Thermal Physics Meeting XVIII

Nov 5th, 2014

I last time

II Heat capacity of a solid

III Kinetic theory of dilute gases

- Gibbs paradox is practically addressed by

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

- Equipartition Theorem (classical result)

For every quadratic term in the Hamiltonian (energy) you get

$$\bar{\epsilon} = \frac{1}{2}kT$$

worth of average energy — this need not only come from momenta.

- Applied this to the ideal gas

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

and to the Einstein Solid

$$\bar{E} = 3NkT = 3\nu RT$$

to find

$$c_v = \frac{1}{\nu}\left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3R.$$

Trouble with diamond at room temperature. Why?

II Let's calculate c_v again

P2/6

We have
$$\bar{R} \sim \left(\frac{V}{N}\right)^{1/3}$$

and
$$\frac{\bar{p}^2}{2m} \sim \bar{\epsilon} = \frac{3}{2}kT$$

or
$$\bar{p} \sim \sqrt{3mkT}$$

So we want
$$\left(\frac{V}{N}\right)^{1/3} = \bar{R} \gg \frac{h}{\sqrt{3mkT}}$$

i.e. T large, concentration small and mass large.

For He at room temp.
$$\tilde{R} \approx 34 \times 10^{-8}\,\text{cm}$$
$$\bar{\lambda} \approx 0.6 \times 10^{-8}\,\text{cm}$$

so classical is pretty good — gets even better for heavier molecules

III Consider a system of f degrees of freedom with
$$E = E(q_1, \ldots, q_f, p_1, \ldots, p_f)$$

and such that:

a. $E = \epsilon_i(p_i) + E'(q_1, \ldots, \hat{p}_i, \ldots p_f)$

and

b. $\epsilon_i(p_i) = b p_i^2$

that is, it has a quadratic dependence on p_i. Then
$$\boxed{\bar{\epsilon}_i = \frac{1}{2}kT}$$

In words, you get a half kT for every quadratic degree of freedom (Note: they don't have to all be momenta.)

Proof:
$$\epsilon_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E}\, \epsilon_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E}\, dq_1 \cdots dp_f}$$

Use hypothesis a, $e^{-\beta E} = e^{-\beta(\epsilon_i + E')}$

so,

$$\bar{\epsilon}_i = \frac{\int e^{-\beta\epsilon_i}\epsilon_i\,dp_i \int e^{-\beta E'}\,dq_1\cdots\hat{dp_i}\cdots dp_f}{\int e^{-\beta\epsilon_i}\,dp_i \int e^{-\beta E'}\,dq_1\cdots\hat{dp_i}\cdots dp_f}$$

$$= \frac{\int e^{-\beta\epsilon_i}\epsilon_i\,dp_i}{\int e^{-\beta\epsilon_i}\,dp_i}$$

$$\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\,dp_i = \int_{-\infty}^{\infty} e^{-\beta b p_i^2}\,dp_i = \beta^{-\frac{1}{2}}\int_{-\infty}^{\infty} e^{-by^2}\,dy$$

where $y = \beta^{1/2} p \Rightarrow dp = \beta^{-1/2}\,dy$

Then

$$\epsilon_i = -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\ln\beta + \ln\int_{-\infty}^{\infty} e^{-by^2}\,dy\right)$$

$$= \frac{1}{2\beta} = \frac{1}{2}kT. \quad \checkmark\checkmark$$

Use our derivative tool

$$\epsilon_i = \frac{-\frac{\partial}{\partial\beta}\left(\int e^{-\beta\epsilon_i}\,dp_i\right)}{\int e^{-\beta\epsilon_i}\,dp_i}$$

$$= -\frac{\partial}{\partial\beta}\ln\left(\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\,dp_i\right)$$

Now we could use $\epsilon_i = bp_i^2$ to do the integral but lets not! Instead let's change variables

A classical stat mech theorem — if kT is comparable to ΔE (= level spacing) it doesn't apply.

<u>Examples</u>:

(1) What is the mean energy of an ideal gas?

There are 3N quadratic degrees of freedom and so

$$\bar{E} = 3N\left(\frac{1}{2}kT\right) = \frac{3}{2}NkT.$$

(2) What are the mean ~~velocity~~ x-comp of velocity and energy E_x of

a light particle in a glass of water on the table?

By symmetry $\bar{v}_x = 0$

but

$$\overline{\tfrac{1}{2}Mv_x^2} = \tfrac{1}{2}kT \Rightarrow \overline{v_x^2} = \frac{kT}{M}$$

why the particle has to be light.

"Brownian motion" helped support the atomic model (another 1905 paper of Einstein's).

(3) What about the mean energy of a 1D harmonic oscillator? Well,

$$E = \frac{p^2}{2m} + \frac{1}{2}K_0 x^2$$

has two quadratic d.o.f. and so,

$$\bar{E} = kT$$

You may recall that our partition function analysis gave us

$$\bar{E} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \left[\tfrac{1}{2}\hbar\omega\right]$$

we neglected this before

In the high temperature limit $\beta\hbar\omega \ll 1$

and

$$\bar{E} = \hbar\omega\left[\frac{1}{1+\beta\hbar\omega+\dots-1} + \frac{1}{2}\right]$$

$$\simeq \hbar\omega\,\frac{1}{\beta\hbar\omega} = kT \checkmark$$

In the low temp. limit $\beta\hbar\omega = \frac{\hbar\omega}{kT} \gg 1$

$$\bar{E} = \hbar\omega\left(\tfrac{1}{2} + e^{-\beta\hbar\omega}\right)$$

which is not classical!

IV Using your recent result what is the molar specific heat of a gas?

$$\bar{E} = \frac{3}{2} NkT = \frac{3}{2} \nu RT$$

So

$$c_v = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_v = \boxed{\frac{3}{2} R}$$

Now, let's return to the Einstein Solid. Using equipartition, what ~~is~~ are the mean energy and heat capacity?

$$\bar{E} = \underbrace{3N}_{\#\text{ of oscillators}} \left[\tfrac{1}{2} kT \times 2 \right]$$

$$= 3NkT$$

But then

$$c_v = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_v = \boxed{3R}$$

If you look at the table on p 254 of our text you'll see this works quite well, except for diamond. Calculate c_v again using our full results on the Einstein Solid:

$$\bar{E} = 3N\hbar\omega\left(\frac{1}{e^{\beta\hbar\omega}-1} + \frac{1}{2}\right)$$

$$c_v = \frac{1}{\nu}\left(\frac{\partial \bar{E}}{\partial T}\right)_v = \frac{1}{\nu}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_v \frac{\partial \beta}{\partial T}$$

$$= -\frac{1}{kT^2\nu}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_v$$

$$= -\frac{3Nk\hbar\omega}{k^2T^2\nu}\left[-\frac{e^{\beta\hbar\omega}\hbar\omega}{(e^{\beta\hbar\omega}-1)^2}\right]$$

or

$$c_v = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$$

with $\frac{\Theta_E}{T} \equiv \frac{\hbar\omega}{kT}$.