ON THE CORRELATION FUNCTION OF VELOCITY DISTRIBUTION OF MOLECULES

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The Laplace–Gauss formula is generalized to the case of three statistical indices and the nature of the forces responsible for the correlation between the thermal velocities of atoms or molecules is discussed.

1. The Maxwellian Velocity Distribution

The Maxwellian velocity distribution of molecules plays a dominant role in modern kinetic theories of the structure of matter.

The components of the thermal velocity of molecules ξ, η, ζ are usually identified with three statistical indices. In this case Maxwell distributions should be regarded as generalizations of the one-dimensional Laplace–Gauss distribution function. Actually we determine the probability of the gaseous system occurring in the phase space $d\xi d\eta d\zeta = d\omega$.

If $n(\xi, \eta, \zeta)$ is the number of molecules with their velocity lying in $d\omega$ and N is the total number of molecules, then the probability mentioned above is $p(\xi, \eta, \zeta) = n(\xi, \eta, \zeta)/N$. Next we denote the probabilities of finding the molecules in the corresponding phase intervals $d\xi$, $d\eta$, $d\zeta$ by $p(\xi)$, $p(\eta)$, and $p(\zeta)$. We shall assume that the probabilities $p(\xi)$, $p(\eta)$, and $p(\zeta)$ are independent; then according to the theorem of multiplication of probabilities we have

$$p(\xi, \eta, \zeta) = p(\xi)\, p(\eta)\, p(\zeta). \tag{1.1}$$

Maxwell justifies this hypothesis of independence of the probabilities in the following way [1]: "But the existence of velocity ξ must not in any way affect the existence of velocity η or ζ, since all these are at right angles to each other and are mutually independent."

Let each probability $p(\xi)$, $p(\eta)$, $p(\zeta)$ obey the Laplace–Gauss formula

$$p(\xi) = c_1 e^{-h\xi^2},\ p(\eta) = c_2 e^{-h\eta^2},\ p(\zeta) = c_3 e^{-h\zeta^2}, \tag{1.2}$$

then after substituting these into (1.1) we obtain the well-known Maxwell distribution

$$p(\xi, \eta, \zeta) = c \exp[-h(\xi^2 + \eta^2 + \zeta^2)].$$

In 1872 L. Boltzmann, having formulated his H theorem, showed that in a gas left to itself molecular collisions would lead to a Maxwell velocity distribution irrespective of the initial distribution. This strengthened the arguments in favor of the universal formula (1.2) and, hence, the hypothesis of independence of the statistical indices. However, the H theorem is derived from the so-called integro-differential equation and in the derivation of this equation Boltzmann had to introduce a hypothesis of random molecular state of the gaseous system which is equivalent to complete statistical independence. In other words Maxwell's concept (1.1) is implicit in the Boltzmann equation.

Moreover, in 1880-1881 Boltzmann published three extensive articles on viscosity, where he proposed a method of solving his equation for calculating viscosity. His investigation did not lead to a simple result and Boltzmann notes that he almost lost hope of obtaining a general solution of his equation.

The shortcomings of Boltzmann's equation are also reflected in Lorentz's article [2] in which certain cases are analyzed where back collisions do not exist.

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The subsequent development of the theory proceeded through a mathematical improvement of the Boltzmann method and now it is called the Chapman—Enskog method.

The solutions of Boltzmann's equation by this method were verified experimentally in 1953 by Grespan and Tompson. They measured the velocities and absorption of ultrasonic waves in rarefied gases. In comparing the results of the experiment with the theory they encountered a paradox that more accurate solutions of Boltzmann's equation lead to the worst results compared to the less accurate solutions.

Trusdel in his work goes even further and casts doubt on the premises of the gas kinetic theory. He speaks of the contemporary crisis in the kinetic theory of gases. In an article with this title he analyzes the current state of the kinetic theory of gases and shows that the problem of convergence of the successive approximations arising in the solution of Boltzmann's equation is by no means trivial. For one specific example he clearly shows that there may be cases when all higher approximations turn out to be worse than the first which is an asymptotic solution.

These contradictions occurring in the kinetic theory of gases must force the investigators to reexamine the validity of the Maxwell—Boltzmann concept.

The problem of narrowness of this concept has been formulated most clearly by A. S. Predvoditelev. In his works on the derivation of the equation of state for condensed media [3, 4] he completely discards the spherical symmetry in the statistics of hidden motions and introduces for the first time a distribution function with correlating statistical indices. He verified the theoretical results of these investigations on abundant experimental material. It was found that Predvoditelev's equation of state is in good agreement with experiment for many liquids and real gases in a wide range of temperatures right up to the critical temperatures. His results encourage further investigations in this direction.

It should be noted that the mathematical aspect of this problem was worked out in the theory of bulk phenomena by K. Pierson and Edgeworth [5], representatives of the English mathematical school. Edgeworth for the first time extended the Laplace—Gauss law to the case of an arbitrary number of statistical indices among which correlation exists; however, his method is of causal—probabilistic nature and is not very clear from the point of view of generalization of formula (1.1).

2. Derivation of Distribution Function with Correlating Statistical Indices

Let us drop Maxwell's hypothesis about the independence of the statistical indices ξ, η, and ζ. Then according to the theorem of multiplication of probabilities formula (1.1) should be rewritten as

$$p(\xi, \eta, \zeta) = p(\xi)\, p(\eta \mid \xi)\, p(\zeta \mid \xi\eta),$$

where $p(\eta/\xi)$ and $p(\zeta/\xi\eta)$ are conditional probabilities. Since statistical indices can be represented in any order, the same formula can be written as

$$p(\xi, \eta, \zeta) = p(\zeta)\, p(\eta \mid \zeta)\, p(\xi \mid \zeta\eta).$$

It is not difficult to comprehend that these two formulas lead to the functional equation

$$p(\xi)\, p(\eta \mid \xi)\, p(\zeta \mid \xi\eta) = p(\zeta)\, p(\eta \mid \zeta)\, p(\xi \mid \zeta\eta). \tag{2.1}$$

Hereafter by statistical indices ξ, η, ζ we shall mean the deviations from the corresponding mean values.

Let us assume that the probabilities $p(\xi)$ and $p(\zeta)$ obey the Laplace—Gauss formula

$$p(\xi) = c_1 e^{-h_1^2 \xi^2}, \quad p(\zeta) = c_1 e^{-h_3^2 \zeta^2}. \tag{2.2}$$

Then according to M. Smolukhovskii's requirement [6] about the oscillating nature of random phenomena the conditional probabilities also must obey the Laplace—Gauss formula, i.e.

$$p(\eta \mid \xi) = c_2 e^{-H_2^2[\eta - f_2(\xi)]^2}, \quad p(\eta \mid \zeta) = c_2 e^{-H_{23}^2[\eta - F_2(\zeta)]^2},$$
$$p(\zeta \mid \xi\eta) = c_3 e^{-H_3^2[\zeta - f_3(\xi, \eta)]^2}, \quad p(\xi \mid \eta\zeta) = c_3 e^{-H_1^2[\xi - F_1(\eta, \zeta)]^2}. \tag{2.3}$$

Unlike formula (2.2) here the mean values of ξ, η, ζ are no longer constant but are functions of other variables. We shall assume that these functions are linear, i.e.

$$f_2(\xi) = a_1\xi,\ f_3(\xi,\ \eta) = a_{13}\xi + b_{13}\eta,$$
$$F_2(\zeta) = c_1\zeta,\ F_1(\eta,\ \zeta) = b_{11}\eta + c_{11}\zeta. \tag{2.4}$$

Substituting formulas (2.2), (2.3), and (2.4) into the functional equation (2.1) and equating terms with equal powers of ξ, η and ζ we obtain the following system of equations:

$$h_1^2 + H_2^2 a_1^2 + H_3^2 a_{13}^2 = H_1^2,\ 2H_3^2 a_{13} b_{13} - 2H_2^2 a_1 = -2H_1^2 b_{11},$$
$$H_2^2 + H_3^2 b_{13}^2 = H_{23}^2 + H_1^2 b_{11}^2,\ -2H_3^2 a_{13} = -2H_1^2 c_{11},$$
$$-2H_3^2 b_{13} = 2H_1^2 b_{11} c_{11} - 2H_{23}^2 c_1,\ H_3^2 = h_3^2 + H_{23}^2 c_1^2 + H_1^2 c_{11}^2. \tag{2.5}$$

We equate each row in (2.5) with numbers A_1, A_{12}, A_2, A_{13}, A_{23}, A_3; then it is not difficult to see that the solution of the functional equation (2.1) has the form

$$p(\xi,\ \eta,\ \zeta) = c\exp[-(A_1\xi^2 + A_{12}\xi\eta + A_2\eta^2 + A_{13}\xi\zeta + A_{23}\eta\zeta + A_3\zeta^2)]. \tag{2.6}$$

Formula (2.6) is more general than Maxwell's formula (1.2) and goes over into the latter if

$$A_{12} = A_{13} = A_{23} = 0,\ A_1 = A_2 = A_3 = h.$$

In order to facilitate subsequent computations we rewrite formula (2.6) in the following form:

$$p = c\exp\left[-\frac{1}{2}(a_{11}\xi^2 + a_{22}\eta^2 + a_{33}\zeta^2 + 2a_{12}\xi\eta + 2a_{13}\xi\zeta + 2a_{23}\eta\zeta)\right] \tag{2.7}$$

and separate out the following term in the square brackets:

$$W = a_{22}\eta^2 + a_{33}\zeta^2 + 2a_{23}\eta\zeta - a_{11}\left(\frac{a_{12}}{a_{11}}\eta + \frac{a_{13}}{a_{11}}\zeta\right)^2.$$

Then formula (2.7) becomes

$$p = ce^{-\frac{1}{2}W}e^{-\frac{1}{2}a_{11}\left[\xi + \left(\frac{a_{12}}{a_{11}}\eta + \frac{a_{13}}{a_{11}}\zeta\right)\right]^2}. \tag{2.8}$$

This form of formula (2.7) is convenient for computing the mean of statistical index ξ. Actually, in the computation of the integral

$$\bar{\xi} = \int_{-\infty}^{\infty} \xi p d\xi$$

indices η and ζ may be regarded as parameters, i.e. they may be assumed constant. Then

$$\bar{\xi} = \int_{-\infty}^{\infty} c_1\xi e^{-\frac{1}{2}a_{11}\left[\xi + \left(\frac{a_{12}}{a_{11}}\eta + \frac{a_{13}}{a_{11}}\zeta\right)\right]^2} d\xi$$

and introducing a new variable

$$t = \sqrt{\frac{a_{11}}{2}}\left[\xi + \left(\frac{a_{12}}{a_{11}}\eta + \frac{a_{13}}{a_{11}}\zeta\right)\right],$$

we obtain

$$\bar{\xi} = -\left(\frac{a_{12}}{a_{11}}\eta + \frac{a_{13}}{a_{11}}\zeta\right). \tag{2.9}$$

This formula is equivalent to the equation of the regression curve of statistical index ξ over η and ζ.

If the regression is strictly linear, then [5]

$$\bar{\xi} = \frac{r_{12} - r_{23}r_{13}}{1 - r_{23}^2}\frac{\sigma_1}{\sigma_2}\eta + \frac{r_{13} - r_{23}r_{12}}{1 - r_{23}^2}\frac{\sigma_1}{\sigma_3}\zeta, \tag{2.10}$$

where the correlation coefficients r_{ij} form the so-called correlation determinant

$$R = \begin{vmatrix} 1 & r_{12} & r_{13} \\ r_{21} & 1 & r_{23} \\ r_{31} & r_{32} & 1 \end{vmatrix}. \tag{2.11}$$

Comparing formulas (2.9) and (2.10) coefficients a_{ij} can be expressed in terms of r_{ij} and σ_1, σ_2, σ_3. This forms the essence of Edgeworth's theorem, so that in our case we have

$$p = c\exp\left[-\frac{1}{2}\left(\frac{R_{11}}{R}\frac{\xi^2}{\sigma_1^2} + \frac{R_{22}}{R}\frac{\eta^2}{\sigma_2^2} + \frac{R_{33}}{R}\frac{\zeta_2}{\sigma_3^2} + \frac{2R_{12}}{R}\frac{\xi\eta}{\sigma_1\sigma_2} + \frac{2R_{13}}{R}\frac{\xi\zeta}{\sigma_1\sigma_3} + \frac{2R_{23}}{R}\frac{\eta\zeta}{\sigma_2\sigma_3}\right)\right]. \tag{2.12}$$

Here R_{ij} denote the minors of the above determinant and σ_1, σ_2, and σ_3 denote the root mean square deviations of the corresponding indices.

For calculating the constants in formula (2.12) we shall make use of the well known relation

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p\,d\xi\,d\eta\,d\zeta = 1. \tag{2.13}$$

Let us compute the double integral

$$I_2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[-\frac{1}{2R}\left(\frac{R_{11}}{\sigma_1^2}\xi^2 + \frac{R_{22}}{\sigma_2^2}\eta^2 + \frac{2R_{12}}{\sigma_1\sigma_2}\xi\eta\right)\right]d\xi\,d\eta,$$

which reduces to a product of two integrals after some simple manipulations:

$$I_2 = \int_{-\infty}^{\infty}\exp\left[-\frac{R_{11}}{2R}\left(\frac{\xi}{\sigma_1} + \frac{R_{12}}{R_{11}}\frac{\eta}{\sigma_2}\right)^2\right]d\xi\int_{-\infty}^{\infty}\exp\left[-\frac{(R_{22}R_{11} - R_{12}^2)}{2RR_{11}}\frac{\eta^2}{\sigma_2^2}\right]d\eta.$$

With the change of variable

$$t = \sqrt{\frac{R_{11}}{2R}}\left(\frac{\xi}{\sigma_1} + \frac{R_{12}}{R_{11}}\frac{\eta}{\sigma_2}\right)$$

the first of these integrals reduces to a tabulated integral. Then we have

$$I_2 = 2\pi\sigma_1\sigma_2 R\sqrt{\frac{R}{(R_{11}R_{22} - R_{12}^2)}}. \tag{2.14}$$

We transform the triple integral in (2.13) into a product of the following two integrals:

$$I_{21} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[-\frac{1}{2R}\left(\bar{R}_{11}\frac{\xi^2}{\sigma_1^2} + 2\bar{R}_{12}\frac{\xi}{\sigma_1}\frac{\eta}{\sigma_2} + \bar{R}_{22}\frac{\eta^2}{\sigma_2^2}\right)\right]d\xi\,d\eta,$$

$$I_1 = \int_{-\infty}^{\infty}\exp\left[-\frac{R_{33}}{2R}\left(\frac{\zeta}{\sigma_3} + \frac{R_{13}}{R_{33}}\frac{\xi}{\sigma_1} + \frac{R_{23}}{R_{33}}\frac{\eta}{\sigma_2}\right)^2\right]d\zeta,$$

where

$$\bar{R}_{11} = \frac{R_{11}R_{33} - R_{13}^2}{R_{33}}, \quad \bar{R}_{12} = \frac{R_{12}R_{33} - R_{13}R_{23}}{R_{33}}, \quad \bar{R}_{22} = \frac{R_{22}R_{33} - R_{23}^2}{R_{33}}.$$

It is not difficult to see that I_{21} is computed in accordance with formula (2.14) and I_1 reduces to a tabulated integral by the change of the variable

$$t = \sqrt{\frac{R_{33}}{2R}}\left(\frac{\zeta}{\sigma_3} + \frac{R_{13}}{R_{33}}\frac{\xi}{\sigma_1} + \frac{R_{23}}{R_{33}}\frac{\eta}{\sigma_2}\right).$$

From Eq. (2.13) we now obtain

$$c = \frac{1}{\sigma_1\sigma_2\sigma_3(2\pi)^{3/2}\sqrt{R}} \times \sqrt{\frac{(R_{11}R_{33} - R_{13}^2)(R_{22}R_{33} - R_{23}^2) - (R_{12}R_{33} - R_{13}R_{23})^2}{R^2R_{33}}}. \tag{2.15}$$

In the derivation of the equation of state for condensed media Predvoditelev used the case of isotropic correlation:

$$R = \begin{vmatrix} 1 & r & r \\ r & 1 & r \\ r & r & 1 \end{vmatrix} = (1-r)^2(1+2r).$$

In this case formula (2.15) gets simplified

$$c = \frac{1}{\sigma_1\sigma_2\sigma_3(2\pi)^{3/2}\sqrt{R}}. \tag{2.16}$$

The simplest case of anisotropic correlation may be

$$R = \begin{vmatrix} 1 & r_1 & r_3 \\ r_1 & 1 & r_2 \\ r_3 & r_2 & 1 \end{vmatrix} = 1 - r_1^2 - r_2^2 - r_3^2 + 2r_1r_2r_3.$$

For this case formula (2.15) becomes

$$c = \frac{1}{\sigma_1\sigma_2\sigma_3(2\pi)^{3/2}\sqrt{1 - r_1^2 - r_2^2 - r_3^2 + 2r_1r_2r_3}}. \tag{2.17}$$

3. Forces Causing Correlation between Statistical Indices of a Gaseous System

In formulating his mechanics H. Hertz used the idea that any mechanical system with any forces acting in and on it can be replaced by a single system containing visible and hidden masses. The same idea was used by Helmholtz in constructing monocyclic motions which he used as the basis for constructing the mechanical analog of entropy.

If T_0 denotes the kinetic energy of the visible masses, then ignoring the cyclic coordinates Lagrange's equation can be written in the form

$$\frac{d}{dt}\frac{\partial T_0}{\partial \dot{q}_i} - \frac{\partial T_0}{\partial q_i} = F_i + \Gamma_i. \tag{3.1}$$

Hence F_i and Γ_i have a definite dependence on the motion of the hidden masses. They may be interpreted as forces acting on the system and within it. One of these F_i does work; the other Γ_i, which is a gyroscopic force equivalent to nonholonomic couplings, does not do any work. From (3.1) we obtain the following equation for the gyroscopic force:

$$\sum_i \Gamma_i dq_i = 0. \tag{3.2}$$

Apparently gaseous systems may exist in which there may be forces doing work and forces not doing work.

Formula (2.9) obtained earlier enables us to write the following formulas for the mean values of ξ, η, ζ:

$$\begin{aligned} \bar{\xi} &= b_{12}\eta + b_{13}\zeta, \\ \bar{\eta} &= b_{12}\xi + b_{23}\zeta, \\ \bar{\zeta} &= b_{13}\xi + b_{23}\eta. \end{aligned} \tag{3.3}$$

If gyroscopic forces are acting in the system, then all possible values of the components ξ, η, ζ must satisfy the relation

$$\Gamma_1\xi + \Gamma_2\eta + \Gamma_3\zeta = 0,$$

where Γ_1, Γ_2, and Γ_3 must depend on the apparent coordinates.

We take the mean of the last relation and assuming that the mean of the product is proportional to the product of the means, we write it in the form

Substituting (3.4) into (3.3) we obtain

$$\bar{\Gamma}_1 \bar{\xi} + \bar{\Gamma}_2 \bar{\eta} + \bar{\Gamma}_3 \bar{\zeta} = 0. \tag{3.4}$$

$$(\bar{\Gamma}_2 b_{12} + \bar{\Gamma}_3 b_{13}) \xi + (\bar{\Gamma}_1 b_{12} + \bar{\Gamma}_3 b_{23}) \eta + (\bar{\Gamma}_1 b_{13} + \bar{\Gamma}_2 b_{23}) \zeta = 0. \tag{3.5}$$

In this equation we require that the following equalities be satisfied:

$$\begin{gathered} \bar{\Gamma}_2 b_{12} + \bar{\Gamma}_3 b_{13} = \bar{\Gamma}_1, \\ \bar{\Gamma}_1 b_{12} + \bar{\Gamma}_3 b_{23} = \bar{\Gamma}_2, \\ \bar{\Gamma}_1 b_{13} + \bar{\Gamma}_2 b_{23} = \bar{\Gamma}_3. \end{gathered} \tag{3.6}$$

After this formula (3.5) becomes

$$\bar{\Gamma}_1 \xi + \bar{\Gamma}_2 \eta + \bar{\Gamma}_3 \zeta = 0.$$

It is not difficult to see that this last formula is equivalent to (3.2); therefore from (3.6) we obtain the following coupling of the coefficients through the averaged components of the gyroscopic forces:

$$b_{12} = \frac{\bar{\Gamma}_1^2 + \bar{\Gamma}_2^2 - \bar{\Gamma}_3^2}{2\bar{\Gamma}_1 \bar{\Gamma}_2},$$

$$b_{13} = \frac{\bar{\Gamma}_1^2 + \bar{\Gamma}_3^2 - \bar{\Gamma}_2^2}{2\bar{\Gamma}_1 \bar{\Gamma}_3},$$

$$b_{23} = \frac{\bar{\Gamma}_2^2 + \bar{\Gamma}_3^2 - \bar{\Gamma}_1^2}{2\bar{\Gamma}_2 \bar{\Gamma}_3}.$$

The formulas obtained here show that since the average values of the components of gyroscopic forces are easily given, b_{12}, b_{13}, b_{23} are thereby determined and vice versa. Thus the presence of gyroscopic forces in the system unambiguously leads to the conclusion that the statistical indices can not be regarded independent. Therefore the distribution of such systems will belong to the class of normal distributions taking account of the correlation among the statistical indices.

NOTATION

ξ, η, ζ are the components of thermal velocity of atoms or molecules;
R is the correlation determinant;
T_0 is the kinetic energy of visible masses;
Γ_i is the gyroscopic force.

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