

## THEORETICAL SUBSTANTIATION OF THE POSSIBILITY OF INDUCING A PONDEROMOTIVE THERMODYNAMIC FORCE IN A SOLID AND A GAS

O. V. Minin

UDC 536.2:517.97

*Based on the principle of least action extended by the author to heat conduction in a solid, owing to the formal analogy between time and absolute temperature stated in the 1980s by means of the formalism of the Hamilton–Jacobi equation an expression is obtained for the ponderomotive thermodynamic force in a solid and a gas.*

1. In 1987 a variational principle for heat conduction was completely formulated [1]. Later [2] it was shown that an analog of the Lagrange function exists and that the density of the Lagrange function for heat conduction in the formalism of integrals over trajectories is equal to

$$L = \rho c_v T \frac{\partial T}{\partial t} + \lambda (\nabla T)^2 - \nabla \cdot (\lambda T \nabla T). \quad (1)$$

In [2] it is proved that this Lagrangian pertains to a singular type since it can be transformed into a balance equation, namely, the heat conduction equation.

A fluctuation functional as an analog of action represents fluctuation of the internal energy accumulated in any interval of time [1]:

$$J(T) = \Delta D = \int_t \int_X \left[ \rho c_v T \frac{\partial T}{\partial t} + \lambda (\nabla T)^2 \right] dX dt - \int_t \int_S \lambda T \nabla_n T dS dt \leq \frac{1}{2} k T^2. \quad (2)$$

Some invariant properties of  $J$  and  $L$  are discussed in [2].

By virtue of an identity transformation,  $L$  can be represented in the following form:

$$\frac{1}{2k} \frac{\partial}{\partial t} [\rho c_v k T^2] + \frac{a}{4k (\rho c_v k T^2)} (\nabla (\rho c_v k T^2))^2 - \nabla \cdot \left( \frac{a}{2k} \nabla (\rho c_v k T^2) \right) = 0, \quad (3)$$

As established in [1], the density of energy fluctuation in the hydrodynamic stage is

$$D(X, t) = k \rho c_v T^2(X, t). \quad (4)$$

Consequently, Eq. (3) acquires the form

$$\frac{1}{2k} \frac{\partial D}{\partial t} + \frac{a}{4kD} (\nabla D)^2 - \nabla \cdot \left( \frac{a}{2k} \nabla D \right) = 0, \quad a = \frac{\lambda}{\rho c_v}. \quad (5)$$

We consider the local dissipative cumulant (LDC) and introduce a small interval of time (for instance,  $\tau \sim 10^{-11} - 10^{-7}$  sec) in order to operate with the LDC and remain within the framework of the hydrodynamic stage:

---

St. Petersburg Institute of Precision Mechanics and Optics, Russia. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 71, No. 5, pp. 917-926, September-October, 1998. Original article submitted June 4, 1996; revision submitted January 28, 1998.

$$K = \Delta D_{\tau}^1 = \int_{\tau} \int_{\Delta V} \left[ \rho c_v T \frac{\partial T}{\partial t} + \lambda (\nabla T)^2 - \nabla \cdot (\lambda T \nabla T) \right] dV dt \leq \frac{1}{2} k T^2, \quad (6)$$

where  $\Delta V$  is some small volume of the solid, which is, generally speaking, indeterminate. However, it is known that the volume should be such that local thermodynamic equilibrium is established in it at any moment on the time scale, but limited each time by the interval  $\tau$ . Such a subdivision of time intervals into small subintervals is used in [3] in determination of the Lagrange and Hamilton functions to provide the condition of maximum probability of transition at each point of the trajectory of the thermodynamic system. As will be seen below, rigorous determination of the small interval  $\tau$  by its lower and upper values is of no crucial importance since abnormally large fluctuations of the internal energy in a solid last for a time  $\Delta t \sim 10^{-13} - 10^{-12}$  sec [4]. This was shown for one-, two-, and three-dimensional crystal lattices with different interaction potentials in computer-aided simulation. According to theoretical and model results of the authors, ordinary deviations of atomic energies from the most probable value correspond, in their terminology, to the "thermal life" of the solid.

Long before the results of [4] it was shown theoretically in [5] that "short-lived large energy fluctuations" of atoms have a lifetime  $\Delta t \sim 10^{-13} - 10^{-12}$  sec. This feature of the energy fluctuation of atoms in a solid indicates that the definition and evaluation of the cumulant  $K$  according to (6) are quite satisfactory since density integration is implemented (definitely) on the introduced interval  $\tau \approx 10^{-11} - 10^{-7}$  sec. In other words, the intervals  $\Delta t \in \tau$  can be considered as the sets approaching zero measure.

Consequently, we have a definition and a satisfactory evaluation of the LDC. Then Eq. (5) can be modified to the form

$$\frac{\partial K}{\partial t} + \frac{1}{2 \frac{k \max T^2}{a}} (\nabla K)^2 - a \nabla^2 K = 0. \quad (7)$$

Expression (7) is similar to the Hamilton–Jacobi equation. In addition to two classical analogs it contains one more term that corresponds to the quantum diffraction term  $(\hbar^2/2m)\rho^{-1/2}\nabla^2\rho^{1/2}$ , which appears in the Schrödinger equation in consideration of action as the phase of the probability wave.

The Hamilton–Jacobi equation was obtained in [3] for the case of non-Gaussian fluctuations in the Boltzmann thermodynamic limit  $k \downarrow$ . Since energy fluctuation is a Markov process (with a Gaussian distribution), the derivative  $\partial K/\partial t = 0$  and at the same time we can set  $\nabla^2 K = 0$ . The multiplier  $1/2(k_{\max} T^2/a) = 1/2G$  does not tend to zero and, consequently, we obtain the eikonal equation

$$(\nabla K)^2 = 0. \quad (8)$$

It is obvious that (8) is the equation of the degenerate eikonal  $K$ . However, despite this we obtain an analog of the law of refraction in geometrical optics. Taking into account that we are considering the process of heat conduction across the phase boundary of two bodies with different thermal conductivities, we can write for any  $\varepsilon$ -neighborhood at the boundary

$$\lambda_1^2 (\nabla K_1)^2 = 0, \quad \lambda_2^2 (\nabla K_2)^2 = 0. \quad (9)$$

According to the infinitesimal estimate (6) we have

$$\lambda_1 T_1 \nabla T_1 = \lambda_2 T_2 \nabla T_2 \quad (10)$$

or

$$\lambda_1 \nabla T_1 = \lambda_2 \nabla T_2 \Rightarrow \frac{\nabla T_1}{\nabla T_2} = \frac{\lambda_2}{\lambda_1}, \quad (11)$$

where  $T_1 = T_2$  is fulfilled by virtue of the energy continuity at the boundary. Consequently, we have obtained the law of refraction of gradients or the continuity condition of the heat flux. The degeneracy of (8) does not allow, unfortunately, derivation of the law of refraction similarly to the method of G. Bruns in geometrical optics described in [6].

If we represent temperature in vector form with the aid of the segment determined by the functions  $T_1(X, t)$  and  $T_2(X, t)$  so that the ensemble of all elements of the type

$$eT(X, t) = [\alpha T_1 + (1 - \alpha) T_2] e, \quad (12)$$

will prescribe some linear manifold [7] with a direction, where  $T_1, T_2 \rightarrow T$ ,  $\alpha \in [0, 1]$ , and  $e$  is the unit vector along this direction, then the condition

$$eT\nabla T = 0 \quad (13)$$

corresponds to orthogonality of the heat flux lines of the isothermal surface  $T(X, t) = \text{const}$  at any point of the front and at any moment of time.

In the context of the developed analogy we must now determine the velocity of isothermal-surface propagation by the Jacobi method. On the one hand, we can formally write

$$dK = kTdT. \quad (14)$$

and on the other hand, the following representation is valid:

$$dK = |\nabla K| dS = |\nabla K| u dt = kT |\nabla T| u dt, \quad (15)$$

whence we have

$$u = \frac{\partial T / \partial t}{|\nabla T|} \quad \text{or} \quad u = \frac{\rho c_v \partial T / \partial t}{\rho c_v |\nabla T|}. \quad (16)$$

and consequently

$$u = \frac{\lambda \nabla^2 T}{\rho c_v |\nabla T|} \quad \text{or} \quad u = - \frac{a \nabla^2 T}{|\nabla T|} e_r. \quad (17)$$

The last formula coincides with an expression obtained by a different method [8].

Developing the envisaged analogy further, we can derive the "pulse" of a temperature field by the same method as in mechanics:

$$p_T = \nabla K \cong \nabla \left( \frac{1}{2} kT^2 \right) = kT\nabla T. \quad (18)$$

In [9] Atkins suggested a hypothesis according to which "for a number of formal reasons temperature can be considered as imaginary time." However, he did not obtain any far-reaching consequences from this assumption. At the same time if we eliminate the imaginary unit and assume that  $t \rightarrow T$ , then, as shown below, we obtain very surprising and, which is most important, correct results and consequences. Then, adopting this analogy we can formally write the "law" of determination of the "force" of the temperature field

$$F_T = \frac{dp_T}{dT} = k\nabla T = \nabla(kT). \quad (19)$$

It is easy to see that the vanishingly small force  $F$  (quasiforce according to [10]) is caused in the present approach by normal thermal fluctuations, and the well-known idea of thermodynamic force shows itself in a new light.

In accordance with the interpretation discussed, the term  $T\rho c_v \Delta V (\partial T / \partial t) dt$  in (6) is similar to the definition of the action  $S = -Et$ , and the succeeding derivative gives

$$H = \frac{dK}{dT} = kT, \quad (20)$$

where  $kT$  is the modulus of any distribution.

Let us ascertain that the canonical Hamilton equations occur. According to the relation

$$H = \sum_i p_i \dot{q}_i - L \quad (21)$$

under the condition  $L = 0$  for heat conduction we obtain

$$kT = kT |\nabla T| \dot{q}_T, \quad \dot{q}_T = \frac{\partial q_T}{\partial T} = \frac{1}{|\nabla T|}, \quad q_T = \frac{T}{|\nabla T|}. \quad (22)$$

Then the relations

$$\dot{p}_T = \frac{\partial p}{\partial T} = k \nabla T = \frac{\partial H / \partial T}{\partial q / \partial T}, \quad (23)$$

$$\dot{q}_T = \frac{\partial q}{\partial T} = \frac{\frac{\partial}{\partial T} (kT)}{\frac{\partial}{\partial T} (kT \nabla T)} = \frac{\partial H / \partial T}{\partial p / \partial T}, \quad (24)$$

must be valid and we obtain a close analogy with the Hamilton equations:

$$\dot{p}_T = \frac{\partial H}{\partial q_T}; \quad \dot{q}_T = \frac{\partial H}{\partial p_T}. \quad (25)$$

As shown in [11], the canonical Hamilton equations can be derived from the generalized variational principle (2.8) in the case of non-Gaussian fluctuations as well.

We will develop this approach further with allowance for the occurrence of non-Gaussian fluctuations due to some external action, the physical nature of which is of no interest to us now. Considering the obtained analog of the Hamilton–Jacobi equation, we assume that the terms  $\partial K / \partial t$ ,  $a \nabla^2 K$  are not equal to zero as a consequence of non-Gaussian fluctuations. Equation (7) is modified to the following form:

$$(\nabla K)^2 = \frac{2k \max T^2}{a} \left( a \nabla^2 K - \frac{\partial K}{\partial t} \right) \quad (26)$$

or

$$p_T = \nabla K = \sqrt{\left( \frac{2k \max T^2}{a} \left( a \nabla^2 K - \frac{\partial K}{\partial t} \right) \right)} \frac{\nabla K}{|\nabla K|}. \quad (27)$$

Thus, we have obtained an analog of the nondegenerate equation of the eikonal (26). In accordance with the developed method the derivative with respect to the temperature  $T$  gives

$$F_T = \frac{\partial}{\partial T} (K) = \sqrt{\left( \frac{k \max T^2}{2a} \right)} \frac{\left( -\frac{\partial}{\partial T} \left( \frac{\partial K}{\partial t} \right) \right)}{\sqrt{\left( a \nabla^2 K - \frac{\partial K}{\partial t} \right)}} \frac{\nabla K}{|\nabla K|}. \quad (28)$$

As established, the local dissipative cumulant (LDC) is

$$K = \int_{\tau} \int_{\Delta V} \left[ \rho c_v T \frac{\partial T}{\partial t} + \lambda (\nabla T)^2 - \nabla \cdot (\lambda \nabla T) \right] dV dt, \quad (29)$$

and then the derivative of the numerator is

$$\frac{\partial}{\partial T} \left( \frac{\partial K}{\partial t} \right) = \rho c_v \Delta V \frac{\partial T}{\partial t}. \quad (30)$$

Consequently, we have an analog of the nondegenerate induced force  $F_T$  or  $f_T$ :

$$f_T = \frac{F_T}{\Delta V} = - \frac{\rho c_v \frac{\partial T}{\partial t}}{\sqrt{\left( a \nabla^2 K - \frac{\partial K}{\partial t} \right) \frac{k \max T^2}{2a}}} \frac{\nabla K}{|\nabla K|}, \quad (31)$$

where  $\nabla K / |\nabla K| = e_k$  is the unit vector coinciding with the gradient of  $K$ . This means that  $f_T$  is the volume density of the force induced in a solid due to an increase (or decrease) in the temperature and due to redistribution of the LDC of functions  $\partial K / \partial t$  and  $\nabla^2 K$  that are not equal to zero. As concerns these two functions, it is pertinent to note that the authors of [4] established in their experiments that spontaneous energy fluctuations of atoms can migrate in a solid due to interference effects (phonons). The latter, overlapping, form migrating packets, and then we can obviously assume that  $\nabla K \neq 0$ ,  $\partial K / \partial t \neq 0$ . When a solid is exposed to an external energetic action, these phenomena will be enhanced because of possible resonant effects.

The physical dimensions of the denominator in (31) correspond to velocity. We assume that in order of magnitude it is equal to the velocity of temperature-field propagation (17). Then (31) can be rewritten in vector form as

$$- f_T \frac{a \nabla^2 T}{|\nabla T|} e_r = - \rho c_v \frac{\partial T}{\partial t} e_k, \quad (32)$$

where  $e_k, e_r$  are unit vectors defined above.

By virtue of the heat conduction equation the term  $a \nabla^2 T$  is equal to  $\partial T / \partial t$ . Then equality (32) is transformed to the form

$$f_T = \rho c_v \nabla T, \quad F_T = \rho c_v \Delta V \nabla T = \nabla U, \quad (33)$$

where  $U$  is the internal energy in the corresponding volume. It is evident that the last formula generalizes relation (19) obtained earlier, and expression (33) is similar to the definition of potential force.

Thus, the two formulas

$$f_T = \rho c_v \nabla T, \quad q = - \lambda \nabla T \quad (34)$$

show that a temperature gradient leads to both the occurrence of a heat flux and the formation of a ponderomotive force. It is easily seen that the vectors  $f_T$  and  $q$  are opposite in direction. However, the formula  $f_T = \rho c_v \nabla T$  is used as an approximation of formula (31).

Using the expression for the force density

$$f_T = \rho c_v \nabla T,$$

we arrive at the magnitude of the heat flux

$$q = a f_T = - c_v \rho a \nabla T = - \lambda \nabla T. \quad (35)$$

It is clear that the relationship between  $\mathbf{q}$  and  $\mathbf{f}_T$  is linear and  $a$  is a constant kinetic coefficient. This corresponds formally to the Onsager representation

$$\mathbf{J} = L\mathbf{X}, \quad (36)$$

where  $\mathbf{J}$  and  $\mathbf{X}$  are the heat flux and the thermodynamic force, respectively;  $L$  is the kinetic coefficient. In this (particular) case it is necessary to write

$$\mathbf{J} = \mathbf{q}; \quad \mathbf{X} = \nabla \left( \frac{1}{T} \right); \quad L = \lambda T^2; \quad \lambda = \frac{L}{T^2}. \quad (37)$$

However we should apparently agree with a constantly arising question: why are  $\mathbf{X}$  and  $\lambda$  such strange parameters representing the force and the coefficient? As will be shown below, it is more reasonable to determine the thermodynamic force by formula (33). Thus, the scalar product of the two opposite vectors  $\mathbf{q}$  and  $\mathbf{f}_T$  gives

$$\mathbf{q} \cdot \mathbf{f}_T = -\lambda \rho c_v (\nabla T)^2. \quad (38)$$

The composition  $\lambda(\nabla T)^2$  is the "trace" of the local entropy production  $\sigma = \lambda(\nabla T)^2/T^2$ . Despite the note about the strange character of the force and the coefficients, we nevertheless use formula (22.54a) in Sec. 22.5 of [12], where  $\lambda$  is determined in terms of the kinetic coefficient  $L_0$ :

$$\lambda = \frac{L_0}{T^2} = \frac{1}{T^2} \int \int_{-\infty}^0 \exp(-\epsilon t) (J_Q^x(x), J_Q^x(x', t)) dx' dt, \quad (39)$$

here, the integral is a two-time retarded Green correlation function. Zubarev [12] represents  $\lambda$ , in fact, according to the Onzager interpretation of the thermodynamic force  $\mathbf{X} = \nabla(1/T)$  in order to match subsequent relations without internal contradictions.

In [12] (Sec. 22.8) the author suggested another definition of the thermodynamic force, namely,  $F_0(k, t) = \beta(k, t)$  (in the case of heat conduction), where  $\beta(k, t)$  are Fourier components in the expansion of the thermodynamic parameter in the space variables, provided that the rate of change of  $F_0(X, t)$  in time is vanishingly small. It should be noted that the new thermodynamic force  $\beta(k, t)$  ( $\beta = 1/T(X, t)$ ) is determined in terms of the formalism so that the linear relations between the fluxes and the forces are retained in constructing a nonequilibrium statistical operator (a distribution function).

Meanwhile, using an original method in passing from the quantum to the "classical version of Eq. (3) and assuming that the local conservation laws are valid," W. M. Visscher [10] obtained a thermal-conductivity coefficient similar to the Green-Kubo and Zubarev formulas. However, he succeeded in doing this by making the assumption that  $\nabla\beta \equiv \nabla(1/T)$  (as applied to the nonequilibrium distribution function) can be considered as a constant quantity in calculating the correlation function and the statistical mean. In fact, W. M. Visscher showed that the thermal conductivity coefficient determined by his formula (9) or the Zubarev formula (39) must not be explicitly related to the factor  $1/T^2$  since the latter stems from a purely mathematical operational procedure. In particular, the author of [10] writes that " $\lambda$  also depends implicitly on  $\nabla\beta$  via the Poisson bracket and this should be considered here, naturally, not as a linear response but as a response that includes the effect of the action of all higher orders of  $\nabla\beta$ ." This concluding remark seems rather controversial.

In the context of the above considerations and references it is, perhaps, reasonable to consider  $\lambda = L_0/T^2$  as an intermediate coefficient that has no physical meaning.

Nevertheless, substituting (39) into formula (38) we arrive at

$$\mathbf{q} \cdot \mathbf{f}_T = - \left[ \int \int_{-\infty}^0 \exp(\epsilon t) (J_Q^x(x), J_Q^x(x', t)) dx' dt \right] \rho c_v \frac{(\nabla T)^2}{T^2}, \quad (40)$$

and the Green's function (up to a sign) plays the role of the thermal diffusivity  $a$ . Here it is seen that the coefficient  $-\left[\int_{-\infty}^0 \int \exp(\epsilon t)(J_Q^x(x), J_Q^x(x', t))dx'dt\right]\rho c_v$  turns out to be positive if the Green's function is negative. In Secs. 15, 17, 18, etc. of [12] Zubarev represents the retarded Green's function with a negative sign. If we assume that this statement is correct, further manipulations will not involve any difficulties or contradictions.

Hence we have

$$\mathbf{f}_T \cdot \mathbf{q} = \frac{\lambda (\nabla T)^2}{T^2} = \sigma. \quad (41)$$

At the same time, substitution of  $\lambda$ , determined in this way, into (38) leads to a correct determination of both the thermal conductivity coefficient  $\lambda$  and the local source of entropy. Extremely curiously (and alarmingly), some kind of antinomy arises here: on the one hand,  $\lambda$  is determined (in our opinion, incorrectly) operationally, but on the other hand, the coefficient is recovered correctly by using another operational procedure. This puzzling fact remains to be explained.

The possibility of representing  $\sigma$  with the aid of  $\mathbf{f}_T = \nabla(\rho c_v T)$  and  $\mathbf{q} = -a\nabla(\rho c_v T)$  allows the local entropy production to be written in the form

$$\sigma = \frac{\lambda (\nabla U)^2}{U^2}, \quad (42)$$

where  $U$  is the density of the internal energy. The entropy flow is

$$\mathbf{J}_S = -\frac{\lambda \nabla T}{T} = -\lambda \nabla \ln U. \quad (43)$$

The local source and the entropy flow can be represented in another way:

$$\sigma = \lambda (\nabla \ln U)^2 = \lambda (\nabla \ln (F + TS))^2 = \lambda \left[ \nabla \left( \ln F \left( 1 + \frac{TS}{F} \right) \right) \right]^2, \quad (44)$$

$$\mathbf{J}_S = -\lambda \nabla \left[ \ln \left( 1 + \frac{TS}{F} \right) F \right], \quad (45)$$

where  $F$  is the density of the free energy.

Using well-known relations of statistical thermodynamics, we substitute  $F$  and  $TS$  into (44):

$$\sigma = \lambda \left( \nabla \ln F + \nabla \ln \left( 1 + \frac{kT \left( \ln Z + T \frac{\partial \ln Z}{\partial T} \right)}{-kT \ln Z} \right) \right)^2, \quad (46)$$

where  $F = -kT \ln Z$ ,  $S = k [\ln Z + T \partial \ln Z / \partial T]$ , and  $Z$  is the statistical integral, while  $\ln Z$  is the volume density of the logarithm of the statistical integral. Simple transformations of (46) yield

$$\sigma = \lambda \left[ \nabla \ln F + \nabla \ln \left( -T \frac{\partial \ln Z}{\ln Z} \right) \right]^2. \quad (47)$$

The analogous formula for the entropy flow  $\mathbf{J}_S$  is

$$\mathbf{J}_S = -\lambda \left[ \nabla \ln F + \nabla \ln \left( -T \frac{\partial \ln Z}{\ln Z} \right) \right]. \quad (48)$$

It is easy to see that the expression  $(\partial \ln Z / \partial T) / \ln Z$  is the "sensitivity" of the logarithm of the integral of states to a change in temperature. For the case of statistical equilibrium of a thermodynamic system with a prescribed number of particles and volume, the statistical integral for the canonical ensemble is

$$Z = \int \exp \left( -\frac{H(p, q)}{kT} \right) \frac{dpdq}{N! \hbar^{3N}}. \quad (49)$$

Since

$$\frac{\partial \ln Z}{\partial T} / \ln Z = \frac{\frac{\partial Z}{\partial T}}{Z \ln Z} \quad (50)$$

and  $Z$  depends explicitly on  $T$  only through the increment of the exponent, we can assume that

$$\nabla \ln \left( T \frac{\frac{\partial Z}{\partial T}}{Z \ln Z} \right) \approx \sigma, \quad (51)$$

because in the subsequent discussion only weakly nonequilibrium states such that  $|\nabla T|/T^2 \ll 1$  are considered.

This approach to a vanishingly small value is confirmed, with a high degree of accuracy, for an ideal gas, which is demonstrated in the next section.

As a result of the assumption made, we obtain

$$\sigma = \lambda [\nabla \ln F]^2, \quad \mathbf{J}_S = -\lambda \nabla \ln F. \quad (52)$$

Representation of the local source and the entropy flow in terms of the "spatial sensitivity" of the free energy and its square  $\lambda(\nabla F/F)$  and  $\lambda(\nabla F/F)^2$  can considerably widen earlier concepts of nonequilibrium thermodynamics. In particular, for the case of heat conduction the Onsager definition

$$\sigma = \mathbf{J}\mathbf{X}; \quad \mathbf{J} = -\lambda \nabla T; \quad \mathbf{X} = \nabla \left( \frac{1}{T} \right) = -\frac{\nabla T}{T^2}, \quad (53)$$

based on use of the temperature and its gradient in introducing the physically nonmeasurable thermodynamic force, is replaced by another by passing to the main thermodynamic potential  $F$ , about which Zubarev has written that "this function determines all the thermodynamic properties of a system" [12, p. 29]. In our opinion, this transition stands up to the Bohr correspondence principle since it brings the method of investigation of nonequilibrium thermodynamic systems back to physical quantities obeying the principle of verification.

2. We consider an ideal gas and write an expression for  $\ln Z_0$ :

$$\ln Z_0 = \frac{3N}{2} (\ln 2\pi + \ln m + \ln kT) + N \ln V - \ln N! \quad (54)$$

or

$$\ln Z_0 = \frac{3N}{2} \left( \ln \frac{2\pi kmTV^{2/3}}{N^{2/3}} \right) \quad (55)$$

provided that  $\ln N! = N \ln N$ .

In order to deal with volume densities, it is necessary to perform some transformations:



$$n = \frac{N}{V}; \ln Z_0 = \frac{\ln Z_0}{V} = \frac{3n}{2} \ln \frac{2\pi kmT}{n^{2/3}};$$

$$F = -kT \frac{3n}{2} \ln \frac{2\pi kmT}{n^{2/3}}; \frac{\partial \ln Z_0}{\partial T} = \frac{3n}{2T}. \quad (56)$$

Consequently, the local entropy production is

$$\sigma = \lambda \left[ \nabla \ln F + \nabla \ln \left( -\frac{T \frac{3n}{2T}}{\frac{3n}{2} \ln \left( \frac{2\pi kmT}{n^{2/3}} \right)} \right) \right]^2 \quad (57)$$

or

$$\sigma = \lambda \left[ \nabla \ln F + \nabla \ln \left( \frac{1}{\ln \left( \frac{n^{2/3}}{2\pi kmT} \right)} \right) \right]^2, \quad (58)$$

or

$$\sigma = \lambda \left[ \nabla \ln F + \nabla \ln \left( \ln \frac{n^{2/3}}{2\pi kmT} \right)^{-1} \right]^2. \quad (59)$$

It is necessary to evaluate the order of magnitude of the second term:

$$2\pi kmT = 6.28 \cdot 1.38 \cdot 10^{-23} \cdot 51 \cdot 10^{-27} T \cong 46 \cdot 10^{-50} T.$$

If  $n \in [10^{15} - 10^{20}]$  and  $T \in [300 - 1000]$  K, then

$$o = \left[ \ln \left( \ln \frac{n^{2/3}}{2\pi kmT} \right) \right]^{-1} \in \left[ \frac{1}{52} \div \frac{1}{56} \right] \quad \text{and} \quad \nabla o \sim 0, \quad (60)$$

whence we obtain with a high degree of accuracy that

$$\sigma = \lambda (\nabla \ln F)^2 = \lambda \left( \frac{\nabla F}{F} \right)^2, \quad (61)$$

$$\mathbf{J}_S = -\lambda \left( \frac{\nabla F}{F} \right) = -\lambda \nabla \ln F. \quad (62)$$

We consider some process of excitation of a weakly nonequilibrium state in the ideal gas. The total entropy after a lapse of time  $t$  is equal to

$$S = \int_t \int_V \sigma dVdt + \int_t \int_V \nabla \cdot \mathbf{J}_S dVdt + S_0. \quad (63)$$

$$S = \int_t \int_V \lambda (\nabla \ln F)^2 dVdt + \int_t \int_V \lambda \nabla \cdot (\nabla \ln F) dVdt + S_0. \quad (64)$$

Since the free-energy density is

$$F = \frac{3}{2} nkT \ln \frac{1}{2\pi kmT} n^{2/3}, \quad (65)$$

the total entropy is

$$S = \int_t \int_V \lambda \left[ \nabla \left( \ln \frac{3}{2} + \ln n + \ln k + \ln T + \ln \ln \frac{n^{2/3}}{2\pi kmT} \right) \right]^2 dVdt + \\ + \int_t \int_V \lambda \nabla \left[ \ln \frac{3}{2} + \ln n + \ln k + \ln T + \ln \ln \frac{n^{2/3}}{2\pi kmT} \right] dVdt + S_0. \quad (66)$$

Using the above evaluation, we obtain

$$S = \int_t \int_V \lambda \left[ \nabla \ln T + \nabla \ln n \right]^2 dVdt + \int_t \int_V \lambda \nabla \cdot \left[ \nabla \ln T + \nabla \ln n \right] dVdt + S_0. \quad (67)$$

Consequently,

$$S \cong \int_t \int_V \lambda (\nabla \ln knT)^2 dVdt + \int_t \int_V \lambda \nabla \cdot (\nabla \ln knT) dVdt + S_0. \quad (68)$$

In conformity with the equation of state of the ideal gas  $p = nkT$  we can write

$$S = \int_t \int_V \lambda \left( \frac{\nabla p}{p} \right)^2 dVdt + \int_t \int_V \lambda \nabla \cdot \left( \frac{\nabla p}{p} \right) dVdt + S_0. \quad (69)$$

According to the first law of thermodynamics

$$p = T \left( \frac{\partial S}{\partial V} \right)_T + \left( \frac{\partial U}{\partial V} \right)_T \cong T \left( \frac{\partial S}{\partial V} \right)_T + \left( \frac{\partial F}{\partial V} \right)_T. \quad (70)$$

Performing volume differentiation, we obtain

$$p = T \int_t \lambda \left[ \frac{|\nabla n|}{n} + \frac{|\nabla T|}{T} \right]^2 dt + T \int_t \lambda \nabla \cdot \left[ \frac{|\nabla n|}{n} + \frac{|\nabla T|}{T} \right] dt + \frac{d}{dV} [-kT \ln Z_0]. \quad (71)$$

The next derivative with respect to  $t$  leads to the expression

$$\frac{d}{dt} \left( \frac{p}{\lambda T} \right) = \left( \frac{\nabla p}{p} \right)^2 + \nabla \cdot \left( \frac{\nabla p}{p} \right) - \frac{d}{dt} \left( \frac{1}{\lambda T} \frac{d}{dV} (kT \ln Z_0) \right) \quad (72)$$

or

$$\frac{d}{dt} \left( \frac{p}{\lambda T} \right) = \left( \frac{\nabla p}{p} \right)^2 + \nabla \cdot \left( \frac{\nabla n}{n} + \frac{\nabla T}{T} \right) - \frac{d^2}{dt dV} \left[ \frac{3kN}{\lambda} \left( \ln 2\pi + \ln k + \ln T - \frac{2}{3} \ln \frac{N}{V} \right) \right]. \quad (73)$$

If  $N$  and  $T$  are constant quantities for a rather short time, then assuming that the third term is equal to zero, we arrive at

$$\frac{d}{dt} \left( \frac{p}{\lambda T} \right) \cong \left( \frac{\nabla p}{p} \right)^2 + \nabla \cdot \left( \frac{\nabla n}{n} + \frac{\nabla T}{T} \right). \quad (74)$$

Based on the restrictions  $|\nabla n| \ll n$  and  $|\nabla T| \ll T$ , we determine that

$$\frac{d}{dt} \left( \frac{p}{\lambda T} \right) \cong \left( \frac{\nabla p}{p} \right)^2, \quad (75)$$

$$f_T = |\nabla p| = p \sqrt{\left(\frac{d}{dt} \left(\frac{p}{\lambda T}\right)\right)}. \quad (76)$$

After differentiation and some transformations we obtain

$$\mathbf{f}_T = \nabla p = \frac{nk}{\sqrt{\lambda}} \sqrt{pT} \left(\frac{dp/dt}{p} - \frac{dT/dt}{T}\right)^{1/2} \mathbf{e}_r. \quad (77)$$

The expression in parentheses is the difference of the corresponding sensitivities in excitation of the nonequilibrium state in some process. If the sensitivity to pressure excitation is higher than to temperature excitation, then the force  $\mathbf{f}_T = \nabla p$  exists and is equal to

$$\mathbf{f}_T = nk\nabla T + kT\nabla n. \quad (78)$$

However, because of the smallness of  $|\nabla n|$  as compared to  $n$  (e.g.,  $|\nabla n| = 10^{10}$  and  $n = 10^{20}$ ), i.e., owing to the introduced limitation related to the weak nonequilibrium state of the system, an expression is obtained for the actual thermodynamic force associated with the corresponding actual flow:

$$\mathbf{f}_T = \rho c_v \nabla T, \quad \mathbf{f}_T = nk\nabla T \quad (\mathbf{q} = -\lambda \nabla T). \quad (79)$$

The force  $\mathbf{f}_T$  induced in a solid and a gas is rather easily detected experimentally. Experiments have been carried out at the St. Petersburg Institute of Precision Mechanics and Optics (SPIPMO) in the department of physics and electrical engineering together with assistant professor N. N. Gubanov. The author thanks him for help and fruitful discussions. The experiments were recorded on a video cassette in 1997 and are available at the department of physics at the SPIPMO.

## NOTATION

$T$ , absolute temperature;  $\lambda$ , thermal-conductivity coefficient;  $c_v$ , specific heat;  $\rho$ , density of the substance;  $k$ , Boltzmann constant;  $D(X, t)$ , volume density of internal-energy fluctuations;  $J(T)$ , internal-energy fluctuation accumulated in some interval of time;  $K = \Delta D_\tau^1$ , local dissipative cumulant (LDC) or local "instantaneous" accumulated fluctuation;  $\mathbf{f}_T$ , volume density of the ponderomotive thermodynamic force;  $U$ , density of the internal energy;  $F$ , density of the free energy;  $Z$ , statistical integral;  $Z_0$ , statistical integral for the case of an ideal gas;  $\ln Z$ , volume density of the logarithm of the statistical integral.

## REFERENCES

1. O. V. Minine, *J. Phys. A: Math. & Gen.*, **20**, 5379-5391 (1981).
2. O. V. Minin, *Zh. Fiz. Khim.*, **54**, 2003-2007 (1990).
3. B. Lavenda and C. Cardella, *J. Phys. A: Math. & Gen.*, **19**, 395-407 (1986).
4. A. I. Slutsker, A. I. Mikhailin, and I. A. Slutsker, *Usp. Fiz. Nauk*, **164**, No. 4, 357-366 (1994).
5. Y. L. Khait, *Physica*, **103A**, 1-34 (1980).
6. M. Born and E. Wolf, *Fundamentals of Optics* [Russian translation], Moscow (1973), pp. 127-130.
7. S. G. Krein (ed.), *Functional Analysis* [in Russian], Moscow (1972), pp. 18-19.
8. A. V. Luikov, *Heat Conduction Theory* [in Russian], Moscow (1967), pp. 20-21.
9. P. Atkins, *Order and Disorder in Nature* [Russian translation], Moscow (1987), pp. 129-130.
10. W. M. Visscher, *Phys. Rev. B*, **10**, 2461-2472 (1974).
11. B. Lavenda and E. Santamato, *J. Stat. Phys.*, **29**, 345-361 (1982).
12. D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* [in Russian], Moscow (1974).