

## 6.1: Separation of Contributions

### Collective Degrees of Freedom

In Section [subsection:Einstein\_Debbye] we have seen that the treatment of condensed phases can be complicated by collective motion of particles. Such effects are absent in an ideal gas that consists of point particles, a model that is reasonable for noble gases far from condensation. For gases consisting of molecules, it does not suffice to consider only translational motion as in Maxwell's kinetic theory of gases. We see this already when considering  $\text{H}_2$  gas, where each molecule can be approximated by a harmonic oscillator (Section [section:harmonic\_oscillator]). Neglect of the vibrational degrees of freedom will lead to wrong results for internal energy, heat capacity, the partition function, and entropy, at least at high temperatures. In fact, an  $\text{H}_2$  molecule is not only an oscillator, it is also a rotor. As a linear molecule it has two rotational degrees of freedom, which also contribute to internal energy and to the partition function.

In principle, we could try to ignore all this and treat each atom as one particle. If the Hamiltonian includes the potentials that characterize interaction between the particles, our equations of motion would be correct. In practice, such a treatment is inconvenient and it is better to group the spatial degrees of freedom according to the type of motion. The  $\text{H}_2$  molecule has 3 translational degrees of freedom, 2 rotational degrees of freedom, and 1 vibrational degree of freedom in the collective motion picture. The sum is 6, as expected for two atoms with each of them having 3 translational degrees of freedom in an 'independent' motion picture. In general, a molecule with  $n$  atoms has  $f_s = 3n$  spatial degrees of freedom, 3 of which are translational, 3 are rotational, except for linear molecules, which have only 2 rotation degrees of freedom, and the rest are vibrational. We note that the number of degrees of freedom in phase space is  $f = 2f_s$  because each spatial degree of freedom is also assigned a momentum degree of freedom.

These considerations take care of particle motion. Further contributions to internal energy and to the partition function can arise from spin. In both closed-shell and open-shell molecules, nuclear spin can play a role. This is indeed the case for  $\text{H}_2$ , which can exist in *ortho* and *para* states that differ in correlation of the nuclear spins of the two hydrogen atoms. For open-shell molecules electron spin degrees of freedom must be considered. This is the case, for instance, for  $\text{O}_2$ , which has a triplet ground state. In this case, rotational and spin degrees of freedom correspond to similar energies and couple. Finally, at sufficiently high temperatures electronic excitation becomes possible and then also makes a contribution to the partition function.

### Factorization of Energy Modes

In many cases, the individual contributions are separable, i.e. the modes corresponding to different types of motions can be treated independently. Roughly speaking, this results from a separation of energy ranges (frequency bands) of the modes and a corresponding separation of time scales. Nuclear spin degrees of freedom have much lower energy than rotational degrees of freedom which usually have much lower energy than vibrational degrees of freedom which have much lower energies than electronic excitation. The independence of nuclear and electron motion is basis of the *Born-Oppenheimer approximation* and the independence of rotational and vibrational motion is invoked when treating a molecule as a rigid rotor. Separability of energy modes leads to a sum rule for the energy contributions for a single closed-shell molecule ,

$$\epsilon_j = \epsilon_{j,\text{trs}} + \epsilon_{j,\text{ns}} + \epsilon_{j,\text{rot}} + \epsilon_{j,\text{vib}} + \epsilon_{j,\text{el}} , \quad (6.1.1)$$

where  $\epsilon_{j,\text{trs}}$ ,  $\epsilon_{j,\text{ns}}$ ,  $\epsilon_{j,\text{rot}}$ ,  $\epsilon_{j,\text{vib}}$ , and  $\epsilon_{j,\text{el}}$  are the translational, nuclear spin, rotational, vibrational, and electronic contributions, respectively. For a monoatomic molecule (atom)  $\epsilon_{j,\text{rot}}$  and  $\epsilon_{j,\text{vib}}$  vanish. If both the number of neutrons and of protons in the nucleus is even, the nucleus has spin  $I = 0$ . In that case the nuclear spin contribution vanishes for an atom, even in the presence of an external magnetic field. If all nuclei have spin zero, the nuclear spin contribution also vanishes for a diatomic or multi-atomic molecule.

If we assume the equipartition theorem to hold, or even more generally, the whole system to attain thermal equilibrium, there must be some coupling between the different modes. If we say that the energy modes are separable, we assume *weak coupling*, which means that for statistical purposes we can assume the modes to be independent of each other. The consequence for the computation of the partition function can be seen by considering a system of  $N$  particles with an  $\alpha$  mode associated with quantum number  $k$  and an  $\omega$  mode associated with quantum number  $r$ . The total energy of a single molecule of this type is  $\epsilon_j = \epsilon_{j,\alpha k} + \epsilon_{j,\omega r}$ . The molecular partition function is given by

$$Z = \sum_k \sum_r e^{-\beta(\epsilon_{\alpha k} + \epsilon_{\omega r})} . \quad (6.1.2)$$

This sum can be rewritten as

$$Z = \sum_k \sum_r e^{-\beta \epsilon_{\alpha k}} \cdot e^{-\beta \epsilon_{\omega r}} \quad (6.1.3)$$

$$= \sum_k e^{-\beta \epsilon_{\alpha k}} \sum_r e^{-\beta \epsilon_{\omega r}} \quad (6.1.4)$$

$$= \sum_k e^{-\beta \epsilon_{\alpha k}} Z_{\omega} = Z_{\omega} \sum_k e^{-\beta \epsilon_{\alpha k}} \quad (6.1.5)$$

$$= Z_{\alpha} Z_{\omega} . \quad (6.1.6)$$

We see that the total partition function is the product of the partition functions corresponding to the individual modes. This consideration can be extended to multiple modes. With Equation 6.1.1 it follows that

$$Z = Z_{\text{trs}} \cdot Z_{\text{ns}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}} \cdot Z_{\text{el}} . \quad (6.1.7)$$

By considering Equation ??? or Equation ??? we see that we can also compute the partition function for a given mode for all  $N$  particles before multiplying the modes. We have already seen that we must set  $z_{\text{trs}} = Z_{\text{trs}}^N / N!$  to heal the Gibbs paradox. What about the other, internal degrees of freedom? If two particles with different internal states are exchanged, they must be considered distinguishable, exactly because their internal state 'tags' them. Hence, for all the other modes we have  $z_{\alpha} = Z_{\alpha}^N$ . Thus,

$$z = \frac{1}{N!} (Z_{\text{trs}} \cdot Z_{\text{ns}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}} \cdot Z_{\text{el}})^N \quad (6.1.8)$$

$$= \frac{Z_{\text{trs}}^N}{N!} \cdot Z_{\text{ns}}^N \cdot Z_{\text{rot}}^N \cdot Z_{\text{vib}}^N \cdot Z_{\text{el}}^N . \quad (6.1.9)$$

Accordingly, we can consider each of the partition functions in turn. We also note that separability of the energies implies factorization of the molecular wavefunction,

$$\psi = \psi_{\text{trs}} \cdot \psi_{\text{ns}} \cdot \psi_{\text{rot}} \cdot \psi_{\text{vib}} \cdot \psi_{\text{el}} \quad (6.1.10)$$

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