(Note the similarity to the pair potential for molecular collisions, Unit ICS.) Near its minimum this potential can be quite accurately approximated as a parabola. When the parabolic-linear spring-potential is introduced in the Schroedinger equation, the resulting energy levels and degeneracy are

$$\varepsilon_{v,\ell} = B_v f_v(\ell) \qquad B_v = h\nu \qquad f_v(\ell) = (\ell + \tfrac{1}{2}) \qquad g_v(\ell) = 1 \qquad \ell = 0,1,2,3$$

This quantum number series, ℓ, also begins with zero, but the minimum energy is not zero, $\varepsilon_{v,0} = h\nu/2$. Each increased energy level represents a larger amplitude (from one side of the parabolic potential to the other) single frequency (simple harmonic) vibration of the atoms about the mean bond distance. The vibrational energy levels are nondegenerate. The vibrational characteristic temperature is given as

$$\theta_v = \frac{B_v}{k} = \frac{h\nu}{k}$$

Diatomic molecules are bound by a single molecular bond. Thus they have only one mode of molecular vibration. The partition function series can be represented as an analytic function without approximation[13]

$$Z_v = \sum_{\ell=0}^{\infty} e^{-(\ell+\frac{1}{2})\,\theta_v/T} = e^{-\theta_v/2T} \sum_{\ell=0}^{\infty} \left(e^{-\theta_v/T}\right)^{\ell} = \frac{e^{-\theta_v/2T}}{1-e^{-\theta_v/T}}$$

Since Z_v is represented as an analytic function, the vibration mode distribution can be determined in general. That is, without recourse to low or high temperature approximations. This is fortunate since vibration characteristic temperatures range from below normal to moderately high temperatures. Therefore, one commonly requires vibrational properties near the various characteristic temperatures. The probability distribution for a vibrational mode is

$$\rho_v(\ell) = \left(1 - e^{-\theta_v/T}\right)\left(e^{-\theta_v/T}\right)^{\ell}$$

Exercise 12. Determine the percentage of particles that are in the 1st, 2nd, and 10th vibrational level at the following temperatures: $T = 0.1\ \theta_v$, θ_v, and $10\ \theta_v$.

The results of Exer. 12 show that the population in the vibrational levels shifts from the lowest toward higher levels as the temperature increases with respect to θ_v.

The contribution of the vibrational mode to the properties of a diatomic gas is determinable from Z_v and its derivatives. Results are listed in Table IIIC-1 and illustrated in the following exercise.

Exercise 13. Derive expressions for $\bar{u}_v$, $\bar{c}_{v,v}$, and $\bar{s}_v$ for a diatomic gas.

---

[13]The infinite series is of the form

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad |x| \le 1$$