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Abstract

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ON THE THEORY OF VIRIAL EXPANSIONS FOR NONIDEAL GASES

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Expansions of thermodynamic functions in powers of the density, or virial expansions, were obtained by Ursell and Mayer ([1]) for classical statistics and generalized by Kahn and Uhlenbeck for quantum statistics ([2]). In the case of classical statistics these expansions were obtained by Bogolyubov ([3]) from chains for distribution functions. In quantum statistics, however, there are no analogous chains, and it is more convenient to use the method of expansion in powers of the activity ([4–7]).

The derivation of the general term for the expansion in powers of the density is usually associated with rather cumbersome computations of a combinatorial or algebraic character. We shall give a simple method for deriving expansions in powers of the density for classical and quantum statistics, based on the application of Cauchy' s theorem for transforming density expansions into series in the activity.

The statistical sum Ξ for the "large" Gibbs ensemble, characterized by the chemical potential μ, is equal to

$$\Xi = \sum_{N\geq 0} \lambda^N Q_N, \qquad \lambda = e^{\mu/\theta}, \tag{1}$$

where Q_N is the statistical sum of the canonical ensemble of N particles in volume V; λ is the absolute activity; μ is the chemical potential.

If the density is small, then in the sum (1) the first terms play the principal role, and (1) may be regarded as an expansion in powers of the absolute activity λ.

With the aid of (1), for the potential $\Omega(\theta, V, \mu)$ we obtain the expansion

$$\Omega = -\theta \ln \Xi = -\theta V \sum_{j\geq 1} b_j \lambda^j, \tag{2}$$

and consequently the pressure is equal to

$$p = -\frac{\Omega}{V} = \theta \sum_{j\geq 1} b_j \lambda^j. \tag{3}$$

The general term in (2) is easily obtained by expanding the logarithm of expression (1) in a series:

$$Vb_j = \sum_{\{n_l\}} (-1)^{\sum_l n_l - 1} \left(\sum_l n_l - 1 \right)! \prod_{l\geq 1} \frac{Q_l^{n_l}}{n_l!} \tag{4}$$

(the summation is over all positive n_l satisfying the condition $\sum_l ln_l = j$).

Using (2), for the mean number of particles and the mean energy we obtain expansions in λ:

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu} = \sum_{j\geq 1} Vjb_j\lambda^j, \tag{5}$$

$$U = \mu\overline{N} + \Omega - \theta \left(\frac{\partial\Omega}{\partial\theta} \right)_{\mu,V} = \theta \sum_{j\geq 1} V \frac{\partial b_j}{\partial\theta} \lambda^j. \tag{6}$$

Equations (3), (5), (6) give the equations of state in parametric form. Formulas (2)–(6) are well known.

To obtain explicit expansions in powers of the density for the pressure and energy from the expansions (3), (6) in powers of the activity, one must solve equation (5) with respect to the activity λ in the form of a series in powers of the density $\frac{1}{v} = \frac{\overline{N}}{V}$ and substitute the results into (3), (6). Usually this involves rather complicated calculations in order to obtain the general term of the expansion. In the present paper we shall solve equation (5) by means of Cauchy’ s integral, which considerably simplifies the calculations.

Represent equation (5) in the form

$$\rho = \lambda f(\rho), \tag{7}$$

which implicitly defines the function $\rho = \rho(\lambda)$.

With the aid of residue theory it is not difficult to verify that

$$\frac{f'(x)}{f(x)} = \frac{1}{2\pi i} \oint \frac{1}{x - \rho(\lambda)} \frac{d\lambda}{\lambda}. \tag{8}$$

The contour of integration in (8) includes the poles $\lambda = 0$ and $\lambda = \lambda_0$, where λ_0 is the root of the equation $x - \rho(\lambda_0) = 0$.

Relation (8) is valid for an arbitrary analytic function $\rho(\lambda)$, if $\rho(0) = 0$, which is the case in our situation. Indeed, the residue at the point λ_0 is equal to

$$\frac{1}{\lambda_0}\frac{1}{(\partial\rho/\partial\lambda)_{\lambda=\lambda_0}} = \frac{f'(x)}{f(x)} - \frac{1}{x},$$

while the residue at the point $\lambda = 0$ is equal to $\frac{1}{x}$.

From equation (8) we see that it is convenient to seek the function $f(x)$ in the form

$$f(x) = b_1 e^{\varphi(x)}, \tag{9}$$

where b_1 has been introduced to preserve dimensionality,

$$b_1 = \frac{Q_1}{V} = \frac{1}{V}\,\mathrm{Sp}\, e^{-T(p)/\theta} = \left(\frac{m\theta}{2\pi\hbar^2}\right)^{3/2} = \frac{1}{\Lambda^3}, \qquad T(p) = \frac{\hbar^2\nabla^2}{2m}$$

(Λ is of the order of the de Broglie wavelength of a particle with energy θ).

Then equation (7) takes the form

$$\rho = \lambda b_1 e^{\varphi(\rho)}, \tag{10}$$

where

$$\varphi'(x) = \frac{1}{2\pi i}\oint \frac{1}{x-\rho(\lambda)}\,\frac{d\lambda}{\lambda}. \tag{11}$$

We shall seek $\varphi(x)$ in the form of a series

$$\varphi(x) = \sum_{k\geq 1}\beta_k x^k; \tag{12}$$

then

$$\sum_{k\geq 1} k\beta_k x^{k-1} = \frac{1}{2\pi i}\oint \frac{1}{x-\rho(\lambda)}\,\frac{d\lambda}{\lambda}. \tag{13}$$

Expanding the subintegral expression in (13) in a series in $x/\rho(\lambda)$, which is possible since $x/\rho(\lambda) < 1$ owing to the fact that the pole λ_0 lies inside the integration contour, and equating coefficients of like powers of x, we obtain for β_k

$$k\beta_k = \frac{-1}{2\pi i}\oint [\rho(\lambda)]^{-k}\frac{d\lambda}{\lambda}. \tag{14}$$

Noting that

$$[\rho(\lambda)]^{-k} = (b_1\lambda)^{-k}\left\{1+\sum_{l\geq 2}\frac{lb_l}{b_1}\lambda^{l-1}\right\}^{-k}, \tag{15}$$

and expanding the second factor in (15) in a series, we finally obtain

$$\beta_k = \sum_{\{n_l\}}(-1)^l\frac{(\sum n_l - 1)!\,(k-1+\sum_l n_l)!}{k!}\prod_{l\geq 0}\frac{\left(\frac{lb_l}{b_1}\right)^{n_l}}{n_l!} \tag{16}$$

(the summation is over positive integers n_l satisfying the condition $\sum_l (l-1)n_l = k$). Thus we obtain the well-known relation between Mayer coefficients b_l and β_k. In classical statistics the coefficients b_l are called reducible integrals, and β_k irreducible integrals. The fact that the function (15) is a generating function for the coefficients β_k was noted already by Mayer[(5)].

It is now not difficult to obtain the equation of state by the usual method

$$\frac{p}{\theta} = \sum_{j\geq 1} b_j\lambda^j = \int_0^\lambda \sum_{j\geq 1} jb_j\lambda^{j-1}d\lambda = \int_0^\lambda \frac{\rho(\lambda)d\lambda}{\lambda},$$

whence, using (10):

$$\frac{p}{\theta} = \int_0^\rho \left(1-\rho\frac{\partial\varphi}{\partial\rho}\right)d\rho = \rho - \sum_{k\geq 1} k\beta_k\int_0^\rho \rho^k d\rho.$$

Finally, for the pressure we obtain the virial expansion

$$\frac{p}{\theta} = \rho + \sum_{k\geq 2} B_k\rho^k, \tag{17}$$

where

$$B_k = -\frac{k-1}{k}\beta_{k-1} \tag{18}$$

are the virial coefficients.

With the aid of (17) it is easy to find the expansion in powers of the density for the mean energy U. We have

$$U = F - \theta \left(\frac{\partial F}{\partial \theta}\right)_{N,V}, \qquad F = \Omega + \mu N.$$

Substituting here Ω and $\overline{N}$ from (2) and (5), we obtain

$$U = \frac{3}{2} N\theta + \overline{N}\theta^2 \sum_{k\geq 1} \frac{1}{k+1} \frac{d\beta}{d\theta} \rho^k. \tag{19}$$

Let us note, incidentally, that with the aid of (11) the equation of state can be written in the form of a contour integral

$$\frac{p(\rho)}{\theta} = -\frac{1}{2\pi i} \oint \frac{d\lambda}{\lambda} \rho(\lambda) \ln \left(1 - \frac{\rho}{\rho(\lambda)}\right). \tag{20}$$

The virial coefficients can be obtained directly from this relation by expanding the logarithmic function in a series.

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Note: Figure translations are in progress. See original paper for figures.