Equipartition Theorem

One important consequence in the canonical ensemble is that for a non-interacting system in which the Hamiltonian can be written in the canonical quadratic form $\mathcal{H} = \sum_i' a q_i^2 + b p_i^2$, each degree of freedom - that is each quadratic term in the Hamiltonian - contributes $\frac{1}{2}kT$ to the mean energy

Proof Let $\mathcal{H} = \sum_i a_i q_i^2 + b_i p_i^2$

Consider the j^{th} co-ordinate degree of freedom. The associated mean energy of this degree of freedom is

$$\langle a_j q_j^2 \rangle = \int d^{3N}q \, d^{3N}p \; e^{-\beta \sum_i (a_i q_i^2 + b_i p_i^2)} \; a_j q_j^2 \,/ Z$$

$$= \int dq_j \; e^{-\beta a_j q_j^2} \, a_j q_j^2 / Z_j$$

$$= -\frac{\partial}{\partial \beta} \ln \int dq_j \; e^{-\beta a_j q_j^2} \sqrt{a_j \beta} \; (a_j \beta)^{-1/2}$$

$$= -\frac{\partial}{\partial \beta} \left[\ln (\beta^{-1/2}) + \ln (\cdots) \right] = kT/2$$

Thus for f degrees of freedom in either q_i or p_i, the general result is $\langle E \rangle = \frac{f}{2} kT$

3.14. The partition function of the mixture at any stage of the reaction is given by

$$Q(N_A, N_B, N_{AB}, V, T) = \frac{1}{N_A!\,N_B!\,N_{AB}!} f_A^{N_A} f_B^{N_B} f_{AB}^{N_{AB}} ,$$

where the symbols N_A, N_B and N_{AB} represent the number of atoms A, atoms B and molecules AB, respectively; this leads to the free energy

$$A = -kT\,\ell n\, Q \approx -kT \sum_j (N_j \ell n\, f_j - N_j\, \ell n N_j + N_j) \qquad (j = A, B, AB). \tag{1}$$

To determine the equilibrium distribution of these numbers, we minimize (1) under the obvious constraints

$$N_A + N_{AB} = const. \quad \text{and} \quad N_B + N_{AB} = const. \tag{2}$$

Varying N_j to $N_j + \delta N_j$, we get

$$\delta A = \ell n(f_A / N_A)\delta N_A + \ell n(f_B / N_B)\delta N_B + \ell n(f_{AB} / N_{AB})\delta N_{AB} = 0 , \tag{3}$$

subject to the constraints

$$\delta N_A + \delta N_{AB} = 0 \quad \text{and} \quad \delta N_B + \delta N_{AB} = 0 . \tag{4}$$

Combining (3) and (4), we obtain the condition for equilibrium, viz.

$$-\ell n(f_A / N_A) - \ell n(f_B / N_B) + \ell n(f_{AB} / N_{AB}) = 0,$$

which may be written as $N_{AB} / N_A N_B = f_{AB} / f_A f_B$, i.e. $n_{AB} / n_A n_B = V f_{AB} / f_A f_B$. In view of the fact that each of the f's, by virtue of the translational degrees of freedom, is proportional to V, the final result is a function of T only.

[redacted]

2.6

(a)

We have

$$Z_1 = \frac{1}{h^3}\int_V d^3q \int_{-\infty}^{\infty} d^3p \exp\left(\frac{-\beta p^2}{2m}\right) = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{V}{\lambda^3}\,.$$

(b)

Using Stirling's formula, $\ln N! \approx N\ln N - N$, we find immediately

$$A = -Nk_BT(\ln\frac{V}{N\lambda^3} + 1)\,.$$

(c)

The desired result follows immediately from

$$Z_G = \sum_N e^{\beta N\mu}\frac{V^N}{N!\lambda^{3N}} = \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]\,.$$

(d)

We have

$$\Omega(N,V,T) = -\langle P\rangle V = -k_BT\ln Z_G\,.$$

Giving

$$\langle P\rangle = \frac{k_BT}{\lambda^3}\exp\frac{\mu}{k_BT}$$

$$\langle N\rangle = \frac{V}{\lambda^3}\exp\frac{\mu}{k_BT}$$

$$\langle S\rangle = \left(k_B - \frac{\mu}{T} - \frac{3k_BT}{\lambda}\frac{\partial\lambda}{\partial T}\right)\frac{V}{\lambda^3}\exp\frac{\mu}{k_BT}\,.$$

Collecting terms we find

$$E = TS - PV + \mu N = \left(k_BT - \mu + \frac{3k_BT}{\lambda}\frac{\partial\lambda}{\partial T} - k_BT + \mu\right)\frac{V}{\lambda^3}\exp\frac{}{k}$$

Using the definition of the thermal wavelength λ we finally obtain.

$$E = \frac{3Nk_BT}{2}\,.$$

(e)

Using

$$\langle(\Delta E)^2\rangle = k_BT^2C_{V,N} = \frac{3Nk_B}{2}$$

and the formula for E we immediately find the desired result

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{E} = \sqrt{\frac{2}{3N}}\,.$$

(f)

We have

$$(\Delta N)^2 = k_BT\frac{\partial\langle N\rangle}{\partial\mu}\,.$$

Differentiating (2.8) with respect to μ then gives

$$\langle(\Delta N)^2\rangle = N\,.$$

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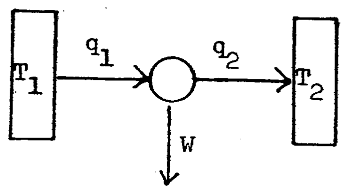
5.23

We have the system



(a) $$W = q_1 - q_2 = C(T_1 - T_f) + C(T_2 - T_f) = C(T_1 + T_2 - 2T_f) \qquad (1)$$

(b) By the second law, $$\Delta S \geqq 0$$

Thus $$\int_{T_1}^{T_f} \frac{CdT}{T} + \int_{T_2}^{T_f} \frac{CdT}{T} = C \ln \frac{T_f^{\,2}}{T_1 T_2} \geqq 0$$

It follows that $$T_f \geqq \sqrt{T_1 T_2}$$

(c) The maximum amount of work will be obtained when $T_f = \sqrt{T_1 T_2}$.

From (1) $$W = C(T_1 + T_2 - 2T_f) = C(\sqrt{T_1} - \sqrt{T_2})^2$$