

The Theory of Simple Gases

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1 An ideal gas in a quantum-mechanical microcanonical ensemble

Consider a gaseous system of N noninteracting, indistinguishable particles confined to a space of volume V and sharing a given energy E . $\Omega(N, V, E)$ denotes the number of distinct microstates accessible to the system under the macrostate (N, V, E) .

For large V , the single-particle energy levels in the system are very close to one another, we may divide the energy spectrum into a large number of “groups of levels”, which may be referred to as **energy cells**. Let ε_i denote the average energy of a level, and g_i the **(arbitrary) number of levels**, in the i th cell; we assume that **all $g_i \gg 1$** . The distribution set $\{n_i\}$ must conform to the conditions

$$\sum_i n_i = N \tag{1}$$

and

$$\sum_i n_i \varepsilon_i = E . \tag{2}$$

$$\Omega(N, V, E) = \sum_{\{n_i\}} W\{n_i\} , \quad (3)$$

where $W\{n_i\}$ is the number of distinct microstates associated with the distribution set $\{n_i\}$, in which summation goes over all distribution sets that conform to conditions (??) and (??).

$$W\{n_i\} = \prod_i w(i) , \quad (4)$$

where $w(i)$ is the number of distinct microstates associated with the i th cell of the spectrum (the cell that contains n_i particles, to be accommodated among g_i levels) while the product goes over all the cells in the spectrum. $w(i)$ is the number of distinct ways in which the n_i identical, and indistinguishable, particles can be distributed among the g_i levels of the i th cell.

the entropy of the system is

$$S(N, V, E) = k \ln \Omega(N, V, E) = k \ln \left[\sum_{\{n_i\}} W\{n_i\} \right] . \quad (5)$$

The logarithm of the sum can be approximated by the logarithm of the largest term in the sum, therefore

$$S(N, V, E) \approx k \ln W\{n_i^*\} \quad (6)$$

where $\{n_i^*\}$ is the distribution set that maximizes the number $W\{n_i\}$; the numbers n_i^* are the most probable values of the distribution numbers n_i . The maximization is to be carried out under the restrictions that the quantities N and E remain constant.

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