

4.9: Statistical Mechanics of Molecular Gases

Separation of translational and internal degrees of freedom

The states of a noninteracting atom or molecule are labeled by its total momentum \mathbf{p} and its internal quantum numbers, which we will simply write with a collective index α , specifying rotational, vibrational, and electronic degrees of freedom. The single particle Hamiltonian is then

$$\hat{h} = \frac{\mathbf{p}^2}{2m} + \hat{h}_{int}, \quad (4.9.1)$$

with

$$\hat{h} |\mathbf{k}, \alpha\rangle = \left(\frac{\hbar^2 \mathbf{k}^2}{2m} + \varepsilon_\alpha \right) |\mathbf{k}, \alpha\rangle. \quad (4.9.2)$$

The partition function is

$$\zeta = \text{Tr} e^{-\beta \hat{h}} = \sum_{\mathbf{p}} e^{-\beta \mathbf{p}^2 / 2m} \sum_j g_j e^{-\beta \varepsilon_j}. \quad (4.9.3)$$

Here we have replaced the internal label α with a label j of energy eigenvalues, with g_j being the degeneracy of the internal state with energy ε_j . To do the \mathbf{p} sum, we quantize in a box of dimensions $L_1 \times L_2 \times \cdots \times L_d$, using periodic boundary conditions. Then

$$\mathbf{p} = \left(\frac{2\pi\hbar n_1}{L_1}, \frac{2\pi\hbar n_2}{L_2}, \dots, \frac{2\pi\hbar n_d}{L_d} \right), \quad (4.9.4)$$

where each n_i is an integer. Since the differences between neighboring quantized \mathbf{p} vectors are very tiny, we can replace the sum over \mathbf{p} by an integral:

$$\sum_{\mathbf{p}} \rightarrow \int \frac{d^d p}{\Delta p_1 \cdots \Delta p_d} \quad (4.9.5)$$

where the volume in momentum space of an elementary rectangle is

$$\Delta p_1 \cdots \Delta p_d = \frac{(2\pi\hbar)^d}{L_1 \cdots L_d} = \frac{(2\pi\hbar)^d}{V}. \quad (4.9.6)$$

Thus,

$$\begin{aligned} \zeta &= V \int \frac{d^d p}{(2\pi\hbar)^d} e^{-\mathbf{p}^2 / 2mk_B T} \sum_j g_j e^{-\varepsilon_j / k_B T} = V \lambda_T^{-d} \xi \\ \xi(T) &= \sum_j g_j e^{-\varepsilon_j / k_B T}. \end{aligned}$$

Here, $\xi(T)$ is the *internal coordinate partition function*. The full N -particle ordinary canonical partition function is then

$$Z_N = \frac{1}{N!} \left(\frac{V}{\lambda_T^d} \right)^N \xi^N(T). \quad (4.9.7)$$

Using Stirling's approximation, we find the Helmholtz free energy $F = -k_B T \ln Z$ is

$$\begin{aligned} F(T, V, N) &= -Nk_B T \left[\ln \left(\frac{V}{N\lambda_T^d} \right) + 1 + \ln \xi(T) \right] \\ &= -Nk_B T \left[\ln \left(\frac{V}{N\lambda_T^d} \right) + 1 \right] + N\varphi(T), \end{aligned}$$

where

$$\varphi(T) = -k_B T \ln \xi(T) \quad (4.9.8)$$

is the internal coordinate contribution to the single particle free energy. We could also compute the partition function in the Gibbs (T, p, N) ensemble:

$$\begin{aligned} Y(T, p, N) &= e^{-\beta G(T, p, N)} = \frac{1}{V_0} \int_0^\infty dV e^{-\beta p V} Z(T, V, N) \\ &= \left(\frac{k_B T}{p V_0} \right) \left(\frac{k_B T}{p \lambda_T^d} \right)^N \xi^N(T) . \end{aligned}$$

Thus, in the thermodynamic limit,

$$\begin{aligned} \mu(T, p) &= \frac{G(T, p, N)}{N} = k_B T \ln \left(\frac{p \lambda_T^d}{k_B T} \right) - k_B T \ln \xi(T) \\ &= k_B T \ln \left(\frac{p \lambda_T^d}{k_B T} \right) + \varphi(T) . \end{aligned}$$

Ideal gas law

Since the internal coordinate contribution to the free energy is volume-independent, we have

$$V = \left(\frac{\partial G}{\partial p} \right)_{T, N} = \frac{N k_B T}{p} , \quad (4.9.9)$$

and the ideal gas law applies. The entropy is

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p, N} = N k_B \left[\ln \left(\frac{k_B T}{p \lambda_T^d} \right) + 1 + \frac{1}{2} d \right] - N \varphi'(T) , \quad (4.9.10)$$

and therefore the heat capacity is

$$\begin{aligned} C_p &= T \left(\frac{\partial S}{\partial T} \right)_{p, N} = \left(\frac{1}{2} d + 1 \right) N k_B - N T \varphi''(T) \\ C_V &= T \left(\frac{\partial S}{\partial T} \right)_{V, N} = \frac{1}{2} d N k_B - N T \varphi''(T) . \end{aligned}$$

Thus, any temperature variation in C_p must be due to the internal degrees of freedom.

The internal coordinate partition function

At energy scales of interest we can separate the internal degrees of freedom into distinct classes, writing

$$\hat{h}_{int} = \hat{h}_{rot} + \hat{h}_{vib} + \hat{h}_{elec} \quad (4.9.11)$$

as a sum over internal Hamiltonians governing rotational, vibrational, and electronic degrees of freedom. Then

$$\xi_{int} = \xi_{rot} \cdot \xi_{vib} \cdot \xi_{elec} . \quad (4.9.12)$$

Associated with each class of excitation is a characteristic temperature Θ . Rotational and vibrational temperatures of a few common molecules are listed in table [tab. \[rvftab\]](#).

Rotations

Consider a class of molecules which can be approximated as an axisymmetric top. The rotational Hamiltonian is then

$$\begin{aligned} \hat{h}_{rot} &= \frac{\mathbf{L}_a^2 + \mathbf{L}_b^2}{2I_1} + \frac{\mathbf{L}_c^2}{2I_3} \\ &= \frac{\hbar^2 L(L+1)}{2I_1} + \left(\frac{1}{2I_3} - \frac{1}{2I_1} \right) \mathbf{L}_c^2 , \end{aligned}$$

where $\hat{\mathbf{n}}_{a,b,c}(t)$ are the principal axes, with $\hat{\mathbf{n}}_c$ the symmetry axis, and $\mathbf{L}_{a,b,c}$ are the components of the angular momentum vector \mathbf{L} about these instantaneous body-fixed principal axes. The components of \mathbf{L} along *space-fixed* axes $\{x, y, z\}$ are written as $L^{x,y,z}$. Note that

$$[L^\mu, \mathbf{L}_c] = n_c^\nu [L^\mu, L^\nu] + [L^\mu, n_c^\nu] L^\nu = i\epsilon_{\mu\nu\lambda} n_c^\nu L^\lambda + i\epsilon_{\mu\nu\lambda} n_c^\lambda L^\nu = 0, \quad (4.9.13)$$

which is equivalent to the statement that $\mathbf{L}_c = \hat{\mathbf{n}}_c \cdot \mathbf{L}$ is a rotational scalar. We can therefore simultaneously specify the eigenvalues of $\{\mathbf{L}^2, L^z, \mathbf{L}_c\}$, which form a complete set of commuting observables (CSCO)¹⁰. The eigenvalues of L^z are $m\hbar$ with $m \in \{-L, \dots, L\}$, while those of \mathbf{L}_c are $k\hbar$ with $k \in \{-L, \dots, L\}$. There is a $(2L+1)$ -fold degeneracy associated with the L^z quantum number.

We assume the molecule is prolate, so that $I_3 < I_1$. We can then define two temperature scales,

$$\Theta = \frac{\hbar^2}{2I_1 k_B}, \quad \tilde{\Theta} = \frac{\hbar^2}{2I_3 k_B}. \quad (4.9.14)$$

Prolateness then means $\tilde{\Theta} > \Theta$. We conclude that the rotational partition function for an axisymmetric molecule is given by

$$\xi_{rot}(T) = \sum_{L=0}^{\infty} (2L+1) e^{-L(L+1)\Theta/T} \sum_{k=-L}^L e^{-k^2(\tilde{\Theta}-\Theta)/T} \quad (4.9.15)$$

Table [rvftab]: Some rotational and vibrational temperatures of common molecules.

molecule	$\Theta_{rot}(K)$	$\Theta_{vib}(K)$
H_2	85.4	6100
N_2	2.86	3340
H_2O	13.7, 21.0, 39.4	2290, 5180, 5400

In diatomic molecules, I_3 is extremely small, and $\tilde{\Theta} \gg k_B T$ at all relevant temperatures. Only the $k=0$ term contributes to the partition sum, and we have

$$\xi_{rot}(T) = \sum_{L=0}^{\infty} (2L+1) e^{-L(L+1)\Theta/T}. \quad (4.9.16)$$

When $T \ll \Theta$, only the first few terms contribute, and

$$\xi_{rot}(T) = 1 + 3e^{-2\Theta/T} + 5e^{-6\Theta/T} + \dots \quad (4.9.17)$$

In the high temperature limit, we have a slowly varying summand. The *Euler-MacLaurin summation formula* may be used to evaluate such a series:

$$\sum_{k=0}^n F_k = \int_0^n dk F(k) + \frac{1}{2} [F(0) + F(n)] + \sum_{j=1}^{\infty} \frac{B_{2j}}{(2j)!} [F^{(2j-1)}(n) - F^{(2j-1)}(0)] \quad (4.9.18)$$

where B_j is the B_j Bernoulli number where

$$B_0 = 1, \quad B_1 = -\frac{1}{2}, \quad B_2 = \frac{1}{6}, \quad B_4 = -\frac{1}{30}, \quad B_6 = \frac{1}{42}. \quad (4.9.19)$$

Thus,

$$\sum_{k=0}^{\infty} F_k = \int_0^{\infty} dx F(x) + \frac{1}{2} F(0) - \frac{1}{12} F'(0) - \frac{1}{720} F'''(0) + \dots \quad (4.9.20)$$

We have $F(x) = (2x+1)e^{-x(x+1)\Theta/T}$, for which $\int_0^{\infty} dx F(x) = \frac{T}{\Theta}$, hence

$$\xi_{rot} = \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15} \frac{\Theta}{T} + \frac{4}{315} \left(\frac{\Theta}{T} \right)^2 + \dots \quad (4.9.21)$$

Recall that $\varphi(T) = -k_B T \ln \xi(T)$. We conclude that $\varphi_{rot}(T) \approx -3k_B T e^{-2\Theta/T}$ for $T \ll \Theta$ and $\varphi_{rot}(T) \approx -k_B T \ln(T/\Theta)$ for $T \gg \Theta$. We have seen that the internal coordinate contribution to the heat capacity is $\Delta C_V = -NT\varphi''(T)$. For diatomic molecules, then, this contribution is exponentially suppressed for $T \ll \Theta$, while for high temperatures we have $\Delta C_V = Nk_B$. One says that the rotational excitations are ‘frozen out’ at temperatures much below Θ . Including the first few terms, we have

$$\begin{aligned} \Delta C_V(T \ll \Theta) &= 12 Nk_B \left(\frac{\Theta}{T} \right)^2 e^{-2\Theta/T} + \dots \\ \Delta C_V(T \gg \Theta) &= Nk_B \left\{ 1 + \frac{1}{45} \left(\frac{\Theta}{T} \right)^2 + \frac{16}{945} \left(\frac{\Theta}{T} \right)^3 + \dots \right\}. \end{aligned}$$

Note that C_V overshoots its limiting value of Nk_B and asymptotically approaches it from above.

Special care must be taken in the case of homonuclear diatomic molecules, for then only even or odd L states are allowed, depending on the total nuclear spin. This is discussed below in §10.7.

For polyatomic molecules, the moments of inertia generally are large enough that the molecule’s rotations can be considered classically. We then have

$$\varepsilon(L_a, L_b, L_c) = \frac{L_a^2}{2I_1} + \frac{L_b^2}{2I_2} + \frac{L_c^2}{2I_3}. \quad (4.9.22)$$

We then have

$$\xi_{rot}(T) = \frac{1}{g_{rot}} \int \frac{dL_a dL_b dL_c d\phi d\theta d\psi}{(2\pi\hbar)^3} e^{-\varepsilon(L_a, L_b, L_c)/k_B T}, \quad (4.9.23)$$

where (ϕ, θ, ψ) are the Euler angles. Recall $\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$, and $\psi \in [0, 2\pi]$. The factor g_{rot} accounts for physically indistinguishable orientations of the molecule brought about by rotations, which can happen when more than one of the nuclei is the same. We then have

$$\xi_{rot}(T) = \left(\frac{2k_B T}{\hbar^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3}. \quad (4.9.24)$$

This leads to $\Delta C_V = \frac{3}{2} Nk_B$.

Vibrations

Vibrational frequencies are often given in units of inverse wavelength, such as cm^{-1} , called a *wavenumber*. To convert to a temperature scale T^* , we write $k_B T^* = h\nu = hc/\lambda$, hence $T^* = (hc/k_B) \lambda^{-1}$, and we multiply by

$$\frac{hc}{k_B} = 1.436 \text{ K} \cdot \text{cm}. \quad (4.9.25)$$

For example, infrared absorption ($\sim 50 \text{ cm}^{-1}$ to 10^4 cm^{-1}) reveals that the ‘asymmetric stretch’ mode of the H_2O molecule has a vibrational frequency of $\nu = 3756 \text{ cm}^{-1}$. The corresponding temperature scale is $T^* = 5394 \text{ K}$.

Vibrations are normal modes of oscillations. A single normal mode Hamiltonian is of the form

$$\hat{h} = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right). \quad (4.9.26)$$

In general there are many vibrational modes, hence many normal mode frequencies ω_α . We then must sum over all of them, resulting in

$$\xi_{vib} = \prod_\alpha \xi_{vib}^{(\alpha)}. \quad (4.9.27)$$

For each such normal mode, the contribution is

$$\begin{aligned}\xi &= \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega/k_B T} = e^{-\hbar\omega/2k_B T} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/k_B T}\right)^n \\ &= \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} = \frac{1}{2 \sinh(\Theta/2T)},\end{aligned}$$

where $\Theta = \hbar\omega/k_B$. Then

$$\begin{aligned}\varphi &= k_B T \ln \left(2 \sinh(\Theta/2T) \right) \\ &= \frac{1}{2} k_B \Theta + k_B T \ln \left(1 - e^{-\Theta/T} \right).\end{aligned}$$

The contribution to the heat capacity is

$$\begin{aligned}\Delta C_V &= N k_B \left(\frac{\Theta}{T} \right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2} \\ &= \begin{cases} N k_B (\Theta/T)^2 \exp(-\Theta/T) & (T \rightarrow 0) \\ N k_B & (T \rightarrow \infty) \end{cases}\end{aligned}$$

Two-level systems : Schottky anomaly

Consider now a two-level system, with energies ε_0 and ε_1 . We define $\Delta \equiv \varepsilon_1 - \varepsilon_0$ and assume without loss of generality that $\Delta > 0$. The partition function is

$$\zeta = e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} = e^{-\beta\varepsilon_0} (1 + e^{-\beta\Delta}). \quad (4.9.28)$$

The free energy is

$$f = -k_B T \ln \zeta = \varepsilon_0 - k_B T \ln (1 + e^{-\Delta/k_B T}). \quad (4.9.29)$$

The entropy for a given two level system is then

$$s = -\frac{\partial f}{\partial T} = k_B \ln (1 + e^{-\Delta/k_B T}) + \frac{\Delta}{T} \cdot \frac{1}{e^{\Delta/k_B T} + 1} \quad (4.9.30)$$

and the heat capacity is $= T (\partial s / \partial T)$,

$$c(T) = \frac{\Delta^2}{k_B T^2} \cdot \frac{e^{\Delta/k_B T}}{(e^{\Delta/k_B T} + 1)^2}. \quad (4.9.31)$$

Thus,

$$\begin{aligned}c(T \ll \Delta) &= \frac{\Delta^2}{k_B T^2} e^{-\Delta/k_B T} \\ c(T \gg \Delta) &= \frac{\Delta^2}{4k_B T^2}.\end{aligned}$$

We find that $c(T)$ has a characteristic peak at $T^* \approx 0.42 \Delta/k_B$. The heat capacity vanishes in both the low temperature and high temperature limits. At low temperatures, the gap to the excited state is much greater than $k_B T$, and it is not possible to populate it and store energy. At high temperatures, both ground state and excited state are equally populated, and once again there is no way to store energy.

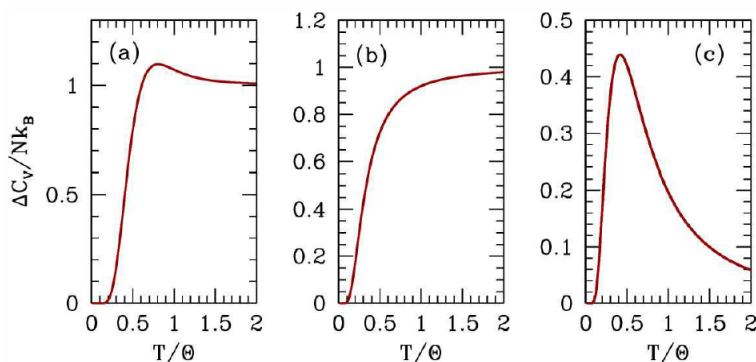


Figure [molgas]: Heat capacity per molecule as a function of temperature for (a) heteronuclear diatomic gases, (b) a single vibrational mode, and (c) a single two-level system.

If we have a distribution of independent two-level systems, the heat capacity of such a system is a sum over the individual Schottky functions:

$$C(T) = \sum_i \tilde{c}(\Delta_i/k_B T) = N \int_0^\infty d\Delta P(\Delta) \tilde{c}(\Delta/T), \quad (4.9.32)$$

where N is the number of two level systems, $\tilde{c}(x) = k_B x^2 e^x / (e^x + 1)^2$, and where $P(\Delta)$ is the normalized distribution function, which satisfies the normalization condition

$$\int_0^\infty d\Delta P(\Delta) = 1. \quad (4.9.33)$$

N_S is the total number of two level systems. If $P(\Delta) \propto \Delta^r$ for $\Delta \rightarrow 0$, then the low temperature heat capacity behaves as $C(T) \propto T^{1+r}$. Many amorphous or glassy systems contain such a distribution of two level systems, with $r \approx 0$ for glasses, leading to a linear low-temperature heat capacity. The origin of these two-level systems is not always so clear but is generally believed to be associated with local atomic configurations for which there are two low-lying states which are close in energy. The paradigmatic example is the mixed crystalline solid $(KBr)_{1-x}(KCN)_x$ which over the range $0.1 \leq x \leq 0.6$ forms an ‘orientational glass’ at low temperatures. The two level systems are associated with different orientation of the cyanide (CN) dipoles.

Electronic and Nuclear Excitations

For a monatomic gas, the internal coordinate partition function arises due to electronic and nuclear degrees of freedom. Let’s first consider the electronic degrees of freedom. We assume that $k_B T$ is small compared with energy differences between successive electronic shells. The atomic ground state is then computed by filling up the hydrogenic orbitals until all the electrons are used up. If the atomic number is a ‘magic number’ ($A = 2$ (He), 10 (Ne), 18 (Ar), 36 (Kr), 54 (Xe), ...) then the atom has all shells filled and $L = 0$ and $S = 0$. Otherwise the last shell is partially filled and one or both of L and S will be nonzero. The atomic ground state configuration $2J+1 L_S$ is then determined by *Hund’s rules*:

1. The LS multiplet with the *largest* S has the lowest energy.
2. If the largest value of S is associated with several multiplets, the multiplet with the *largest* L has the lowest energy.
3. If an incomplete shell is not more than half-filled, then the lowest energy state has $J = |L - S|$. If the shell is more than half-filled, then $J = L + S$.

The last of Hund’s rules distinguishes between the $(2S+1)(2L+1)$ states which result upon fixing S and L as per rules #1 and #2. It arises due to the atomic spin-orbit coupling, whose effective Hamiltonian may be written $\hat{H} = \Lambda \mathbf{L} \cdot \mathbf{S}$, where Λ is the Russell-Saunders coupling. If the last shell is less than or equal to half-filled, then $\Lambda > 0$ and the ground state has $J = |L - S|$. If the last shell is more than half-filled, the coupling is *inverted*, $\Lambda < 0$, and the ground state has $J = L + S$.¹¹

The electronic contribution to ξ is then

$$\xi_{elec} = \sum_{J=|L-S|}^{L+S} (2J+1) e^{-\Delta \epsilon(L,S,J)/k_B T} \quad (4.9.34)$$

where

$$\Delta\epsilon(L, S, J) = \frac{1}{2} \Lambda \left[J(J+1) - L(L+1) - S(S+1) \right]. \quad (4.9.35)$$

At high temperatures, $k_B T$ is larger than the energy difference between the different J multiplets, and we have $\xi_{elec} \sim (2L+1)(2S+1) e^{-\beta\epsilon_0}$, where ϵ_0 is the ground state energy. At low temperatures, a particular value of J is selected – that determined by Hund's third rule – and we have $\xi_{elec} \sim (2J+1) e^{-\beta\epsilon_0}$. If, in addition, there is a nonzero nuclear spin I , then we also must include a factor $\xi_{nuc} = (2I+1)$, neglecting the small hyperfine splittings due to the coupling of nuclear and electronic angular momenta.

For *heteronuclear* diatomic molecules, molecules composed from two different atomic nuclei, the internal partition function simply receives a factor of $\xi_{elec} \cdot \xi_{nuc}^{(1)} \cdot \xi_{nuc}^{(2)}$, where the first term is a sum over molecular electronic states, and the second two terms arise from the spin degeneracies of the two nuclei. For *homonuclear* diatomic molecules, the exchange of nuclear centers is a symmetry operation, and does not represent a distinct quantum state. To correctly count the electronic states, we first assume that the total electronic spin is $S = 0$. This is generally a very safe assumption. Exchange symmetry now puts restrictions on the possible values of the molecular angular momentum L , depending on the total nuclear angular momentum I_{tot} . If I_{tot} is even, then the molecular angular momentum L must also be even. If the total nuclear angular momentum is odd, then L must be odd. This is so because the molecular ground state configuration is $1\Sigma^+_{sg}$.¹²

The total number of nuclear states for the molecule is $(2I+1)^2$, of which some are even under nuclear exchange, and some are odd. The number of even states, corresponding to even total nuclear angular momentum is written as g_g , where the subscript conventionally stands for the (mercifully short) German word *gerade*, meaning 'even'. The number of odd (Ger. *ungerade*) states is written g_u . Table [nucspin] gives the values of $g_{g,u}$ corresponding to half-odd-integer I and integer I .

The final answer for the rotational component of the internal molecular partition function is then

$$\xi_{rot}(T) = g_g \zeta_g + g_u \zeta_u, \quad (4.9.36)$$

where

$$\zeta_g = \sum_{L \text{ even}} (2L+1) e^{-L(L+1) \Theta_{rot}/T}$$

$$\zeta_u = \sum_{L \text{ odd}} (2L+1) e^{-L(L+1) \Theta_{rot}/T}.$$

For hydrogen, the molecules with the larger nuclear statistical weight are called *orthohydrogen* and those with the smaller statistical weight are called *parahydrogen*. For H_2 , we have $I = \frac{1}{2}$ hence the ortho state has $g_u = 3$ and the para state has $g_g = 1$. In D_2 , we have $I = 1$ and the ortho state has $g_g = 6$ while the para state has $g_u = 3$. In equilibrium, the ratio of ortho to para states is then

$$\frac{N_{H_2}^{ortho}}{N_{H_2}^{para}} = \frac{g_u \zeta_u}{g_g \zeta_g} = \frac{3 \zeta_u}{\zeta_g}, \quad \frac{N_{D_2}^{ortho}}{N_{D_2}^{para}} = \frac{g_g \zeta_g}{g_u \zeta_u} = \frac{2 \zeta_g}{\zeta_u}. \quad (4.9.37)$$

Table [nucspin]: Number of even (g_g) and odd (g_u) total nuclear angular momentum states for a homonuclear diatomic molecule. I is the ground state nuclear spin.

$2I$	g_g	g_u
odd	$I(2I+1)$	$(I+1)(2I+1)$
even	$(I+1)(2I+1)$	$I(2I+1)$

Incidentally, how do we derive the results in Table [tabgggu]? The total nuclear angular momentum I_{tot} is the quantum mechanical sum of the two individual nuclear angular momenta, each of which are of magnitude I . From elementary addition of angular momenta, we have

$$I \otimes I = 0 \oplus 1 \oplus 2 \oplus \cdots \oplus 2I. \quad (4.9.38)$$

The right hand side of the above equation lists all the possible multiplets. Thus, $I_{tot} \in \{0, 1, \dots, 2I\}$. Now let us count the total number of states with *even* I_{tot} . If $2I$ is even, which is to say if I is an integer, we have

$$g_g^{(2I=even)} = \sum_{n=0}^I \left\{ 2 \cdot (2n) + 1 \right\} = (I+1)(2I+1) , \quad (4.9.39)$$

because the degeneracy of each multiplet is $2I_{tot} + 1$. It follows that

$$g_u^{(2I=even)} = (2I+1)^2 - g_g = I(2I+1) . \quad (4.9.40)$$

On the other hand, if $2I$ is odd, which is to say I is a half odd integer, then

$$g_g^{(2I=odd)} = \sum_{n=0}^{I-\frac{1}{2}} \left\{ 2 \cdot (2n) + 1 \right\} = I(2I+1) . \quad (4.9.41)$$

It follows that

$$g_u^{(2I=odd)} = (2I+1)^2 - g_g = (I+1)(2I+1) . \quad (4.9.42)$$

This page titled [4.9: Statistical Mechanics of Molecular Gases](#) is shared under a [CC BY-NC-SA](#) license and was authored, remixed, and/or curated by [Daniel Arovas](#).