Statistical Physics Tutorial 1 — J L Gouws

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1. We have:

$$z\frac{\partial \ln \mathfrak{Z}}{\partial z} = z\frac{\partial \mathfrak{Z}}{\partial z}/\mathfrak{Z} = \frac{z}{\mathfrak{Z}}\sum_N N z^{N-1} Z_N = \sum_N N\frac{z^N Z_N}{\mathfrak{Z}} = \sum_N N\frac{e^{\beta\mu N}\sum_r e^{-\beta E_r}}{\mathfrak{Z}} = \sum_N N P_N = \langle N\rangle$$

2. The cannonical partition function for an ideal gas is:

$$\begin{aligned}
Z_N &= \frac{1}{h^3 N!}\int d^{3N}p\ d^{3N}q e^{-\beta H} \\
&= \frac{1}{\lambda^{3N}N!}\int d^{3N}q \exp\left\{-\beta\sum_{i<j} u_{ij}\right\} \\
&= \frac{1}{\lambda^{3N}N!}\int d^{3N}q e^{-\beta\times 0} \\
&= \frac{1}{\lambda^{3N}N!}\int d^{3N}q \\
&= \frac{V^N}{\lambda^{3N}N!}
\end{aligned}$$

Since there is no interaction between ideal gas molecules. We can use this to evaluate the grand partion function for an ensemble of ideal gas samples:

$$\begin{aligned}
\mathfrak{Z} &= \sum_{N=0}^{\infty} z^N\frac{V^N}{\lambda^{3N}N!} \\
&= \sum_{N=0}^{\infty}\frac{(zV/\lambda^3)^N}{N!} \\
&= e^{zV/\lambda^3}
\end{aligned}$$

We also have that:

$$P = \frac{k_B T}{V}\ln\mathfrak{Z} = z\frac{k_B T}{\lambda^3} \implies \frac{P}{k_B T} = \frac{z}{\lambda^3}$$

and:

$$\langle N\rangle = z\frac{\partial}{\partial z}\left[\frac{zV}{\lambda^3}\right] = \frac{zV}{\lambda^3} \implies \frac{\langle N\rangle}{V} = \frac{z}{\lambda^3}$$

From which we deduce:

$$\frac{P}{k_B T} = \frac{\langle N\rangle}{V} \implies PV = \langle N\rangle k_B T$$

3. We have:

$$\frac{1}{\lambda^3}\sum_{l=1}^{\infty} b_l z^l = \frac{P}{k_B T} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} a_l \times \left(\lambda^3 \frac{\langle N\rangle}{V}\right)^l$$
$$\Longrightarrow \sum_{l=1}^{\infty} b_l z^l = \sum_{l=1}^{\infty} a_l \times \left(\sum_{k=1}^{\infty} k b_k z^k\right)^l \tag{1}$$

Now we match coefficients of z. The only way to get a z term on the right handside is if $l = k = 1$:

$$b_1 z = a_1 \times b_1 z \Longrightarrow a_1 = 1$$

Also note that:

$$b_1 = \frac{1}{V}\int_V d^3 r = 1 \Longrightarrow a_1 = b_1 = 1$$

For the z^2 terms, the only way to get z^2 on the right of Eq. 1 is if $l = 1$ and $k = 2$ or if $l = 2$ and $k = 1$

$$\begin{aligned} b_2 z^2 &= a_1 \times (2b_2 z^2) + a_2 \times (b_1 z^1)^2 \\ \Longrightarrow b_2 &= 2b_2 + a_2 \\ \Longrightarrow a_2 &= -b_2 \end{aligned}$$

Where I used the fact that $a_1 = b_1 = 1$. For the z^3 terms, the only way to get z^3 on the right of Eq. 1 is if $l = l$ and $k = 3$ or if $l = 2$ and $k = 1, 2$ (cross multiplied terms) or if $l = 3$ and $k = 1$.

$$\begin{aligned} b_3 z^3 &= a_1 \times (3b_3 z^3) + a_2 \times (b_1 z \times 2b_2 z^2 + 2b_2 z^2 \times b_1 z) + a_3 \times (b_1 z)^3 \\ \Longrightarrow b_3 &= 3b_3 + (-b_2)(4b_2) + a_3 \\ \Longrightarrow a_3 &= 4b_2^2 - 2b_3 \end{aligned}$$

4. We wish to find $a_2 = -b_2$, to this end note that:

$$\begin{aligned} b_2 &= \frac{\lambda^3}{2!V\lambda^{3\times 2}} \int d^3q_1 \int d^3q_2 f_{12} \\ &= \frac{1}{2V\lambda^3} \int d^3q_1 \int d^3(q_2 - q_1) \left[e^{-\beta V(|q_2 - q_1|)} - 1 \right] \\ &= \frac{1}{2V\lambda^3} \int d^3q_1 \int d^3x \left[e^{-\beta V(|x|)} - 1 \right] \end{aligned}$$

Where $x = q_2 - q_1$. Provided that the interaction range of the potential is short the integrals can be treated as approximately independent. This follows from the fact that if q_1 starts differing largely from q_2, the integrand dependent on x becomes negligible ($V \longrightarrow 0$). Thus the integral over x cannot vary much with changing q_1. Hence:

$$\begin{aligned} b_2 &\approx \frac{1}{2V\lambda^3} \left(\int d^3q_1 \right) \left(\int d^3x \left[e^{-\beta V(|x|)} - 1 \right] \right) \\ &= \frac{1}{2\lambda^3} \int d^3x \left[e^{-\beta V(|x|)} - 1 \right] \\ &= \frac{1}{2\lambda^3} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr \left[e^{-\beta V(|r|)} - 1 \right] \\ &= \frac{2\pi}{\lambda^3} \int_0^{\infty} r^2 dr \left[e^{-\beta V(|r|)} - 1 \right] \end{aligned}$$

Now we can use this to evaluate a_2.

$$\begin{aligned} a_2 = -b_2 &= -\frac{2\pi}{\lambda^3} \int_0^{\infty} (e^{-\beta V(r)} - 1) r^2 dr \\ &= -\frac{2\pi}{\lambda^3} \int_0^{\alpha} (0 - 1) r^2 dr - \frac{2\pi}{\lambda^3} \int_{\alpha}^{\infty} (1 - 1) r^2 dr \\ &= \frac{2\pi}{\lambda^3} \int_0^{\alpha} r^2 dr \\ &= \frac{2\pi\alpha^3}{3\lambda^3} \end{aligned}$$

5. Doing a similar calculation to the above:

$$
\begin{aligned}
a_2 &= -\frac{2\pi}{\lambda^3}\int_0^\infty (e^{-\beta V(r)} - 1) r^2 dr \\
&= -\frac{2\pi}{\lambda^3}\left[\int_0^\alpha (0-1) r^2 dr + \int_\alpha^{2\alpha} (e^{\beta v_0/kT} - 1) r^2 dr - \int_{2\alpha}^\infty (1-1) r^2 dr\right] \\
&= -\frac{2\pi}{\lambda^3}\left[-\frac{\alpha^3}{3} + (e^{\beta v_0} - 1)\left(\frac{8\alpha^3}{3} - \frac{\alpha^3}{3}\right)\right] \\
&= -\frac{2\pi\alpha^3(7e^{v_0/kT} - 8)}{3\lambda^3}
\end{aligned}
$$

It can been seen from this that a_2 is negative for low T, and is positive for high T when the exponential is large and small respevtively. Thus a_2 does change sign with temperature.