

Entropy of a Classical Ideal Gas of Distinguishable Atoms—C.E. Mungan, Spring 2011

Reference: R.H. Swendsen, J. Stat. Phys. **107**, 1143 (June 2002).

Incorrect calculation

The partition function for translations of one atom of mass m in a box of volume V is

$$Z_1 = \frac{V(2\pi mkT)^{3/2}}{h^3} \quad (1)$$

at temperature T . Here h is Planck's constant and k is Boltzmann's constant. But the partition function for N distinguishable, noninteracting particles in the classical limit is

$$Z_N = Z_1^N. \quad (2)$$

Therefore the entropy of the gas is

$$S = kT \left(\frac{\partial \ln Z_N}{\partial T} \right)_{V,N} + k \ln Z_N = Nk \left\{ \ln \left[V \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{3}{2} \right\} \quad (3)$$

where the gas's internal energy is $U = 3NkT / 2$.

The following argument shows that Eq. (3) violates the second law of thermodynamics. Consider two subsystems each individually in equilibrium with values $\{U_1, V_1, \text{ and } N_1\}$ and $\{U_2, V_2, \text{ and } N_2\}$. Bring them into thermal contact but suppose they are otherwise isolated so that their total energy $U = U_1 + U_2$ is constant. Let the total entropy of the combined system be $S = S_1 + S_2$. Then the equilibrium condition is found by solving

$$\left(\frac{\partial S}{\partial U_1} \right)_{V_1, V_2, N_1, N_2} = 0 \quad (4)$$

which leads to the expected result,

$$\frac{U_1}{N_1} = \frac{U_2}{N_2} \Rightarrow T_1 = T_2. \quad (5)$$

Next poke a hole in the wall between the two subsystems. The thermal equilibrium remains unchanged but now particles flow between them (subject to the constraint of fixed total number $N = N_1 + N_2$) until diffusive equilibrium is found from

$$\left(\frac{\partial S}{\partial N_1} \right)_{V_1, V_2, T_1, T_2} = 0 \quad (6)$$

which incorrectly predicts

$$V_1 = V_2 \quad (7)$$

instead of the expected result

$$\frac{V_1}{N_1} = \frac{V_2}{N_2}. \quad (8)$$

Clearly the problem is that we *should* have V/N where V appears in Eq. (3). Thus that expression for S *cannot* be correct.

Correct calculation

For particles confined to a volume V , the probability density for the location of a particle is $1/V$. For an ideal gas, each particle is independent of the others, and hence the probability density for distributing N_1 particles in a subvolume V_1 , and N_2 in V_2 , is given by the binomial distribution

$$W = \frac{N!}{N_1!N_2!} \left(\frac{V_1}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N_2}. \quad (9)$$

where $N = N_1 + N_2$ and $V = V_1 + V_2$ are both constants. But the logarithm can be written as

$$\ln W = \ln \Omega_c(V_1, N_1) + \ln \Omega_c(V_2, N_2) - \ln \Omega_c(V, N) \quad (10)$$

where

$$\Omega_c(V, N) \equiv \frac{V^N}{N!}. \quad (11)$$

Noting that the last term in Eq. (10) is an uninteresting constant, this result suggests that we can identify Eq. (11) as a “configurational” multiplicity of each individual subsystem. To get the entire entropy, we now multiply by the usual “momentum” contribution (by integrating the surface area of a hypersphere),

$$\Omega_p(U, N) = \frac{(2\pi mU)^{3N/2}}{(3N/2)!} \quad (12)$$

assuming $N \gg 1$ (so that we can drop some factors of 1). Hence in phase space we get

$$\Omega(U, V, N) = \frac{\Omega_c(V, N)\Omega_p(U, N)}{h^{3N}} \quad (13)$$

for 3 spatial dimensions. Substituting in Eqs. (11) and (12), and defining

$$S = k \ln \Omega(U, V, N) \quad (14)$$

gives the same Sackur-Tetrode equation for *distinguishable* particles as for *indistinguishable* ones, namely

$$S = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right\} \quad (15)$$

using Stirling's approximation. Owing to the factorial in the denominator of Eq. (11), V/N now appears in the argument of the logarithm in Eq. (15), so that we will correctly predict Eq. (8) and the second law of thermodynamics is saved.