10.40 Thermodynamics **Fall 2003**

Problem Set 8

Problem 1

═══

Compute $U/(RT)$ of a mole of diatomic ideal gas molecules treating the vibrational mode classically. Assume that the vibrational frequency is 10^{13} s^{-1}, and take the reference state as $\underline{E} = 0$ when the system is in its ground state (degeneracy of 1 and no important excited electronic states). In a few words, explain the significance of the difference between the quantum and classical results.

Solution:
From quantum mechanics, the energy levels of a harmonic oscillator are:

$$\varepsilon_n = \left(n + \tfrac{1}{2}\right)h\nu \quad \text{for } n = 0, 1, 2, \ldots$$

Then using the definition of the ensemble average, we can calculate the contribution from the vibrational mode of a single diatomic molecule to the internal energy as:

$$\left\langle \underline{U}_V \right\rangle = \sum_i \left(P_N(\varepsilon_i)\right)\varepsilon_i = \frac{\displaystyle\sum_{i=0}^{\infty}\varepsilon_i e^{(-\beta\varepsilon_i)}}{\displaystyle\sum_{i=0}^{\infty} e^{(-\beta\varepsilon_i)}} = \frac{\displaystyle\sum_{i=0}^{\infty}\left(n+\tfrac{1}{2}\right)h\nu\, e^{\left(-\beta\left(n+\tfrac{1}{2}\right)h\nu\right)}}{Q_N}$$

However, this problem asks us to compute U/RT treating the vibrational mode classically. Therefore, we can assume that the energy of each possible state forms a continuum and can be integrated. We also assume that the classical Hamiltonian applies, so that the contribution from a single molecule is:

$$\left\langle \underline{U}_V \right\rangle = \frac{\displaystyle\int \ldots \int H(\boldsymbol{q},\boldsymbol{p}) e^{(-\beta H(\boldsymbol{q},\boldsymbol{p}))}d\boldsymbol{q}d\boldsymbol{p}}{\displaystyle\int \ldots \int e^{(-\beta H(\boldsymbol{q},\boldsymbol{p}))}d\boldsymbol{q}d\boldsymbol{p}}$$

$$H(\boldsymbol{q},\boldsymbol{p}) = T(\boldsymbol{p}) + \Phi(\boldsymbol{q})$$

In the above equation, $H(\boldsymbol{r},\boldsymbol{p})$ is the Hamiltonian that describes the energy of the particle as a function of its position and momentum. If we consider the vibrational mode classically, we envision a diatomic molecule as two particles attached by a spring. For a spring, Hooke's Law gives $F = -k_s x$, where k_s is the spring constant. The kinetic energy and potential energies of a spring are given by

$$T(\boldsymbol{p}) = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\Phi(\boldsymbol{q}) = -\int F(x)\,dx = \frac{1}{2}k_s x^2$$

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}k_s x^2$$

Plugging this expression into our previous integral gives:

$$\langle \underline{U}_V \rangle = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)e^{\left(-\beta\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)\right)}dxdp}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{\left(-\beta\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)\right)}dxdp}$$

Performing the integration, noting that

$$\int_{-\infty}^{\infty}e^{-a^2 x^2}x = \frac{\sqrt{\pi}}{a}$$

$$\int_{-\infty}^{\infty}x^2 e^{-a^2 x^2}x = \frac{1}{2}\frac{\sqrt{\pi}}{a^3}$$

We get

$$\langle \underline{U}_V \rangle = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)e^{\left(-\beta\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)\right)}dxdp}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{\left(-\beta\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)\right)}dxdp} = \frac{2\pi m^{1/2}\Big/\beta^2 k_s^{1/2}}{2\pi m^{1/2}\Big/\beta k_s^{1/2}} = \frac{1}{\beta} = k_B T$$

For a system made up of N molecules:

$$\underline{U}_V = Nk_B T = RT \quad \rightarrow \quad \frac{\underline{U}_V}{RT} = 1$$

The same answer could have been found by noting that for a single molecule, the partition function is

$$q_V = c\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{\left(-\beta\left(\frac{p^2}{2m} + \frac{1}{2}k_s x^2\right)\right)}dxdp$$

where the constant c is needed as a quantum correction. Noting that the spring constant $k_s^{1/2} = 2\pi\nu m^{1/2}$, we find

$$q_V = \frac{2\pi c m^{1/2}}{\beta k_s^{1/2}} = \frac{2\pi c m^{1/2}}{\beta 2\pi\nu m^{1/2}} = \frac{c}{\beta\nu} = \frac{c k_B T}{\nu}$$

and by inspection, we conclude that $c = h$, Planck's constant. Then, we use the relation

$$\underline{U}_V = k_B T^2\left(\frac{\partial \ln q_V^N}{\partial T}\right)_{\underline{V},N} = \frac{Nk_B T^2}{q_V}\left(\frac{\partial q_V}{\partial T}\right)_{\underline{V},N} = Nk_B T$$

There is one final point to mention. In the stat mech notes from class, the ground state is taken to be the separated atoms of the molecule at rest. This corresponds to the bottom of a well whose depth is D_e, the dissociation energy of the molecule. For this reason, we write the electronic partition function in its ground state as:

$$q_e = \omega_{e1} e^{-D_e / kT}$$

However, for this problem, we are told that the reference energy is $\underline{E} = 0$ when the system is in its ground state, and there is a degeneracy of 1. Therefore, $q_e = e^{0/kT} = 1$ and the electronic mode does not contribute to the internal energy. Since the translational and rotational modes were already treated classically in their development, the final expression for $\underline{U}/RT$ when all modes are treated classically is:

$$\frac{\underline{U}}{RT} = \underbrace{\frac{3}{2}}_{trans} + \underbrace{\frac{2}{2}}_{rot} + \underbrace{1}_{vib} = \frac{7}{2}$$

Students should realize that the reason for the ½RT contribution from the various degrees of freedom is due to the equipartition rule. In other words, each time a ½ x^2 or ½ p^2 term appears in the Hamiltonian, it results in a contribution of ½RT to the internal energy of the particle. The translational mode is made up of 3 degrees of freedom, each with a momentum term but with no potential energy term. The rotational term also contains a momentum term only (in this case, two for the two degrees of freedom). Since the single vibrational degree of freedom contains both a momentum and potential energy term in the Hamiltonian when it is treated as a classical spring, it contributes 2x(½)RT to the internal energy. If some other model were used to describe the Hamiltonian classically (ex. Leonard-Jones potential in the case of a non-ideal gas), then the vibrational contribution would not necessarily be RT.

The same result as the classical case is found for the quantum case of the vibrational mode at T gets very large:

$$\lim_{T \to \infty} \frac{U_V^{quant}}{RT} = \lim_{T \to \infty} \left(\frac{\theta_v}{2T} + \frac{\theta_v/T}{e^{\theta_v/T} - 1} \right) = 1$$

This is because at higher temperatures, a large number of the vibrational energy levels are filled, so that the energy difference between them is small and the levels can be approximated as a continuum. However, at lower temperatures, like those normally encountered in engineering problems, an appreciable number of energy levels are not filled so that a classical approximation does not give accurate results. The quantum expression for the vibrational mode is needed since it gives more accurate results at these conditions.