Lecture 15 - Equipartition theorem

What's Important:
- equipartition theorem
- applications: ideal gas, harmonic oscilator, 3D lattice

Text: Reif

Skip Secs. 7.1 to 7.4

Cheap tricks: equipartition theorem

A simple expression for the mean energy per degree of freedom arises when the total energy of a system
- is quadratic in its variables; *e.g.* $K = p^2/2m$ or $V = kx^2/2$
- separates into single-variable expressions, such as $K = p_1{}^2/2m_1 + p_2{}^2/2m_2$.

For a given degree of freedom (labeled by an index *i*), let us write the energy as

$$\varepsilon_i = b\, p_i^2$$

where p_i could be a coordinate or its time derivative. Then

$$\bar{\varepsilon}_i = \frac{\int \varepsilon_i \exp(-ß[E_{rem} + \varepsilon_i])dq_1..dq_f dp_1..dp_f}{\int \exp(-ß[E_{rem} + \varepsilon_i])dq_1..dq_f dp_1..dp_f}$$

where $E_{\rm rem}$ is the remaining energy in the system, other than ε_i:

$$E_{\rm rem} = E - \varepsilon_i.$$

Because the energy separates into a piece that depends on p_i, and the residue which does not, we can write

$$\bar{\varepsilon}_i = \frac{\int \varepsilon_i \exp(-ß\varepsilon_i)dp_i \int \exp(-ßE_{rem})dq_1...dp_f}{\int \exp(-ß\varepsilon_i)dp_i \int \exp(-ßE_{rem})dq_1...dp_f}$$

The integrals **not** involving p_i obviously all cancel, leaving us with

$$\bar{\varepsilon}_i = \frac{\int bp_i^2 \exp(-ßbp_i^2)dp_i}{\int \exp(-ßbp_i^2)dp_i}$$

Now, the integral in the numerator can be expressed as

$$\int p_i^2 e^{-ßbp_i^2} dp_i = -\frac{\partial}{\partial ß}\int e^{-ßbp_i^2} dp_i = -\frac{\partial}{\partial ß} I(ß)$$

permitting the mean energy of mode *i* to be written in the compact form

$$\bar{\varepsilon}_i = \frac{-\frac{\partial}{\partial ß} I(ß)}{I(ß)} = -\frac{\partial}{\partial ß} \ln I(ß).$$

To evaluate this expression, we use a formal trick seen elsewhere in this course, where we isolate the *ß*-dependence of the logarithm before taking its derivative:

$$\ln I(\beta) = \ln \int e^{-\beta b p^2} dp = \ln \left[(\beta b)^{-1/2} \int e^{-y^2} dy \right]$$

$$= -\tfrac{1}{2} \ln \beta b + \ln \int e^{-y^2} dy$$

Clearly, the remaining integral has no *ß*-dependence, and is just a numerical constant (important if we want to know the logarithm, but not for its derivative). Thus,

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial \beta} \left[-\frac{1}{2} \ln \beta b + const \right]$$

$$= -\left(-\frac{1}{2} \right) \frac{\partial}{\partial \beta} \left[\ln \beta + \ln b + const \right]$$

$$= \frac{1}{2\beta}$$

$$= \frac{k_B T}{2}$$

This result was obtained previously within the context of the translational motion of particles in an ideal gas. We now find that it is applicable to any degree of freedom whose contribution to the energy is

- quadratic
- independent of other modes of motion.

This is referred to as the **equipartition theorem**.

Ideal gas, again

The kinetic energy is quadratic in momenta, so the mean kinetic energy is

$$\bar{K} = \frac{f}{2} k_B T .$$

Harmonic oscillator in 1D

Each oscillator has energy

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

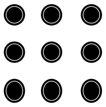
Hence

$$\bar{E} = 2 \cdot \frac{1}{2} k_B T = k_B T .$$

(This result neglects quantum effects, see following lecture).

Particles on a 3D lattice

Place N particles on a lattice



and permit them to oscillate about their equilibrium positions according to Hooke's law:

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{3N} \frac{kx_i^2}{2}$$

From the equipartition theorem,

$$\bar{E} = 3N \cdot \frac{1}{2} k_B T + 3N \cdot \frac{1}{2} k_B T = 3Nk_B T$$

This result can be tested by measuring the heat capacity (here at constant volume)

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{\partial}{\partial T} 3Nk_B T = 3Nk_B$$

For a mole of particles (N = Avogadro's number = N_o), this predicts

$$c_v = 3(N_o k_B) = 3R,$$

where R is the universal gas constant, or

$$c_v = 3 \times 8.31 = 24.9 \text{ J/K}.$$

The prediction for the molar specific heat of solids is called the Dulong-Petit rule, and it agrees very well with experiment for many solids.

Solid	c_p (at 25 °C)
Cu	24.5
Si	25.5
Pb	26.4

Note: c_v is hard to measure for solids because of the difficulty in fixing the volume. Experimentally, c_v is about 5% smaller than c_p.