Thermal Physics

Meeting XVII

Nov 3rd, 2014

I Last time

II Gibbs paradox

III Equipartition (at last)

IV Specific heats of gases and solids

I

- Can interpret canonical ensemble not only as ensemble of systems at fixed T but alternatively as an ensemble of systems with fixed mean energy $\bar{E}$

- Two key properties of the partition function:

(i) $Z_{tot} = Z_1^N$

(ii) $E \rightarrow E^* = E + \epsilon_0$

$$Z \rightarrow Z^* = e^{-\beta\epsilon_0} Z$$

or $\ln Z \rightarrow \ln Z^* = \ln Z - \beta\epsilon_0$

- Evaluated Z for monatomic ideal gas in the classical limit to find

$$\ln Z' = N\left[\ln V - \tfrac{3}{2}\ln\beta + \tfrac{3}{2}\ln\left(\tfrac{2\pi m}{h^2}\right)\right]$$

$$\bar{E} = \tfrac{3}{2}NkT$$

$$\bar{p}V = NkT$$

$$S = Nk\left[\ln V - \tfrac{3}{2}\ln\beta + \tfrac{3}{2}\ln\left(\tfrac{2\pi m}{h^2}\right) + \tfrac{3}{2}\right]$$

$$= k\left(\ln Z' + \beta\bar{E}\right) \quad \text{Wrong!}$$

II If we double the system we expect

$$S = S' + S'' = 2S'$$

While for the doubled gas we find,

$$S = 2Nk\left[\ln 2V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi M}{h^2}\right) + \frac{3}{2}\right]$$

and

$$S - 2S' = 2Nk\ln 2V - 2Nk\ln V = 2Nk\ln 2$$

Let

$$Z = \frac{Z'}{N!} = \zeta^N / N!$$

$$\ln Z = N\ln\zeta - \ln N!$$

$$\cong N\ln\zeta - N\ln N - N$$

and

$$\boxed{S = kN\left[\ln\frac{V}{N} \overset{-}{\cancel{+}} \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi M}{h^2}\right) + \frac{5}{2}\right]}$$

But the entropy can't actually have increased. We have failed to take into account the indistinguishability of the atoms! This is a quantum aspect ultimately but has a simple classical fix.

Were we otherwise justified in treating the gas classically? Yes! Let $\bar{R}$ be the mean separation of atoms — it's classical if

momentum!!

$$\bar{R}\,\bar{p} \gg h$$

or

$$\bar{R} \gg \lambda = \frac{h}{\bar{p}}$$

the de Broglie wavelength.

III Now, for a molecule of mass m in a dilute gas

$$\epsilon = \underset{\substack{\uparrow \\ \text{Classical}}}{\frac{\vec{p}^2}{2m}} + \underset{\nwarrow\ \text{quantum}}{\epsilon_s^{(int)}}$$

$$P_s(\vec{r},\vec{p})\, d^3\vec{r}\, d^3\vec{p} \propto e^{-\beta[\vec{p}^2/2m + \epsilon_s^{(int)}]}\, d^3\vec{r}\, d^3\vec{p}$$

If we sum over the internal states this just modifies the proportionality constant

$$P(\vec{r},\vec{p})\, d^3\vec{r}\, d^3\vec{p} \propto e^{-\beta\, \vec{p}^2/2m}\, d^3\vec{r}\, d^3\vec{p}$$

Let

$f(\vec{r},\vec{v})\, d^3\vec{r}\, d^3\vec{v}$ = mean # of molecules with com between $\vec{r}$ and $\vec{r}+d\vec{r}$, and vel between $\vec{v}$ and $\vec{v}+d\vec{v}$.

Then

$$f(\vec{r},\vec{v})\, d^3\vec{r}\, d^3\vec{v} = C e^{-\beta \frac{m\vec{v}^2}{2}}\, d^3\vec{r}\, d^3\vec{v}$$

and requiring that

$$\int_{(\vec{r})}\int_{(\vec{v})} f\, d^3\vec{r}\, d^3\vec{v} = N$$

allows us to determine C. We find

$$CV\left(\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2}\, dv_x\right)^3$$

$$= CV\left(\frac{2\pi}{\beta m}\right)^{3/2} = N$$

or $C = n\left(\frac{\beta m}{2\pi}\right)^{3/2}$, $n = \frac{N}{V}$.

Hence,

$$f(\vec{v})\, d^3\vec{r}\, d^3\vec{v} = n\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m \vec{v}^2} d^3\vec{r}\, d^3\vec{v}$$

$$= n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} d^3\vec{r}\, d^3\vec{v}$$

Usually divide by $d^3\vec{r}$ and just talk about the velocity distribution.

<u>Ex</u>: What is the distribution of the x-components of velocity?

$g(v_x)\, dv_x$?