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Citation: *American Journal of Physics* **49**, 125 (1981); doi: 10.1119/1.12540

View online: <http://dx.doi.org/10.1119/1.12540>

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Quantum statistics of an ideal molecular gas

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(Received 3 December 1979; accepted 23 July 1980)

For an ideal gas of molecules with internal degrees of freedom, we express the canonical and grand canonical partition functions in terms of the molecular partition function. The derivation is simple and the result is exact. The many-body ground state is included naturally and Bose-Einstein condensation appears without the need of special measures. The canonical partition function has a form which generalizes its classical approximation, and we use it for a discussion of multiply occupied molecular states.

In this paper we give a very simple derivation of a formula for the grand canonical partition function Ξ of an ideal molecular gas, which apparently has escaped the textbooks¹⁻¹² although it has been used in a different context in the research literature.¹³

We start from the usual expression for $\ln \Xi$ at temperature T , chemical potential μ , and volume V (e.g., Ref. 9, p. 160)

$$\ln \Xi = \pm \sum_j \ln [1 \pm \lambda \exp(-\beta \epsilon_j)]. \quad (1)$$

The sum is taken over a complete set of orthogonal energy eigenstates of a single molecule with corresponding energies ϵ_j . The upper (lower) sign applies to fermions (bosons) and $\lambda = \exp(\beta \mu)$ is the absolute activity, whilst $\beta = (kT)^{-1}$.

We obtain the formula immediately by expanding the logarithm and interchanging the order of the two summations:

$$\ln \Xi = \beta p V = \sum_{n=1}^{\infty} (\mp 1)^{n+1} \frac{q(n\beta)}{n} \lambda^n. \quad (2)$$

Here

$$q(\beta) = \sum_j \exp(-\beta \epsilon_j) \quad (3)$$

is the molecular partition function.

The interchange of the order of summations is permissible and the resulting series (2) is convergent providing $\lambda < 1$ ($\mu < 0$). (We take the zero of energy in the molecular ground state.) Thus the result always applies to bosons but not to strongly degenerate fermions.

From Eq. (2) we may find other thermodynamical functions as, for example,

$$N = \lambda (\partial \ln \Xi / \partial \lambda)_{\beta, V} = \sum_{n=1}^{\infty} (\mp 1)^{n+1} q(n\beta) \lambda^n, \quad (4a)$$

$$E = -(\partial \ln \Xi / \partial \beta)_{\lambda, V} = - \sum_{n=1}^{\infty} (\mp 1)^{n+1} q'(n\beta) \lambda^n, \quad (4b)$$

for the average number of molecules N and the average energy E . In Eq. (4b) $q'(n\beta)$ is the derivative of the function $q(n\beta)$ with respect to its argument $n\beta$. We may also obtain the contribution of any selected molecular state j by replacing $q(n\beta)$ by $\exp(-n\beta \epsilon_j)$. From Eq. (4a) we find, for example,

$$N_j = \frac{1}{\exp[\beta(\epsilon_j - \mu)] \pm 1}, \quad (5)$$

which represents the Fermi-Dirac and Bose-Einstein dis-

tributions. This result may of course be obtained directly from Eq. (1), but its relation to the expansion (4a) is brought out clearly here.

The results (2) and (4) are exact. In particular, the many-body ground state of a boson gas is included, and Eqs. (2) and (4) describe Bose-Einstein condensation. To see this explicitly we split q into the contribution of the (possibly degenerate) molecular ground state g_0 and that of the excited states q_e ,

$$q(\beta) = g_0 + q_e(\beta). \quad (6)$$

We then find

$$\beta p V = \pm g_0 \ln(1 \pm \lambda) + \sum_{n=1}^{\infty} (\mp 1)^{n+1} \frac{q_e(n\beta)}{n} \lambda^n, \quad (7a)$$

$$N = g_0 \frac{\lambda}{1 \pm \lambda} + \sum_{n=1}^{\infty} (\mp 1)^{n+1} q_e(n\beta) \lambda^n. \quad (7b)$$

For bosons the first term of Eq. (7b) is the average number of particles in the many-body ground state,

$$N_0 = g_0 \lambda / (1 - \lambda), \quad (8)$$

and this may be macroscopically large (Bose-Einstein condensation). The first term of Eq. (7a) can be written in terms of N_0 ,

$$g_0 \ln \frac{N_0 + g_0}{g_0}. \quad (9)$$

It is always negligible, as is the corresponding term for fermions.

A monatomic gas is a special case for which the (very good) approximation $q_e(\beta) \propto \beta^{-3/2}$ immediately leads to the usual expansions (e.g., Ref. 4, p. 200)

$$\beta p V = q_e(\beta) \sum_{n=1}^{\infty} (\mp 1)^{n+1} \lambda^n / n^{5/2}, \quad (10a)$$

$$N = g_0 \frac{\lambda}{1 \pm \lambda} + q_e(\beta) \sum_{n=1}^{\infty} (\mp 1)^{n+1} \frac{\lambda^n}{n^{3/2}}, \quad (10b)$$

$$E = (3/2) p V. \quad (10c)$$

The first term of Eq. (10b) may be ignored for fermions.

We obtain the canonical partition function Q_N for N molecules by substituting the series (2) into the relation

$$\exp(\beta p V) = \sum_{N=0}^{\infty} Q_N \lambda^N \quad (11)$$

and identifying the coefficients of λ^N . For bosons the result is

$$Q_N = \sum_s Q(s), \quad (12a)$$

$$Q(\mathbf{s}) = \prod_{n=1}^N \frac{[q(n\beta)/n]^{s_n}}{s_n!} \quad (12b)$$

The sum is taken over all sets of non-negative integers $\mathbf{s} = (s_1, s_2, s_3, \dots, s_N)$ satisfying the condition

$$\sum_{n=1}^N ns_n = N. \quad (13)$$

The set \mathbf{s} is related to the population of the molecular states. The population structure of an N -body state may be characterized by a set of non-negative integers $\mathbf{p} = (p_1, p_2, p_3, \dots, p_N)$ such that p_n is the number of molecular states occupied by precisely n molecules; and the set \mathbf{s} is then a lower bound for sets \mathbf{p} of the states contributing to $Q(\mathbf{s})$, in the sense that the set of inequalities

$$\sum_{n=l}^N np_n \geq \sum_{n=l}^N ns_n \quad l = 1, 2, 3, \dots, N \quad (14)$$

must be satisfied, with strict equality for $l = 1$.

To see this we note that a factor $q(n\beta)$ gives rise to molecular states occupied by n molecules. But a product $q(n\beta)q(m\beta)$ produces states occupied by $(n+m)$ molecules, in addition to distinct states with n and m molecules. Similar remarks apply to products of several factors (including powers).

The first term of the sum (12),

$$Q(N, 0, 0, \dots, 0) = q^N/N! \quad (15)$$

is the classical approximation to Q_N . [We write $q(\beta)$ as q for short.] In the classical regime where $q \gg N$ it is a good approximation in the sense that

$$|\ln Q_N - \ln(q^N/N!)| \ll \ln Q_N. \quad (16)$$

The term (15) contains the full contribution of all N -body states with but singly occupied molecular states. It also contains contributions with multiply occupied states, but these do not appear with their full weight in $q^N/N!$.

The higher terms of Eq. (12) provide the remaining contributions with multiply occupied states, and it is interesting to assess the importance of these corrections to Eq. (15). To this end we find the largest term in the sum (12) by use of Lagrange's method of undetermined multipliers: it occurs for $\mathbf{s} = \mathbf{s}^*$ with

$$s_n^* = [q(n\beta)/n]\lambda^n. \quad (17)$$

[The activity enters through the restraint (13) by comparison with Eq. (4a).] The maximum term is

$$Q(\mathbf{s}^*) = \prod_{n=1}^N \frac{[q(n\beta)/n]^{s_n^*}}{s_n^{*!}}, \quad (18)$$

and we note in passing that this is a good approximation to Q_N as an implicit function of T , V , and N . Thus it is easily checked that differentiation with respect to N yields an identity for the chemical potential.

The magnitude of $Q(\mathbf{s}^*)$ is conveniently approximated as

$$Q(\mathbf{s}^*) \simeq \frac{q^N}{N!} \exp\left(\sum_{n=2}^N s_n^*\right) \quad (19a)$$

providing

$$\sum_{n=2}^N ns_n^* \ll N. \quad (19b)$$

To obtain Eq. (19a) we have approximated $N!/s_1^{*!}$ by $N^{N-s_1^*}$

and eliminated s_1^* by use of Eq. (13), then introduced $\lambda = s_1^*/q \simeq N/q$ and used Stirling's approximation.

As an example we consider one mole of argon gas at room temperature and atmospheric pressure. In this case the maximum term is

$$Q(\mathbf{s}^*) \simeq 10^{10^{15}} q^N/N! \quad (20a)$$

with

$$s_2^* \simeq 10^{16}, \quad s_3^* \simeq 4 \times 10^8, \quad s_4^* \simeq 20, \quad s_n^* = 0 \quad \text{for } n \geq 5, \quad (20b)$$

and with s_1^* given by Eq. (13). This example and the general result (17) show that under most circumstances of practical interest the vast majority of terms contributing significantly to Q_N have several molecules in multiply occupied states, even when the classical approximation to Q_N applies. The opposite proposition is sometimes (e.g., Ref. 9, p. 71) assumed in a facile derivation of the classical approximation to Q_N in which the molecules are first treated as independent subsystems, and the result is subsequently corrected for the fact that molecules are indistinguishable.

For fermions the canonical partition function is given by Eq. (12) with $q(n\beta)$ replaced by $(-1)^{n+1}q(n\beta)$. It can be written

$$Q_N = \sum_{\mathbf{s}} (-1)^{N+|\mathbf{s}|} Q(\mathbf{s}), \quad (21a)$$

with

$$|\mathbf{s}| \equiv \sum_{n=1}^N s_n. \quad (21b)$$

The first term is again the classical approximation (15), and this is corrected for the erroneously included multiply occupied states by the higher terms. Unfortunately, these corrections are large in magnitude compared to Eq. (15) and have alternating signs, yet the sum must be positive and smaller than Eq. (15); so an accurate summation is difficult. However, when the condition (19b) applies we may approximate the combined Eqs. (12) and (21) by the expression

$$Q_N \simeq \frac{q^N}{N!} \sum_{\mathbf{s}} \prod_{n=2}^N \frac{[(\mp 1)^{n+1} q(n\beta) N^n / (nq^n)]^{s_n}}{s_n!} \quad (22)$$

and extend the summation to all non-negative values of $s_2, s_3, s_4, \dots, s_N$ as an additional approximation. The result is

$$Q_N \simeq \frac{q^N}{N!} \exp\left[\sum_{n=2}^N (\mp 1)^{n+1} \frac{q(n\beta)}{n} \left(\frac{N}{q}\right)^n\right]. \quad (23)$$

It agrees within a maximum term approximation with Eq. (19a) for a boson gas since λ can be identified with its classical value $\lambda \simeq N/q$ when Eq. (19b) applies.

For a fermion counterpart of the numerical example given above for bosons Eq. (23) provides the estimate

$$Q_N \simeq 10^{-10^{15}} q^N/N!. \quad (24)$$

This example shows that for a typically classical gas the contribution to q^N of terms with but singly occupied molecular states is negligibly small compared to q^N , a conclusion which may be contrasted with the argument of Ref. 3, p. 63.

Some of our findings for the classical approximation may of course be inferred from results of the grand canonical ensemble or by even simpler means. However, we believe

that the present more direct and detailed treatment may be of interest.

The results here described may be used to advantage even for monatomic gases. In our view the new forms in terms of the molecular partition function are valuable because they are exact, fairly general, physically transparent, and very easily derived. Their main limitation is that they cannot in practice describe a strongly degenerate fermion gas although Eq. (21) applies.

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