0)}p, N^{(0)}q$ we find a power series expansion in x giving

$$P(x) = e^{\frac{-x^2}{2N^{(0)}pq}}$$

which is Gaussian as desired.

(c) Write the binomial distribution,

$$P(N) = \frac{N^{(0)}!}{N!(N^{(0)} - N)!} p^N (1-p)^{N(0)-N}$$

which in the limits $p << 1$ and $N << N^{(0)}$ gives Poisson,

$$P(N) \approx \frac{(N^{(0)})^N}{N!} p^N e^{-N^{(0)}p}$$

□

Exercise 2. Consider a classical system of noninteracting, diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian of a single molecule is given by

$$H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{1}{2}K|\mathbf{r}_1 - \mathbf{r}_2|^2.$$

Study the thermodynamics of this system, including the dependence of the quantity $\langle r_{12}^2 \rangle$ on T.

Solution. Start with the partition function,

$$Q_1 = \int d\omega e^{-\beta E}$$

Since we are in phase space, $d\omega - \frac{dr^6 dp^6}{h^6}$,

$$Q_1 = \int\int d^6 r d^6 p e^{-\beta\frac{p_1^2}{2m} - \beta\frac{p_2^2}{2m} - \beta\frac{1}{2}K|\overline{r_2} - \overline{r_1}|^2} = \frac{1}{h^6}\Big(\frac{2\pi m}{\beta}\Big)^3 \int e^{-\frac{1}{2}\beta K|\overline{r_2} - \overline{r_1}|^2}$$

Changing variables,

$$Q_1 = \frac{1}{h^6}\Big(\frac{2\pi m}{\beta}\Big)^3 \int d^3\bar{x} d^3\bar{y} e^{\frac{-1}{2}\beta K x^2} = \frac{V}{h^6}\Big(\frac{2\pi m}{\beta}\Big)^3 \Big(\frac{2\pi}{K\beta}\Big)^{\frac{3}{2}} = V f(T)$$

so,

$$Q(z, V, T) = e^{zVf(T)}$$

Now the thermodynamics follow from trivial calculations,

$$P = zkTf(T)$$

$$N = zVf(t) = V\beta P$$

$$U = zVkT^2 f'(T) = \frac{9}{2}VP = \frac{9}{2}NkT$$

$$A = NkT\ln(z) - zVkTf(T) = NkT\frac{\mu}{kT} - PV = N\mu - PV$$

$$S = -Nk\ln(z) + zVkf(T) + zVkTf'(T) = \frac{PV}{T} + \frac{U}{T} - \frac{Nk\mu}{kT}$$

Now to evaluate $\langle \bar{r}^2 \rangle = \langle x^2 \rangle$

$$\langle x^2 \rangle = \frac{\int dx_1 dx_2 dx_3 (x_1^2 + x_2^2 + x_3^2) e^{-\frac{1}{2}k(x_1^2+x_2^2+x_3^2)}}{\int dx_1 dx_2 dx_3 e^{-\frac{\beta}{2}K(x_1^2+x_2^2+x_3^2)}}$$

I evaluated this in Maple,

$$\langle x^2 \rangle = \frac{3kT}{K}$$

$\square$

Exercise 3. Show that for a system in the grand canonical ensemble

$$\{\overline{(NE)} - \overline{N}\overline{E}\} = \left(\frac{\partial U}{\partial N}\right)_{T,V} \overline{(\Delta N)^2}.$$

Solution. Start with 4.5.1,

$$\left(\frac{\partial \bar{N}}{\partial \beta}\right)_{\alpha,V} = \overline{-NE} + \bar{N}\bar{E}$$

Rewriting,

$$-kT^2\left(\frac{\partial \bar{N}}{\partial T}\right)_{z,V} = -kT\left(\frac{\partial U}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial U}{\partial \bar{N}}\right)_{T,V}\overline{(\Delta N)^2}$$

$\square$