SOVIET PHYSICS JETP VOLUME 36, NUMBER 1 JANUARY, 1973

THE BOLTZMANN H-THEOREM FOR AN IMPERFECT GAS

Yu. L. KLIMONTOVICH

Moscow State University

Submitted February 17, 1972

Zh. Eksp. Teor. Fiz. **63**, 150–156 (July, 1972)

An expression is derived in the pair collision approximation for the entropy density S of a non-equilibrium imperfect gas. As expression for the Boltzmann H-function is found in the same approximation on basis of the Boltzmann kinetic equation for an imperfect gas[1]. In the equilibrium state the expression for S is given by the first two terms of the virial expansion of entropy with respect to density.

1. INTRODUCTION

It was shown earlier[1] that complete allowance for the interaction of the particles in a gas, within the framework of the pair-collision approximation, leads to additional terms in Boltzmann's classical kinetic equation. The corresponding additional terms appear also in Boltzmann's quantum kinetic equation. The first attempt to determine these terms was made apparently by Green[2]. This problem was considered with great success in[3-5].

In the case of a spatially homogeneous distribution of the gas particles, Boltzmann's classical kinetic equation takes the form

$$\frac{\partial f_1(\mathbf{p}_1, t)}{\partial t} = J_1 + J_2. \tag{1.1}$$

Here J_1 is Boltzmann's collision integral. We write it in the form proposed by Bogolyubov[6]

$$J_1 = n\int \frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1} f_1(\mathbf{P}_1(-\infty),t)f_1(\mathbf{P}_2(-\infty),t)\,d\mathbf{r}_2\,d\mathbf{p}_2, \tag{1.2}$$

$\mathbf{P}_1$ and $\mathbf{P}_2$ are the initial moment of the two particles colliding at the instant of time t, while n = N/V is the average particle concentration. The additional collision integral J_2 is defined by

$$J_2 = -n\frac{\partial}{\partial t}\int\limits_0^\infty\int \tau\frac{\partial\Phi}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}\frac{d}{d\tau}f_1(\mathbf{P}_1(-\tau),t) \tag{1.3}$$
$$\times f_1(\mathbf{P}_2(-\tau),t)\,dx_2 d\tau, \quad x = (\mathbf{r}, p)$$

Owing to the presence of the additional integral J_2, the integral

$$I(t) = n\int \varphi(\mathbf{p}_1)(J_1 + J_2)\,d\mathbf{p}_1$$

vanishes only at $\varphi = 1, \mathbf{p}_1$. At $\varphi = \mathbf{p}_1^2/2m$ we have

$$n\int\frac{\mathbf{p}_1^2}{2m}(J_1+J_2)\,d\mathbf{p}_1 = -\frac{n^2}{2}\frac{\partial}{\partial t}\int \Phi(1,2)f_1(\mathbf{P}_1(-\infty),t)$$
$$\times f_1(\mathbf{P}_2(-\infty),t)\,dx_2 d\mathbf{p}_1.$$

In the pair-collision approximation, consequently, the expression for the density of the internal energy of the gas takes the form[1]

$$U = n\int\frac{\mathbf{p}_1^2}{2m}f_1 d\mathbf{p}_1 + \frac{n^2}{2}\int\Phi(1,2)f_1(\mathbf{P}_1(-\infty),t)f_1(\mathbf{P}_2(-\infty),t)\,dx_2\,d\mathbf{p}_1. \tag{1.4}$$

We see that the sum of the average kinetic and potential energies is conserved.

Any thermodynamic function of the gas can be represented by a series in powers of the density. This pertains also to the distribution functions f_1 and f_2, which are averaged statistical characteristics. Within the framework of the pair-collision approximation, we can obtain only the first two terms of the expansions with respect to the density. In this approximation we can therefore represent the distribution function f_1 in the form

$$f_1 = f_1^0 + nf_1^1.$$

Here $f_1^{(0)}$ is the distribution function of an ideal gas and f_1^1 is the contribution to f_1 as a result of the non-ideality of the gas. Since allowance for the non-ideality means allowance for the correlation of the particle positions, the function f_1^1 is determined by the correlation function

$$g_2 = f_2 - f_1 f_1. \tag{1.5}$$

The general connection between the functions f_1 and g_2 is the same for both the classical and the quantum cases. When only pair collisions are taken into account, it takes the form

$$f_1(p_1,t) = C\left(f_1^0 + (N-1)\int g_2(x_1,x_2,t)\frac{d\mathbf{r}_1\,dx_2}{V^2}\right). \tag{1.6}$$

This expression can be obtained in the pair-collision approximation, e.g., with the aid of the equations of[1] for the functions f_1 and f_2. We do not present the derivation, since the meaning of (1.6) is clear: the first term describes the distribution function of an ideal gas, and the second takes into account the influence of the pair correlation of the particle under consideration with the N − 1 surrounding particles.

When writing (1.6), we used the following normalization of the distribution functions:

$$\int f_1\frac{dx_1}{V} = 1, \quad \int f_2\frac{dx_1 dx_2}{V^2} = 1. \tag{1.7}$$

The quantity C in (1.6) is determined from the normalization condition. From (1.7) we get

$$\int g_2\frac{dx_1}{V} = \int g_2\frac{dx_2}{V} = 0. \tag{1.8}$$

Owing to the presence of the factor (N − 1), the second term in (1.6), in spite of Eq. (1.8), makes a finite contribution in the limit as N → ∞, V → ∞, with N/V = const.

Using the expression for the normalization constant

C, we can represent (1.6) in the first approximation in the density as follows:

$$f_1(\mathbf{p}_1, t) = f_1{}^0 + n \int \left\{ \int g_2 d\mathbf{p}_2 - \int g_2 d\mathbf{p}_1\, d\mathbf{p}_2 f_1{}^0(\mathbf{p}_1, t) \right\} \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V}. \qquad (1.9)$$

In the equilibrium state, the distributions with respect to coordinates and momenta are independent for a classical gas, and it follows from (1.9) that in this case $f_1 = f_1^0$, i.e., f_1 is the Maxwell distribution. When the quantum corrections are taken into account, we have $f_1 \neq f_1^0$ even in the equilibrium state [7]. Thus, e.g., in the expression for the energy density (1.4), the influence of the correlation function becomes manifest in the general case both in the expression for the kinetic energy and in the expression for the potential energy. In the first expression, the correlations enter via the first distribution function f_1, and in the second (in the potential energy) they enter via the second distribution function f_2. To take complete account of the non-ideality, it is necessary to consider both contributions. A similar situation arises also in the calculation of the entropy for a non-ideal gas.

Usually for a Boltzmann gas the entropy density is determined by the expression (cf., e.g.,[8-11])

$$S_\mathrm{B} = -kn \int f_1 \ln f_1 \frac{dx_1}{V}. \qquad (1.10)$$

For non-equilibrium states, this expression takes partial account of the contribution of the correlations, since, according to (1.9), f_1 depends on g_2. However, this account is incomplete. Indeed, for the equilibrium state of a classical gas, expression (1.10) coincides with the entropy of an ideal gas. At the same time, for a non-ideal gas the entropy can also be represented in the form of a series in the density. A contribution of the order of n^2 to the entropy density, within the framework of the pair-collision approximation, is not equal to zero even in the equilibrium state. This indeed demonstrates the incompleteness of expression (1.10) for a non-ideal gas.

The purpose of the present article is to derive for the entropy an expression that takes full account of the non-ideality of the gas within the framework of the pair collisions. In Sec. 2 we determine the additional contribution made to formula (1.10) by the correlation of the particles. In Sec. 3 we carry out the corresponding generalization of Boltzmann's H-theorem.

2. ENTROPY DENSITY FOR A NON-IDEAL GAS IN THE PAIR-COLLISION APPROXIMATION

We represent the expression for the entropy density S in the form

$$S = S_\mathrm{B} + \Delta S, \qquad (2.1)$$

where ΔS is the additional contribution to S as a result of the correlations, which enter via the second distribution function f_2.

To determine ΔS we proceed as follows. We write down the expression for S_B for two particles in the form

$$-2\frac{k}{2}\int \ln(f_1 f_1) f_1 f_1 \frac{dx_1\, dx_2}{V^2} = -k \int \ln(f_1 f_1) f_2 \frac{dx_1\, dx_2}{V^2}.$$

We have used here the normalization conditions (1.7). When the correlation of the particle pair is taken into account, this expression takes the form

$$-k\int f_2 \ln f_2 \frac{dx_1\, dx_2}{V^2}.$$

Since the number of pairs is $N(N-1)/2$, these two expressions lead to an expression for that part of the entropy density which is due to the correlation of the particles:

$$\Delta S = -\frac{kn^2}{2}\int f_2 \ln \frac{f_2}{f_1 f_1} \frac{dx_1\, dx_2}{V}. \qquad (2.2)$$

Let us examine this expression for the equilibrium case. In this case we can integrate in (2.2) with respect to the momenta. As a result we obtain

$$\Delta S = -\frac{kn^2}{2}\int f_2(\mathbf{r}_1, \mathbf{r}_2) \ln f_2(\mathbf{r}_1, \mathbf{r}_2) \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V}. \qquad (2.3)$$

Here $f_2 = C \exp(-\Phi(1, 2)/kT)$. The normalization constant is

$$C = \left(\int e^{-\Phi/kT} \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V^2}\right)^{-1} \sim 1 - \frac{r_\mathrm{cor}^3}{V}. \qquad (2.4)$$

Here r_cor is the correlation radius. As $V \to \infty$ we have $C \to 1$. However, we can put $C = 1$ in (2.3) only as the first factor under the integral sign. Indeed,

$$\frac{kn^2}{2}\ln C \int f_2 \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V} = \frac{knN}{2}\ln C = \frac{kn^2}{2}\int (e^{-\Phi/kT} - 1)\frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V},$$

I.e., this quantity is of the same order as the remaining terms in (2.3). Taking this into account, we can write (2.3) in the form

$$\Delta S = \frac{kn^2}{2}\int \left[\frac{\Phi}{kT} e^{-\Phi/kT} + (e^{-\Phi/kT} - 1)\right] d\mathbf{r}, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \qquad (2.5)$$

For the model of spheres with weak attraction we have

$$\Delta S = -kn^2 b - \pi k n^2 \int_{r_0}^{\infty} \frac{\Phi^2}{(kT)^2} r^2 dr.$$

Here $b = 2\pi r_0^3/3$ is the Van der Waals constant.

Expression (2.5) follows also from the Gibbs canonical distribution. The first term is determined by the contribution of the internal energy and the second by the free energy, since

$$\Delta F = -2\pi k T n^2 \int_0^{\infty} (e^{-\Phi/kT} - 1) r^2\, dr.$$

The general expression (2.2) can be represented also in the nonequilibrium case in the form of a sum of two parts, one of which determines the contribution of the internal energy on going to the equilibrium state, and the other the contribution of the free energy. To this end, we represent the functions f_1 and f_2 in the form

$$f_1 = \left(\int F_1 \frac{dx_1}{V}\right)^{-1} F_1;\ f_2 = \left(\int F_2 \frac{dx_1\, dx_2}{V^2}\right)^{-1} F_2;\ F_2 - F_1 F_1 = G_2. \qquad (2.6)$$

In the equilibrium state we have

$$F_2 = e^{-\Phi/kT}, \quad G_2 = e^{-\Phi/kT} - 1. \qquad (2.7)$$

Expression (2.7) differs from (2.6) in that here $C = 1$, i.e., the contribution of the correlation is not included in the normalization constant. Taking (2.6) into account, recognizing that

$$\int F_1 \frac{dx_1}{V} = 1 + O(n)$$

and neglecting the terms n^3, we reduce (2.2) to the form

$$\Delta S = -\frac{kn^2}{2}\int\left[\ln\frac{F_2}{F_1F_1} - G_2\right]\frac{dx_1\,dx_2}{V}. \tag{2.8}$$

In the equilibrium state, using (2.7), we arrive again at expression (2.5). We see that the first term in (2.8) is the non-equilibrium analog of the contribution of the free energy.

In the perturbation-theory approximation in g_2/f_1f_2, we obtain from (2.2) and (2.8)

$$\Delta S = -\frac{kn^2}{2}\int\frac{g_2^2}{2f_1f_1}\frac{dx_1\,dx_2}{V} = -\frac{kn^2}{2}\int\frac{G_2^2}{2F_1F_1}\frac{dx_1\,dx_2}{V} \tag{2.9}$$

Expression (2.8) and (2.9) coincide with those given in[12].

3. H-FUNCTION FOR A NON-IDEAL GAS

It is seen from (2.2) and (2.8) that the correlation enters in the expression for ΔS via f_2 and via $\ln f_2$. To take into account the contribution of the correlation function under the logarithm sign when determining the H function, we proceed the following manner. Using the kinetic equation (1.1), we write down an equation for the function $f_1(p_1, t)f_1(p_2, t)$. We multiply this expression by

$$\left(-\frac{kn}{2}\ln(f_1f_1) - \frac{kn^2}{2}V\ln\frac{f_2}{f_1f_1}\right)\frac{dx_1\,dx_2}{V^2}$$

and integrate with respect to x_1 and x_2. Neglecting terms of the order of n^3 in the right- and left-hand sides, we obtain

$$-kn\int\frac{\partial f_1}{\partial t}\ln f_1\frac{dx_1}{V} - \frac{kn^2}{2}\int\frac{\partial}{\partial t}(f_1f_1)\ln\frac{f_2}{f_1f_1}\frac{dx_1\,dx_2}{V} = -kn\int J_1\ln f_1\frac{dx_1}{V}$$
$$-kn\int J_2\ln f_1\frac{dx_1}{V} \equiv I_1 + I_2. \tag{3.1}$$

The integral J_1 coincides with the Boltzmann collision integral, and therefore

$$I_1 = -kn\int J_1\ln f_1\frac{dx_1}{V} \geqslant 0. \tag{3.1'}$$

We transform the second term of the right-hand side of (3.1). Using the expression (1.3) after integrating by parts with respect to p_1 and symmetrizing, we obtain the expression

$$-\frac{kn^2}{2}\int_0^\infty\!\!\int\left(\frac{\partial\Phi}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{p}_1} + \frac{\partial\Phi}{\partial\mathbf{r}_2}\frac{\partial}{\partial\mathbf{p}_2}\right)\ln f_1f_1\cdot$$
$$\cdot\tau\frac{d}{d\tau}\frac{\partial}{\partial t}S_{-\tau}(1,2)f_1(\mathbf{p}_1,t)f_1(\mathbf{p}_2,t)\frac{dx_1\,dx_2}{V}d\tau.$$

We perform transformations analogous to those made in[1] in the derivation of the conservation law (29). Under the integral sign I_2, we change over to new variables, $x_1, x_2 \to X_1(-\tau), X_2(-\tau)$ and recognize that

$$-\left[\left(\frac{\partial\Phi}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{p}_1} + \frac{\partial\Phi}{\partial\mathbf{r}_2}\frac{\partial}{\partial\mathbf{p}_2}\right)\ln(f_1f_1)\right]_{X_1(-\tau),X_2(-\tau)} = \left[\frac{d}{d\tau}\ln(f_1f_1)\right]_{X_1(-\tau),X_2(-\tau)},$$

integrate by parts with respect to τ, and then change back to the variables x_1 and x_2. As a result we obtain the expression

$$-\frac{kn^2}{2}\int_0^\infty\!\!\int\ln(f_1f_1)\frac{\partial}{\partial t}\frac{d}{d\tau}S_{-\tau}(1,2)f_1f_1\frac{dx_1dx_2}{V}d\tau.$$

Integrating with respect to τ and recognizing that in the zeroth approximation in the retardation the second correlation function is

$$g_2(x_1, x_2) = f_1(\mathbf{P}_1(-\infty), t)f_1(\mathbf{P}_2(-\infty), t) - f_1f_1,$$

we obtain the expression

$$I_2(t) = -\frac{kn^2}{2}\int\ln(f_1f_1)\frac{\partial g}{\partial t}\frac{dx_1dx_2}{V}. \tag{3.2}$$

We use Eq. (1.2) of[1] for the function f_2:

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1\frac{\partial}{\partial\mathbf{r}_1} + \mathbf{v}_2\frac{\partial}{\partial\mathbf{r}_2} - \frac{\partial\Phi}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{p}_1} - \frac{\partial\Phi}{\partial\mathbf{r}_2}\frac{\partial}{\partial\mathbf{p}_2}\right)f_2 = \frac{\partial f_1f_1}{\partial t}, \tag{3.3}$$

in order to rewrite (3.2) in a form more convenient for our purposes. We multiply (3.3) by $\ln f_2$ and integrate with respect to x_1 and x_2. As a result we obtain

$$\int\ln f_2\frac{\partial g_2}{\partial t}\frac{dx_1dx_2}{V} = 0. \tag{3.4}$$

It follows from (3.2) and (3.4) that

$$I_2(t) = -\frac{kn^2}{2}\int\ln\frac{f_2}{f_1f_1}\frac{\partial g_2}{\partial t}\frac{dx_1dx_2}{V}. \tag{3.5}$$

Taking (3.1) and (3.5) into account, we obtain

$$-kn\int\ln f_1\frac{\partial f_1}{\partial t} - \frac{kn^2}{2}\int\ln\frac{f_2}{f_1f_1}\frac{\partial f_2}{\partial t}\frac{dx_1dx_2}{V} = I_1(t) \geqslant 0. \tag{3.6}$$

The operator $\partial/\partial t$ in the left-hand side can be taken outside the integral signs, by recognizing that

$$-kn\int f_1\frac{\partial\ln f_1}{\partial t}\frac{dx_1}{V} = 0;$$
$$\int f_2\frac{\partial}{\partial t}\left(\ln\frac{f_2}{f_1f_1}\right)\frac{dx_1dx_2}{V} = -\int\frac{\partial g}{\partial t}\frac{dx_1dx_2}{V} = 0. \tag{3.7}$$

The last equation follows from (3.3). The result is the inequality

$$dS/dt \equiv -dH/dt = I_1(t) \geqslant 0,$$

where

$$H = kn\int f_1\ln f_1\frac{dx_1}{V} + \frac{kn^2}{2}\int f_2\ln\frac{f_2}{f_1f_1}\frac{dx_1\,dx_2}{V} \tag{3.8}$$

is the Boltzmann H-function with complete account taken of the interaction of the particles within the framework of the pair-collision approximation. The additional term in (3.8) for S coincides with expression (2.2).

If we replace f_1, f_2, and g_2 by the functions F_1, F_2, and G_2 defined by formulas (2.6) and (2.7), then we obtain for the H-function instead of (3.8) the following expression:

$$H = kn\int f_1\ln f_1\frac{dx_1}{V} + \frac{kn^2}{2}\int\left(F_2\ln\frac{F_2}{F_1F_1} - G_2\right)\frac{dx_1dx_2}{V}.$$

This expression coincides with that given in[12].

The results can be generalized for the ternary- and quaternary-collision approximations. The solution of this problem, however, entails many difficulties, one of which is due to the appearance of divergences in the corresponding collision integrals.

---

[1] Yu. L. Klimontovich, Zh. Eksp. Teor. Fiz. 60, 1352 (1971) [Sov. Phys.-JETP 33, 732 (1971)].

[2] H. S. Green, Proc. Roy. Soc. A66, 325 (1953).

[3] L. Kadanoff and G. Baym, Quantum Statistical Mechanics, Benjamin, 1962.

[4] K. Baerwinkel and S. Grossmann, Zs. Phys. 198, 277 (1967).

[5] K. Baerwinkel, Naturforschung 24a, 22, 28 (1969).

[6] N. N. Bogolyubov, Problemy dinamicheskoĭ teorii v statisticheskoĭ fizike (Problems of Dynamic Theory in Statistical Physics), Gostekhizdat, 1946; Izbrannye

trudy (Selected Works), II, Naukova dumka, Kiev, 1970.

[7] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964, Sec. 33 [Addison-Wesley, 1969].

[8] Kerson Huang, Statistical Mechanics, Wiley, 1963.

[9] M. N. Kogan, Dinamika razrezhennogo gaza (Dynamics of Rarefied Gases), Nauka, 1967, Sec. 2, 5.

[10] K. P. Gurov, Osnovanie kineticheskoĭ teorii (Fundamentals of Kinetic Theory), Sec. 5, Nauka, 1966.

[11] V. P. Silin, Vvedenie v kineticheskuyu teoriyu gazov (Introduction to Kinetic Gas Theory), Nauka, 1971, Sec. 5.

[12] Yu. L. Klimontovich, Trudy konferentsii po teorii plazmy (Proc. of Conference on Plasma Theory), Kiev (in press), 1972.

Translated by J. G. Adashko
17