Substitution gives an expression for the probability of an energy level

$$\rho_{el}(\varepsilon)\Big|_{\substack{T=0_\circ \\ \varepsilon<\varepsilon_F^\circ}} = \frac{n_{el}(\varepsilon)}{N_{el}} = \frac{3}{2}\,\frac{\varepsilon^{\frac{1}{2}}}{(\varepsilon_F^\circ)^{3/2}} \qquad \rho_{el}(\varepsilon)\Big|_{\substack{T=0_\circ \\ \varepsilon>\varepsilon_F}} = 0$$

A speed distribution is obtained by substituting

$$\varepsilon = \frac{m_e^* V^2}{2} \qquad \varepsilon_F^\circ = \frac{m_e^* V_F^2}{2} \qquad d\varepsilon = m_e^* V dV$$

into

Ans. 1. To go from Cartesian to spherical velocity coordinates, we express $dV_x\, dV_y\, dV_z \Rightarrow V^2 \sin\theta\, d\theta\, d\phi\, dV$ where $0 \le V \le \infty$, $0 \le \theta \le \pi$, and $0 \le \phi \le 2\pi$. Then the probability integral is

$$1 = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \rho(\bar{V})V^2 \sin\theta\, d\phi\, d\theta\, dV$$

The speed distribution is obtained by integrating the velocity distribution over θ and ϕ. This gives $\int_0^{2\pi}\int_0^{\pi} \sin\theta\, d\phi\, d\theta = 4\pi$. So

$$\rho(V) = 4\pi V^2\, \rho(\bar{V}) = \frac{4\pi}{(2\pi RT)^{3/2}}\, V^2\, e^{-V^2/2RT}$$

Ans. 2. The most probable speed is determined by setting

$$\frac{d}{dV}\rho(V) = \frac{4\pi}{(2\pi RT)^{3/2}}\frac{d}{dV}\left[V^2\, e^{-V^2/2RT}\right] = \frac{4\pi\, e^{-V^2/2RT}}{(2\pi RT)^{3/2}}\left(2V - \frac{2V^3}{2RT}\right) = 0$$

This gives $\qquad V_{mp}^2 = 2RT, \qquad V_{mp} = \sqrt{2RT}.$

Ans. 3. The velocity distribution specifies direction as well as magnitude of particle translational energy. It corresponds to the probability of each specific energy *state*. The speed distribution specifies only the magnitude of particle energy. It corresponds to the probability of each energy *level*. There are very few states of low energy. Thus the probability of the low energy states (velocities) can be relatively high even while these levels (speeds) are not probable. The most probable level (speed) is achieved when the increasing numbers of states per level can no longer compensate for the decreasing probability of the higher energy states.

Ans. 4. As defined, the average kinetic energy requires a determination of the average speed squared. Transforming to dimensionless form, we find

$$\widehat{V^2} = \int_0^\infty V^2\, \rho(V)dV = \frac{4\pi}{(2\pi RT)^{3/2}}\int_0^\infty V^2 V^2\, e^{-V^2/2RT} = \frac{4\pi}{(2\pi RT)^{3/2}}\,(2RT)^{5/2}\int_0^\infty x^4\, e^{-x^2}\, dx$$

$$= \frac{4\pi}{(\pi)^{3/2}}\,(2RT)\left(\frac{3\sqrt{\pi}}{8}\right) = 3RT$$

Thus, since $R = \bar{R}/M = k/m^*$, $\hat{\varepsilon}_{ke} = m^* V^2/2 = 3m^* kT/(2m^*) = (3/2)\,kT$. And the toal energy for a mole of molecules is

$$\bar{u}_{ke} = N_A\, \hat{\varepsilon}_{ke} = \frac{3}{2}\, N_A kT = \frac{3}{2}\,\bar{R}T,$$

which is the same as that determined for the translational mode in Unit IIIC.