PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

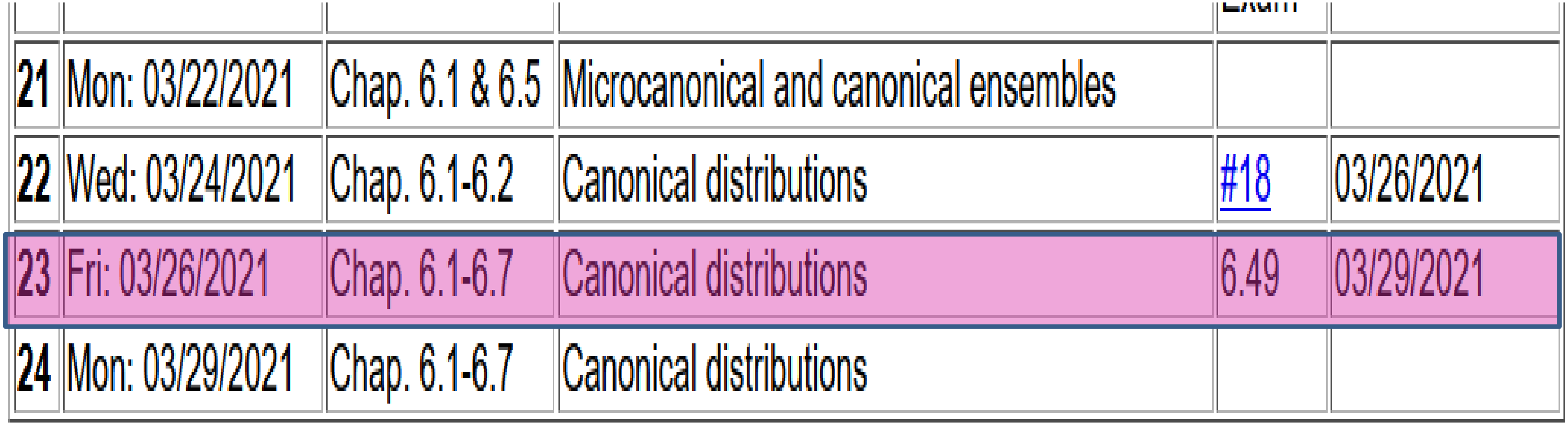
Record!!!

Discussion for Lecture 23:

Introduction to statistical mechanics – Single particle and multi particle systems

Reading: Chapter 6.1-6.7

1. Partition function for a simple free particle
2. Partition function for a complex free particle
3. Partition function for multiple particles; distinguishable or indistinguishable



21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	#18	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions		

Homework problem from textbook:

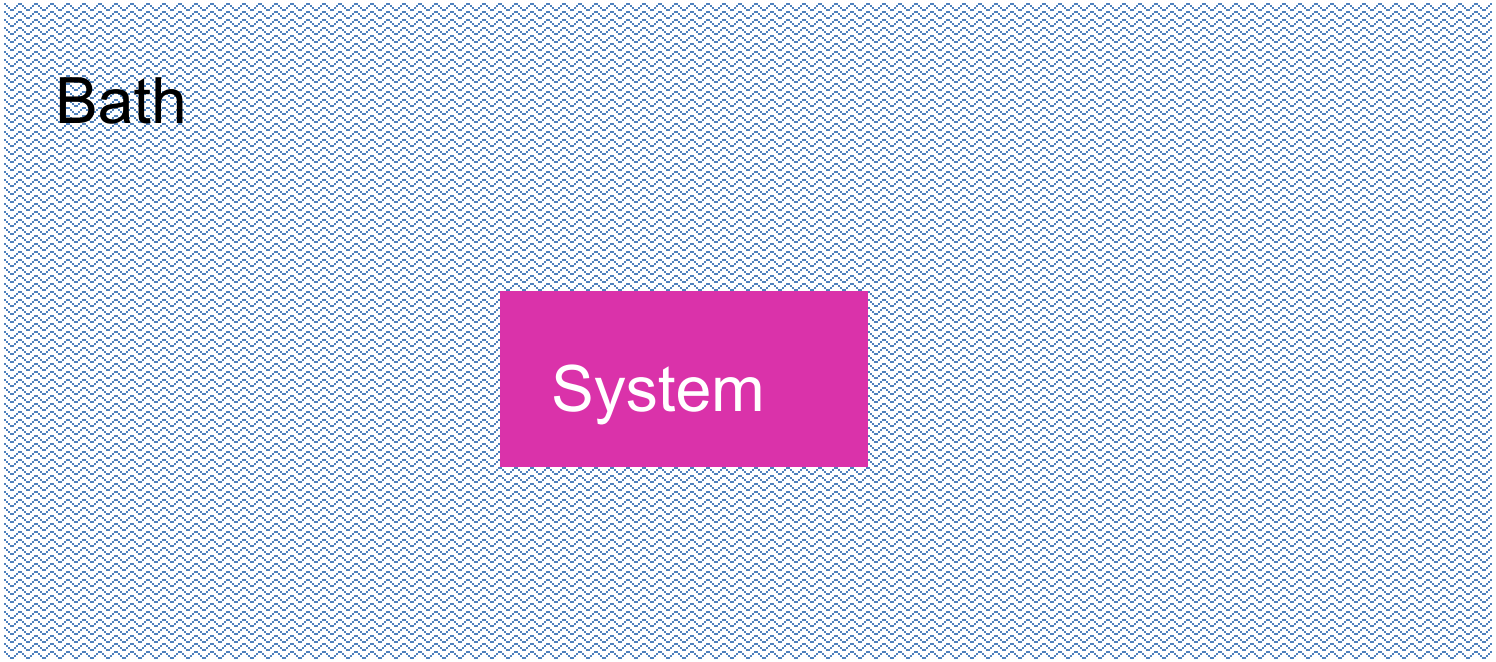
6.49 For a mole of nitrogen (N_2) gas at room temperature and atmospheric pressure, compute the following: U, H, F, G, S, and μ. The rotational constant ε for N_2 is 0.00025 eV. The electronic ground state is non degenerate.

Your questions –

From Kristen -- 1. While I mostly understand the proof of the equipartition theorem, I am still a bit unsure about what it is actually telling us/why it is important. 2. What does Vrms (the root-mean-square speed) actually mean and how can we drive its equation from the equipartition formula?

From Rich -- What do you use for Uint and Fint when calculating the Cv or F from the partition function?

Canonical ensemble for system in bath



$$\mathcal{P}_s = \frac{e^{-U_s/kT}}{Z} \quad \text{where } Z = \sum_s e^{-U_s/kT}$$

Examples for systems of single particles:

First consider a single atom of mass *m* in box of volume *V*

Its energy depends on only on its momentum **p** in terms of its kinetic energy

$$U_s \equiv U_{\mathbf{p}} = \frac{p^2}{2m}$$

$$\sum_s e^{-U_s/kT} \to \frac{1}{h^3}\int d^3r \int d^3p \; e^{-p^2/(2mkT)} = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} dp_x e^{-p_x^2/(2mkT)}\right)^3$$

V

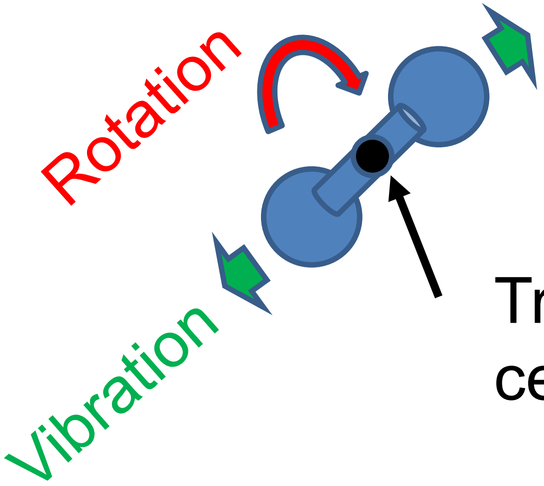
$$= \frac{V}{h^3}\left(2\pi mkT\right)^{3/2}$$

Planck’s constant for compatibility with QM

See Appendix B

$$Z_{1\,\mathrm{trans}}(T,V) = \frac{V}{h^3}\left(2\pi mkT\right)^{3/2}$$

Now consider the motions of a more complicated system such as a diatomic molecule



Translations of center of mass

$$U_s = U_{trans}(\mathbf{p}) + U_{rot}(j) + U_{vib}(\nu)$$

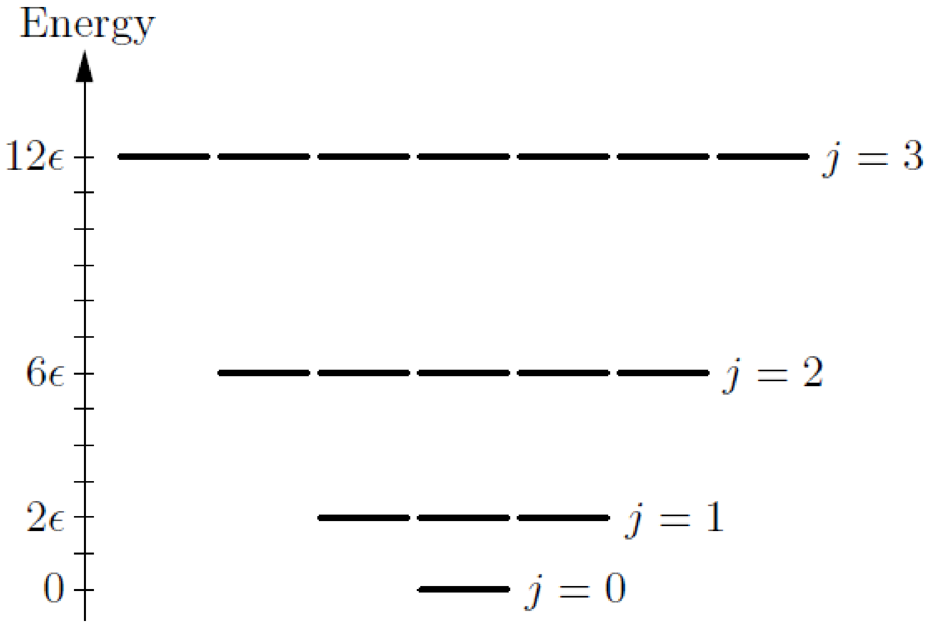
Rotations of a diatomic molecule

Quantum mechanics tells us that the rotational energy levels of rotating diatomic molecule has discrete states specified by integers $j = 0, 1, 2, 3...$

$U_{rot}(J) = j(j+1)\epsilon$ each with degeneracy $2j+1$

$$Z_{rot}(T) = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT}$$

Figure 6.6. Energy level diagram for the rotational states of a diatomic molecule. Copyright ©2000, Addison-Wesley.



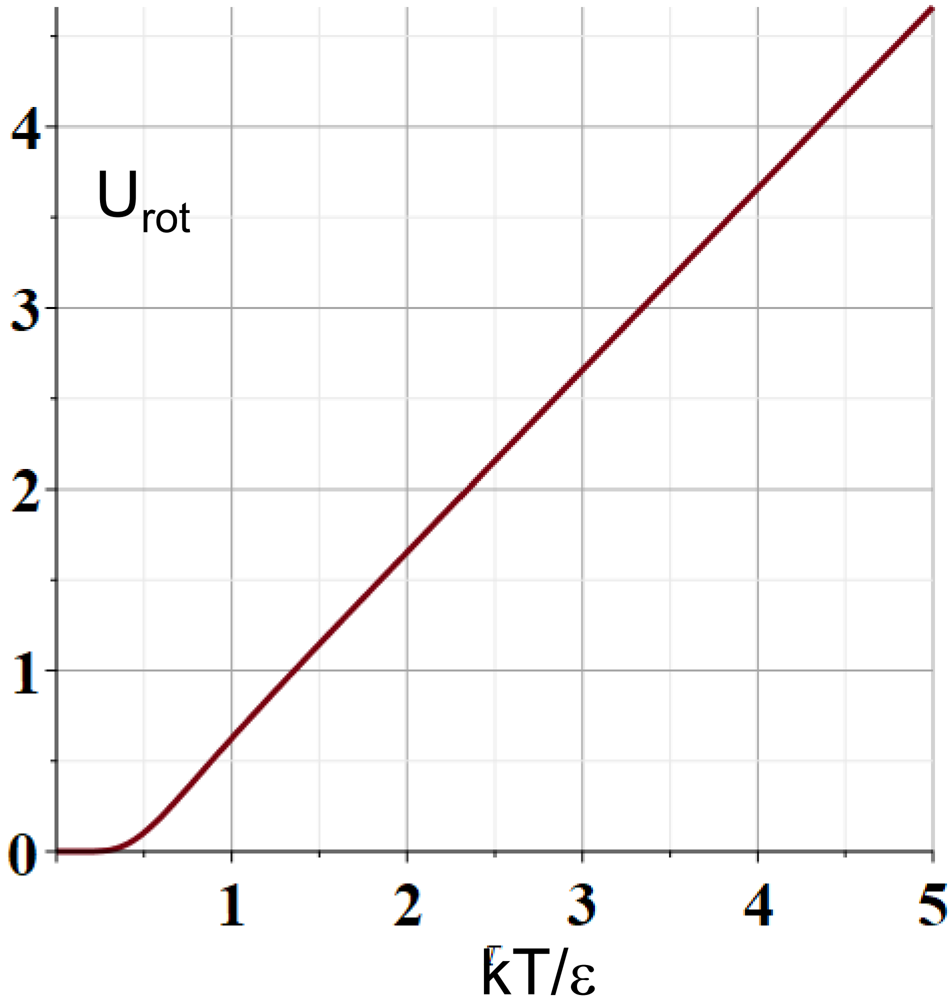
Rotations of a diatomic molecule -- continued

$$Z_{rot}(T)=\sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}$$

$$F_{rot}(T)=-kT\ln\left(Z_{rot}(T)\right)$$

$$S_{rot}(T)=-\left(\frac{\partial F_{rot}}{\partial T}\right)_{N,V}$$

$$U_{rot}(T)=F_{rot}(T)+TS_{rot}(T)$$



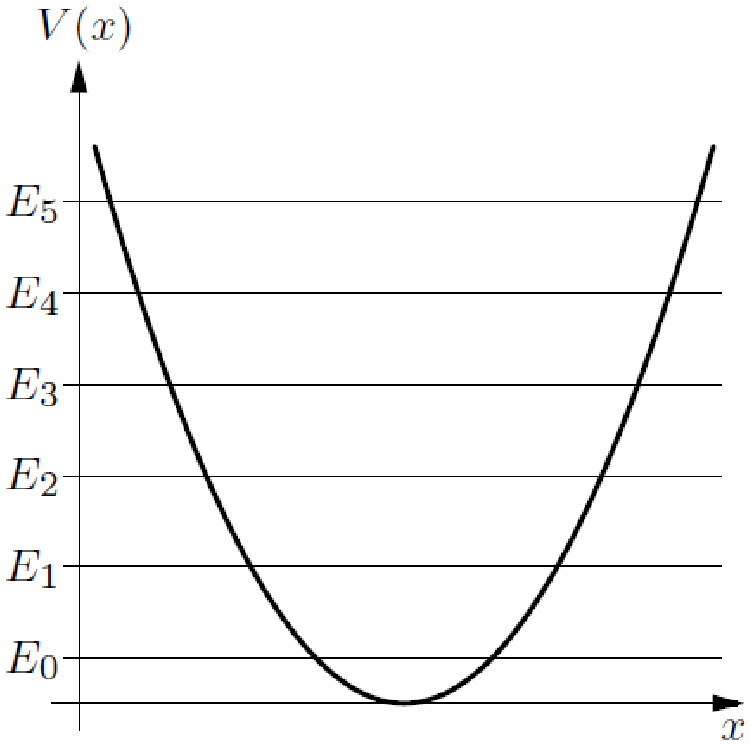
Vibrations of a diatomic molecule (see Appendix A)

$$U_{vib} = \frac{p_r^2}{2\mu_r} + \frac{1}{2}\mu_r\omega^2 x_r^2$$

$$U_{vib}(\nu) = \hbar\omega\left(\nu + \frac{1}{2}\right)$$

$$Z_{vib}(T) = \sum_{\nu=0}^{\infty} e^{-(\nu+1/2)\hbar\omega/kT}$$

$$= \frac{e^{-\hbar\omega/2kT}}{1-e^{-\hbar\omega/kT}}$$



Digression on geometric summation

$$Z_{vib}(T) = \sum_{\nu=0}^{\infty} e^{-(\nu+1/2)\hbar\omega/kT}$$

$$= \frac{e^{-\hbar\omega/2kT}}{1-e^{-\hbar\omega/kT}}$$

Some details: $e^{-(\nu+1/2)\hbar\omega/kT} = e^{-\hbar\omega/(2kT)}\left(e^{-\hbar\omega/(kT)}\right)^{\nu}$

$$\sum_{\nu=0}^{\infty} x^{\nu} = \frac{1}{1-x} \quad \text{for } x<1$$

Vibrations of a diatomic molecule

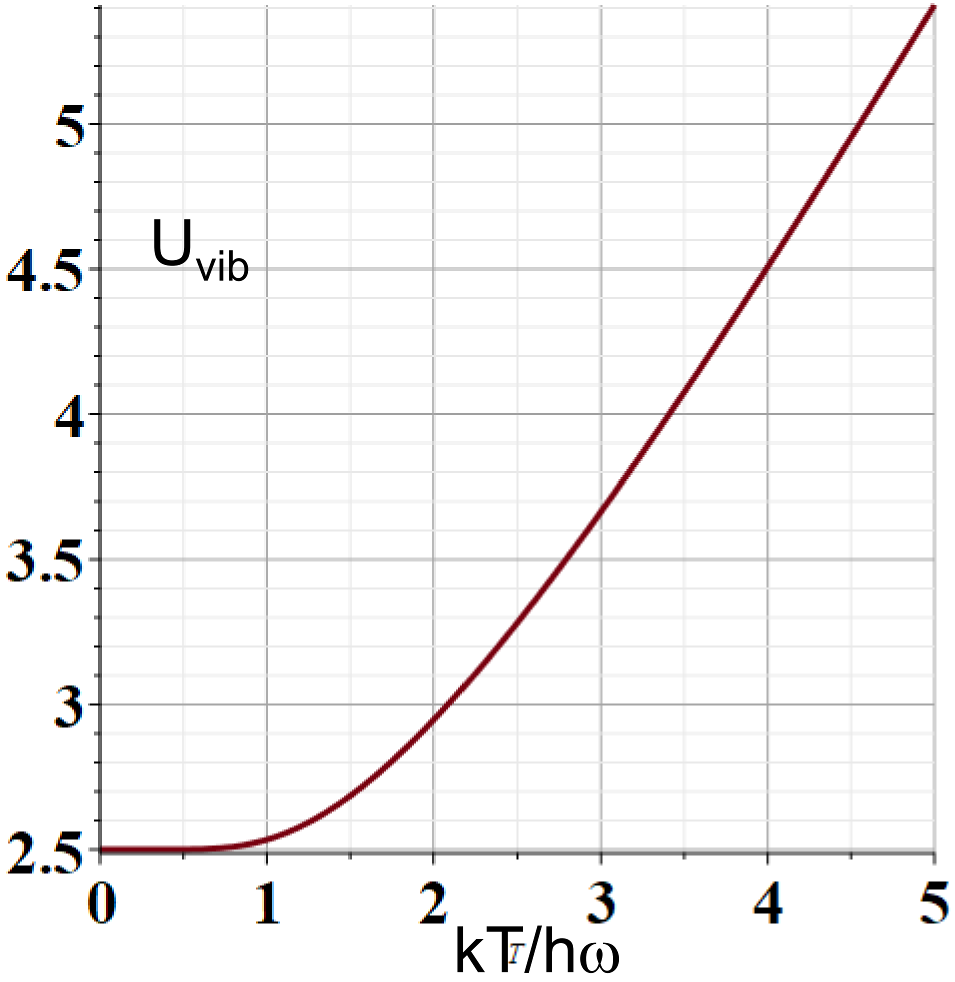
$$Z_{vib}(T) = \ = \frac{e^{-\hbar\omega/2kT}}{1-e^{-\hbar\omega/kT}}$$

$$F_{vib}(T) = -kT\ln\left(Z_{vib}(T)\right)$$

$$S_{vib}(T) = -\left(\frac{\partial F_{vib}}{\partial T}\right)_{N,V}$$

$$U_{vib}(T) = F_{vib}(T) + TS_{vib}(T)$$

$$= \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT}-1}\right)$$



Partition function for single molecule including translational and "internal" motions

$$Z_1(T,V) = Z_{1\,\mathrm{trans}}(T,V)Z_{1\,\mathrm{rot}}(T)Z_{1\,\mathrm{vib}}(T)$$

Now suppose that there are N particles. Last time we suggested that if the particles are not interacting, then

$Z_N=(Z_1)^N$

It turns out that this approach is correct if the particles are distinguishable. However, for indistinguishable particles, the correct N particle partition function should be

$$Z(T,V,N) = \frac{1}{N!}\left(Z_1(T,V)\right)^N$$

$$Z(T,V,N) = \frac{1}{N!}\left(Z_1(T,V)\right)^N$$

$$F(T,V,N) = -kTN\ln\left(Z_1(T,V)\right) + kT\ln N!$$

$$\approx -kTN\ln\left(Z_1(T,V)\right) + kTN(\ln N - 1)$$

$$Z_1(T,V) = Z_{1\,\mathrm{trans}}(T,V)Z_{1\,\mathrm{rot}}(T)Z_{1\,\mathrm{vib}}(T)$$

$$Z_{1\,\mathrm{trans}}(T,V) = \frac{V}{h^3}\left(2\pi mkT\right)^{3/2}$$

First consider the mono atomic case:

$$Z(T,V,N)=\frac{1}{N!}\left(Z_1(T,V)\right)^N$$

$$F(T,V,N)=-kTN\ln\left(Z_1(T,V)\right)+kTN(\ln N-1)$$

$$=-kTN\ln\left(\frac{V}{h^3}\left(2\pi mkT\right)^{3/2}\right)+kTN(\ln N-1)$$

$$=-kTN\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)+1\right)$$

$$S=-\left(\frac{\partial F}{\partial T}\right)_{N,V}=Nk\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right)$$

$$U=F+TS=\frac{3}{2}NkT$$

$$C_V=\frac{3}{2}Nk$$

Now consider a complex molecule with

$$Z_1(T,V) = Z_{1\ \mathrm{trans}}(T,V)Z_{1\ \mathrm{int}}(T) \qquad \text{where } Z_{1\ \mathrm{int}}(T) \ = Z_{1\ \mathrm{rot}}(T)\ Z_{1\ \mathrm{vib}}(T)$$

$$F(T,V,N) = -kTN\left(\ln\left(Z_{1\ \mathrm{trans}}(T,V)\right) + \ln\left(Z_{1\ \mathrm{int}}(T,V)\right)\right) + kTN(\ln N - 1)$$

$$= F_{trans}(T,V,N) - kTN\ln\left(Z_{1\ \mathrm{int}}(T,V)\right)$$

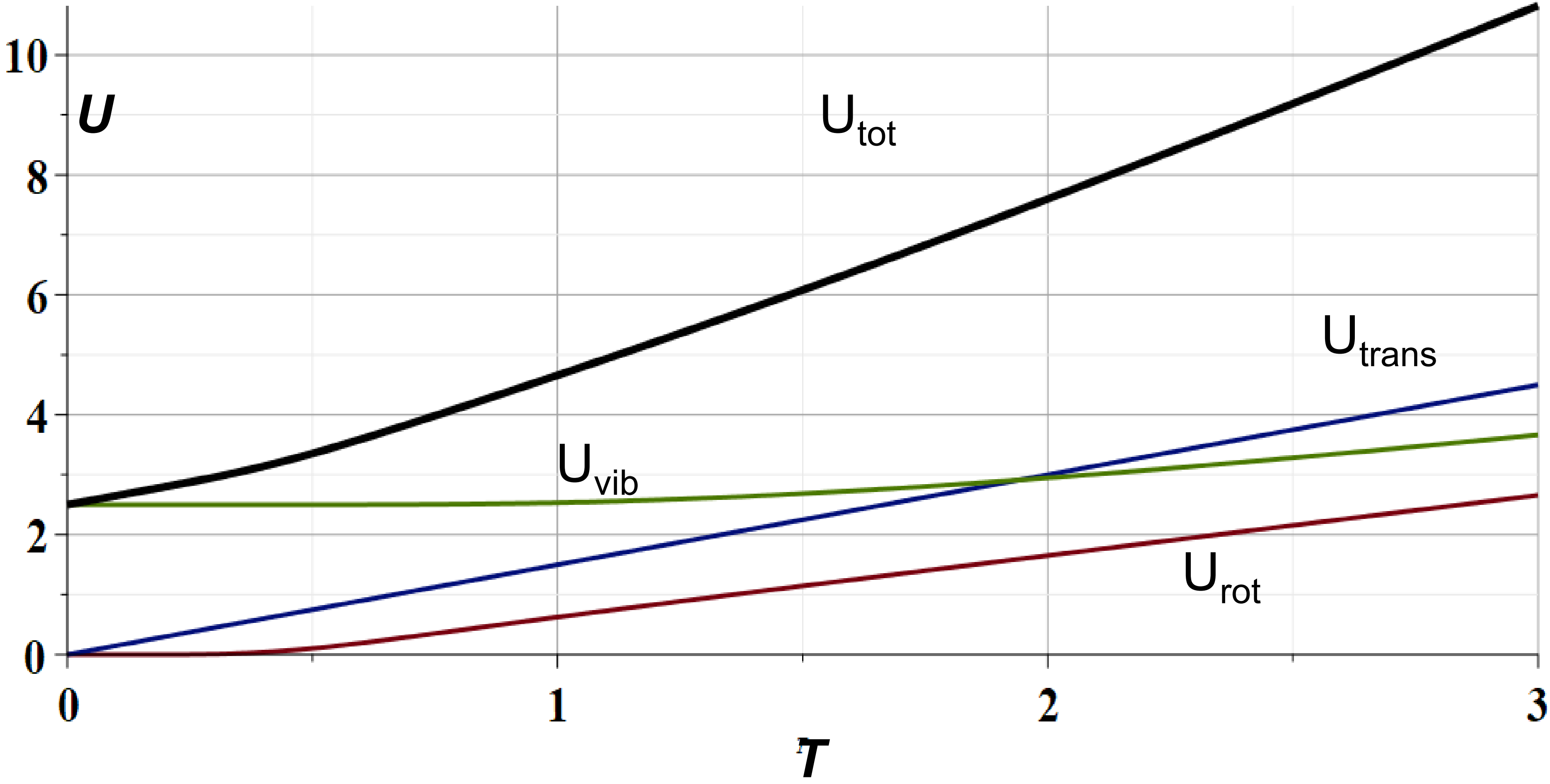
$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = S_{trans} + kN\ln\left(Z_{1\ \mathrm{int}}(T,V)\right) + \frac{kTN}{Z_{1\ \mathrm{int}}(T,V)}\left(\frac{\partial Z_{1\ \mathrm{int}}}{\partial T}\right)_{N,V}$$

$$= S_{trans} + S_{\mathrm{int}}$$

$$U = F + TS = U_{trans} + U_{\mathrm{int}} = U_{trans} + U_{rot} + U_{vib}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = C_{Vtrans} + C_{Vrot} + C_{Vvib}$$

Plot of internal energy as a function of temperature for model diatomic molecule



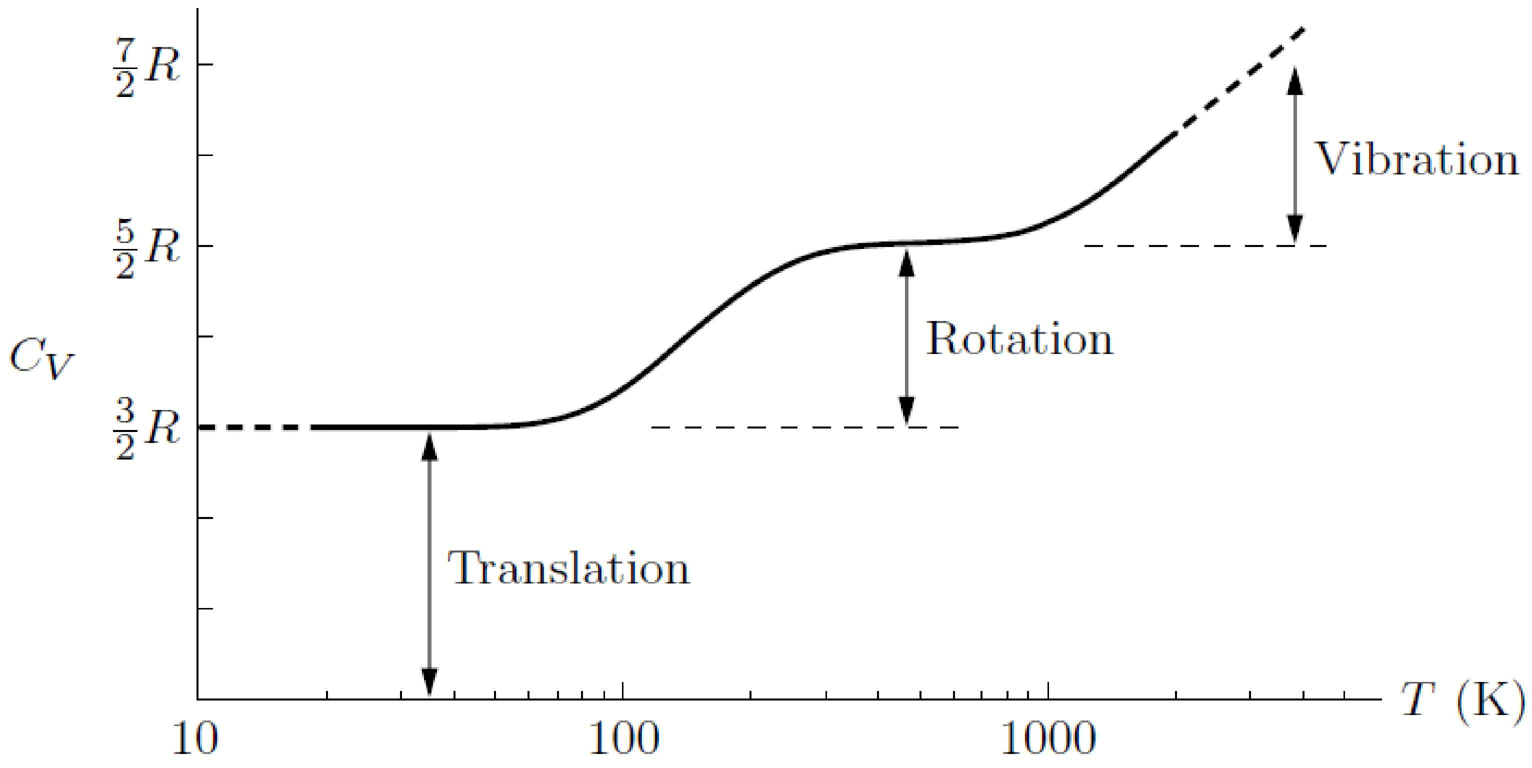


Figure 1.13. Heat capacity at constant volume of one mole of hydrogen (H_2) gas. Note that the temperature scale is logarithmic. Below about 100 K only the three translational degrees of freedom are active. Around room temperature the two rotational degrees of freedom are active as well. Above 1000 K the two vibrational degrees of freedom also become active. At atmospheric pressure, hydrogen liquefies at 20 K and begins to dissociate at about 2000 K. Data from Woolley et al. (1948). Copyright ©2000, Addison-Wesley.