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# The joint analysis of general aspects of the phenomenological thermodynamics and the kinetic Boltzmann theory

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#### Abstract

The question of agreement of the kinetic moment theory with the first principle continuum thermodynamics is considered. The characteristics of distribution function describing local non-equilibrium state of monatomic gases are analyzed. In the first approach on non-equilibrium variables the equations making more exact the results of Chapman and Enskog are received. The paradox of heat conduction is eliminated and the coincidence of theoretical and experimental data on dispersion of sound speed in inert gases is improved.  $© 2002$  Elsevier Science Ltd. All rights reserved.

### 1. Introduction

The great many of the publications  $[1-7]$  is devoted to development of a locally non-equilibrium thermodynamics resulting in a hyperbolic equation of heat conduction. The new approaches are offered periodically. Some of them require revision of conventional physical concepts. For example, in last version of the extended thermodynamics of irreversible processes the concepts of production of the heat flux, of the vector flux of heat flux are entered and the balance equation of a heat flux similar to balance equations of mass, impulse and energy is postulated [3]. In the generalized Boltzmann kinetic theory [8] the equations of mass transfer, impulse and energy undergo the changes. The additional term of a non-divergent type enters in them. Thereof the mass of each material volume of the medium during non-equilibrium processes takes the variable values.

Obtained by different methods the results are the important logical step for understanding of locally nonequilibrium processes. However, despite the variety of used methods, solution of a so difficult problem is still far from the complication.

The development of the theory of locally non-equilibrium processes apart from only scientific value has large applied importance. Using the hyperbolic equation of heat conduction, it is possible to increase accuracy of calculations of supersonic flows, especially when the flow velocity is more than or equal to the speed of heat propagation. The updated relations can also benefit from the description of fast proceeding processes of combustion, when the flame spread from the initial source of reaction appreciably depends on speed of transfer of a emerging heat.

## 2. General aspects of the kinetic and phenomenological theories

The most general-purpose method permitting to receive the constitutive relations for gases at arbitrary Knudsen numbers is the method of the moments [9]. The general scheme of this method consists in the following. It is assumed that the distribution function is given by

$$
f(t, \mathbf{x}, \mathbf{C}) = F[\mathbf{C}, A(t, \mathbf{x})],\tag{1}
$$

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## Nomenclature



where  $A = (A_1, A_2, \ldots)$  – set (finite or infinite) of some variables. By means of relation (1) the macroscopic characteristics of gas are expressed by functions  $A(t, x)$ . Then by the help of the Boltzmann equation the set of equations of the moments closed concerning parameters  $A(t, x)$  is derived. As a rule, the balance equations of mass, impulse and energy are included in the set of equations of moments. If it is not enough, the additional equations of the moments are taken, selection of which is arbitrary to a certain extent.

In the kinetic theory the criteria of selection of parameters  $A(t, x)$  are not elaborated yet (usually it is done because of reason of simplicity [9]). Such criteria are contained in the thermomechanics of continuums [10]. Therefore at usage of kinetic moment theory it is necessary to combine both approaches – kinetic and phenomenological.

Remark. The need of the coordination of general aspects of the kinetic and phenomenological theories are deep roots. In particular, without engaging some minimum number of *phenomenological* equations of state it is impossible to construct the contansive kinetic theory. To show it, we consider the elementary case

of spatial-uniform stationary state of rarefied gas, behavior of which is described by the Boltzmann equation

$$
J(f, f) = 0.\t\t(2)
$$

The general solution of the Eq. (2) is the function, the logarithm of which linearly depends on independent collisional invariants m,  $m\xi$ ,  $m\xi^2/2$  [11,12]

$$
\ln f(\xi) = m\gamma_1 + m\xi \cdot \gamma_2 - m\xi^2 \gamma_3/2. \tag{3}
$$

Here  $\gamma_1$ ,  $\gamma_3$  are some positive numbers, and  $\gamma_2$  is a fixed vector. To find values of given variables, there is not enough of determination of densities, barycentric velocity, specific internal energy per unit mass, stress tensor and velocity of heat conduction

$$
\rho \equiv \int mf \, d\xi, \quad \mathbf{v} \equiv \rho^{-1} \int m\xi f \, d\xi,
$$
  

$$
u \equiv (2\rho)^{-1} \int m(\xi - \mathbf{v})^2 f \, d\xi,
$$
  

$$
T \equiv -\int mCCf \, d\xi, \quad C \equiv \xi - \mathbf{v}.
$$
 (4)

The phenomenological equations of state for equilibrium gas are necessary:  $1$ 

$$
T = -pI, \quad p = \rho R\theta, u = u(\theta), \quad du = c d\theta.
$$
 (5)

Due to these equations it is possible to establish that by the help of the Boltzmann kinetic equation it is possible to describe flow of monatomic gases only, at equilibrium of which the absolute temperature has the following molecular-kinetic sense:

$$
\theta = (3R\rho)^{-1} \int mC^2 f(\xi) d\xi.
$$

And only after that the equilibrium distribution function (3) receives the traditional view of the Maxwellian distribution function

$$
f_0 = (\rho/m)(2\pi R\theta)^{-3/2} \exp[-C^2/(2R\theta)].
$$
 (6)

## 2.1. Structure of the distribution function

In the continuum mechanics the thermodynamic state is identified with some set of parameters, which are convenient for dividing by two parts: thermodynamic variables  $z$  and non-equilibrium variables  $\chi$  (the thermodynamic variables characterize the condition of gas at equilibrium). Each function of a thermodynamic state depends on t and x by parameters z and  $\chi$ . In particular, for the stress tensor we have

$$
T(t, x) = T[z(t, x), \chi(t, x)].
$$
\n(7)

In the Boltzmann kinetic theory the stress tensor is determined as

$$
T(t, x) = -\int mCCf(t, x, C) dC.
$$
 (8)

Having compared expressions  $(1)$ ,  $(7)$ ,  $(8)$ , we come to conclusion that it is necessary to take thermodynamic and non-equilibrium variables as independent parameters  $A(t, x)$ :

$$
f(t, \mathbf{x}, \mathbf{C}) = F[\mathbf{C}, z(t, \mathbf{x}), \chi(t, \mathbf{x})]. \tag{9}
$$

By the principle of material frame indifference if in one reference frame is

$$
T = \Im(z, \chi), \tag{10}
$$

then in any other reference frame is

$$
T^* = \mathfrak{I}(z^*, \chi^*). \tag{11}
$$

The replacement of frame is described by the equations

$$
\boldsymbol{T}^* = \boldsymbol{Q}(t) \cdot \boldsymbol{T} \cdot \boldsymbol{Q}^T(t), \quad \boldsymbol{C}^* = \boldsymbol{Q}(t) \cdot \boldsymbol{C}.
$$
 (12)

From Eqs. (8) and (12) the relation follows

$$
\int mCCf^*(t^*, \mathbf{x}^*, \mathbf{C}^*) d\mathbf{C} = \int mCCf(t, \mathbf{x}, \mathbf{C}) d\mathbf{C}.
$$
 (13)

The analysis of equalities  $(9)$ – $(13)$  results in a conclusion that

$$
F(\mathbf{C}^*, \mathbf{z}^*, \chi^*) = F(\mathbf{C}, \mathbf{z}, \chi). \tag{14}
$$

Differently, at replacement of a frame the distribution function should save not only numerical value, but also form of function relation from arguments  $C$ , z and  $\gamma$ .

#### 2.2. State parameters of non-equilibrium gas

The comprehensive information about state of the medium is yielded by the principle of determinism. According to this principle the value of any physical quantity  $H$ , describing the properties of the given point of the medium  $X$  in the given instant  $t$ , can be calculated, if the law of motion of the medium  $x(\tau, Y)$  and law of change of temperature  $\theta(\tau, Y)$  are known in all points Y in all prior instants  $\tau \leq t$ 

$$
H(t, X) = \prod_{\tau = -\infty}^{\tau = t} \frac{\left[x(\tau, Y), \theta(\tau, Y)\right]}{\forall Y}.
$$
 (15)

The main difficulty in application of the principle of determinism is included in its generality. Even the monatomic gases in different conditions show different properties. Generally speaking, the exact state equations should have a rather complex structure.

In a modern thermodynamics the greatest expansion has received the supposition that the condition of each point of the medium in the given instant is quite determined by parameters, the values of which are taken in the same point and in the same instant. The number of such parameters is generally indefinite. However at the description of the outlined group of physical phenomena it is possible to limit the number of state parameters by finite value ensuring the acceptable conformity of the computational and empirical data.

We expand the law of motion  $x(\tau, Y)$  and law of change of temperature  $\theta(\tau, Y)$  in the Taylor series on power  $(\tau - t)$ ,  $(Y - X)$  and keep the linear members, for which the required balance equations are the differential not above the second-order equations. Additionally we

<sup>&</sup>lt;sup>1</sup> On the basis of physical sense of the distribution function the strict definition can be given for density only. For the remained values it is necessary to use the additional heuristic reasons (for example, to compare the phenomenological balance equations of mass, impulse and energy with equations which are obtained from the kinetic equation by multiplication of the independent collisional invariants and the following integration over the space of velocity). But the concept of barycentric velocity is not such obvious. Sometimes the value v is defined taking into account the effect of self-diffusion [13–15]. Landau supposes that such step is logically acceptable, but inexpedient from the physical point of view, because in this case barycentric velocity is not coinciding with the impulse of mass unit [16].

take into account an isotropy and invariance of properties of gases at quasi-static isochoric–isothermal shearing strains. Omitting the bulky calculations, we will give only the final result

$$
T = T(\rho, \theta, \dot{\theta}, \nabla \theta, D).
$$

The similar expressions take place for vector of the heat flux and the internal energy.

Thus, in the considered approximation the nonequilibrium gas state is described by parameters

$$
\mathbf{z} = (\rho, \theta), \quad \chi = (\dot{\theta}, \nabla \theta, \mathbf{D}), \tag{16}
$$

which differ from the state parameters of classical hydrogasdynamics by presence of the total time derivative of absolute temperature  $\dot{\theta}$ .

#### 3. Hydrodynamic equations

Let us proceed from the Boltzmann equation

$$
\frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \cdot \xi + \frac{\partial f}{\partial \xi} \cdot \boldsymbol{b} = J(f, f). \tag{17}
$$

The function (9) is decomposed to components:

$$
f = f_z(\mathbf{C}, z) + f_\chi(\mathbf{C}, z, \chi), \tag{18}
$$

$$
f_z(\mathbf{C}, z) \equiv F(\mathbf{C}, z, \chi = 0), \tag{19}
$$

$$
f_{\chi}(\mathbf{C}, \mathbf{z}, \chi) \equiv F(\mathbf{C}, \mathbf{z}, \chi) - F(\mathbf{C}, \mathbf{z}, \chi = 0). \tag{20}
$$

The component (19) depends on velocities of particles and thermodynamic variables. The component (20) besides depends on non-equilibrium variables. Therefore,  $f_z$  is locally equilibrium part and  $f_\chi$  is the locally nonequilibrium part of the distribution function. It is understandable that in the equilibrium conditions

$$
f_{\chi}(\mathbf{C}, \mathbf{z}, \chi = 0) = 0. \tag{21}
$$

The decomposition (18) results in decomposition of the stress tensor (8) by components:

$$
T(z, \chi) = T_z(z) + T_\chi(z, \chi),
$$
  
\n
$$
T_z(z) \equiv -\int mCCf_z dC,
$$
\n(22)

$$
T_{\chi}(z,\chi) \equiv -\int mCC f_{\chi} dC. \qquad (23)
$$

For specific internal energy

$$
u \equiv 0.5\rho^{-1} \int mC^2 f \,dC \tag{24}
$$

the similar decomposition takes place

$$
u(z, \chi) = u_z(z) + u_\chi(z, \chi), \qquad (25)
$$

$$
u_z(z) \equiv 0.5\rho^{-1} \int mC^2 f_z dC, \qquad (26)
$$

$$
u_{\chi}(z,\chi) \equiv 0.5\rho^{-1} \int mC^2 f_{\chi} dC.
$$
 (27)

The explicit view of a function  $f_z(\mathbf{C}, z)$  can be established if to consider the spatial-uniform stationary state of gas. In this case the Eq. (17) by virtue of a condition (21) accepts the view  $J(f_z, f_z) = 0$ . Therefore  $f_z$ coincides with the Maxwellian distribution function (6). Proceeding from definitions (4), (22), (26) by the help of relations (6), (18) and phenomenological relations (5) we receive

$$
\rho = \int mf_z dC, \quad \int mf_x dC = 0, \quad \int mC f_x dC = 0,
$$
  

$$
T_z = -p_z I, \quad p_z = \rho R\theta, \quad u_z = 3R\theta/2.
$$
 (28)

Therefore, the absolute temperature and the thermodynamic pressure should be determined by the formulas

$$
3R\theta/2 = 0.5\rho^{-1} \int mC^2 f_z dC,
$$
  
\n
$$
p_z = \int mC^2 f_z dC/3.
$$
\n(29)

The difference of these formulas from the traditionally postulated relations consists of the fact that the integrands in expressions (29) contain not the full distribution function, they contain its locally equilibrium component. Therefore the total pressure  $p \equiv -\text{tr}T/3$  differs from thermodynamic pressure  $p_z$  by the locally nonequilibrium component-dynamic pressure  $p_1 = p - p_2 =$  $-\text{tr}T_{\gamma}/3$ . Due to expressions (8) and (24) it is possible to receive relation  $p = 2\rho u/3$ , which links the total pressure to the internal energy. The similar relation takes place for the components:  $p_z = 2\rho u_z/3$ ,  $p_\chi = 2\rho u_\chi/3$ .

Without indicating the reasons the supposition is usually done that the locally non-equilibrium component of internal energy is identically equal to zero. For example, in the monograph [11] it is marked: ''Certainly, the other choice of such conditions is admitted also, but the considered choice results in more suitable form of the theory''. However, as shown in the work [5], the value  $u<sub>x</sub>$  significantly influences the symmetry of the law of conservation and transformation of energy. Therefore the question about its existence is open. For example, in the Boltzmann theory the internal energy is determined only by the kinetic energy of the heat motion of particles. However it at all does not mean that the potential energy of interaction of particles is identically equal to zero. At certain conditions (dense gases) the potential energy ceases to be negligibly small. Also in the course of fast proceeding processes (for example, at propagation of ultrasonic oscillations) the locally equilibrium and locally non-equilibrium components of internal energy become commensurable by value.

3.1. First approximation of the locally non-equilibrium component of the distribution function

The locally non-equilibrium component of the distribution function may be presented as

$$
f_{\chi}=f_0(\boldsymbol{C},z)\phi(\boldsymbol{C},z,\chi).
$$

 $V = (V \t V)$ 

By virtue of equalities (6) and (14) it is possible to apply the theorem for scalar-valued isotropic functions [17] to the function  $\phi$ . Having entered the denotations

$$
X_1 = (A_1, \ldots, A_{12}),
$$
  
\n
$$
X_1 = \dot{\theta}, \quad X_2 = \nabla \theta \cdot \mathbf{C}, \quad X_3 = \mathbf{tr} \mathbf{D},
$$
  
\n
$$
X_4 = \mathbf{C} \cdot \mathbf{D} \cdot \mathbf{C}, \quad X_5 = \mathbf{C}^2, \quad X_6 = \nabla \theta^2,
$$
  
\n
$$
X_7 = \mathbf{tr} \mathbf{D}^2, \quad X_8 = \mathbf{tr} \mathbf{D}^3, \quad X_9 = \mathbf{C} \cdot \mathbf{D}^2 \cdot \mathbf{C},
$$
  
\n
$$
X_{10} = \nabla \theta \cdot \mathbf{D} \cdot \nabla \theta, \quad X_{11} = \nabla \theta \cdot \mathbf{D}^2 \cdot \nabla \theta,
$$
  
\n
$$
X_{12} = \nabla \theta \cdot \mathbf{D} \cdot \mathbf{C},
$$

let us have

$$
\phi = \phi[z, X(C, \chi)].
$$

As a first approximation on non-equilibrium variables  $\chi$ we discover

$$
\phi \cong \left[ \left( \frac{\partial \phi}{\partial X} \right) \cdot \left( \frac{\partial X}{\partial \chi} \right) \right]_{\chi=0} \cdot \chi.
$$

Having calculated the appropriate derivative, we receive

$$
f_{\chi} = f_0[\Phi_1 \dot{\theta} + \Phi_2 \mathbf{C} \cdot \nabla \theta + \Phi_3 tr \mathbf{D} + \Phi_4 (\mathbf{C} \mathbf{C}) : \mathbf{D}], \qquad (30)
$$

where  $(i = 1, 2, 3, 4)$ 

$$
\Phi_i(\rho, \theta, \mathbf{C}^2) = [\partial \phi / \partial X_i]_{\chi=0}.
$$
\n(31)

It is easy to notice that the expression (30) contains, as particular case, first approximation of Chapman– Enskog [11]. To find the relation (31) in the explicit view it is possible, for example, properly to modify the Chapman–Enskog method or to take advantage of the variational Tamm's method [9]. However, to receive closed system of the macroscopic equations, it is enough to know that the values  $\Phi_i$  are even functions of the components of vector C.

## 3.2. Constitutive relations

Proceeding from relations (6) and (30), we calculate values (23) and (27) and vector of the heat flux

$$
q \equiv 0.5 \int mC^2 C f \, dC.
$$

In view of the fact that tr $\mathbf{D} = \nabla \cdot \mathbf{v} = -\dot{\rho}/\rho$ , we receive

$$
u_{\chi} = \alpha_{\theta}(\rho, \theta)\dot{\theta} + \alpha_{\rho}(\rho, \theta)\dot{\rho}, \quad \mathbf{q} = -\lambda(\rho, \theta)\nabla\theta,
$$
  

$$
\boldsymbol{T}_{\chi} = -(2\rho/3)\Big\{\alpha_{\theta}(\rho, \theta)\dot{\theta} + [\alpha_{\rho}(\rho, \theta) - \mu(\rho, \theta)/\rho^2]\dot{\rho}\Big\}\boldsymbol{I}
$$
  

$$
+ 2\mu(\rho, \theta)\boldsymbol{D}.
$$
 (32)

For the description of the evolution of parameters (16) there are enough of the balance equations of mass, impulse and energy which by the usual manner are concluded from the Eq. (17).

As at  $\dot{\theta} = 0$  the distribution function (30) becomes the first approximation of Chapman–Enskog, and the included in the constitutive relations (32) coefficients  $\alpha_{\theta}$ ,  $\alpha_q$ ,  $\lambda$ ,  $\mu$  depend only on density and temperature, it is possible to take advantage of the known results of Chapman–Enskog [11]

$$
\zeta \equiv 2\rho^2 \alpha_\rho/3 = 0, \quad \lambda = 15R\mu/4. \tag{33}
$$

Theoretically coefficient  $\alpha_{\theta}$  can be defined after the laborious calculations grounded on the appropriate modification of the Chapman–Enskog method. It is possible to act easier and to estimate value of a coefficient  $\alpha_{\theta}$  by direct comparison theoretical and empiric data about the dispersion of the sound speed in inert gases.

#### 3.3. Matching with experiment

One of the tasks, the solution of which directly is connected to the paradox of heat conduction, is the task about the dispersion of the acoustic waves. Having entered the dimensionless values

$$
\bar{k} = ka_0/\omega, \quad \bar{\omega} = 3\mu\omega/(5p_z), \quad \bar{\alpha}_\theta = 20\alpha_\theta p_z/(9R\mu)
$$

and having taken into account relations (33), it is easy to deduce by the standard method [7] the dimensionless dispersion relation

$$
\begin{aligned} & [10/3 - 3\mathrm{i}/(2\bar{\omega})]\bar{k}^4 + \left[\bar{\omega}^{-2} - 2\bar{\alpha}_\theta/3 \\& + \mathrm{i}(23/6 + \bar{\alpha}_\theta/2)\bar{\omega}^{-1}\right]\bar{k}^2 - \left[\bar{\omega}^{-2} + \mathrm{i}\bar{\alpha}_\theta/(2\bar{\omega})\right] = 0 \end{aligned}
$$

and then by the empiric data of Meyer and Sesler<sup>2</sup> to find the value  $\bar{\alpha}_\theta = 5/4$ . As result for inert gases the following value of the thermal constitutive coefficient is received:

$$
\alpha_{\theta} = 9\mu/(16\rho\theta). \tag{34}
$$

The classical ( $\bar{\alpha}_{\theta} = 0$ ) and updated ( $\bar{\alpha}_{\theta} = 5/4$ ) theoretical curves are shown in Fig. 1. As we see, at low frequencies  $\bar{\omega}$  both the theoretical curves are practically merging. The difference appears at  $\bar{\omega} \rightarrow \infty$ : according to the classic theory the phase speed  $\bar{a}$  tends to infinity, whereas according to the updated data the phase speed is finite.

<sup>&</sup>lt;sup>2</sup> According to the experience for  $\bar{\omega} \rightarrow \infty$  the  $\bar{a} = 2$  equality is to be carried out, where  $\bar{a} = a/a_0$ ,  $a = \omega/\text{Re } k$  and  $a_0 =$  $\sqrt{5R\theta/3}$  [18,19].



Fig. 1. The dependence of the phase sound speed on the dimensionless frequency: (1) classic curve; (2) updated curve;  $\phi$ empiric data for inert gases [12].

The updated constitutive relations (32) result in the following heat conduction equation for the fixed medium:

$$
\rho \alpha_{\theta} \partial^2 \theta / \partial t^2 + \rho c \partial \theta / \partial t = \lambda \nabla^2 \theta + \nabla \lambda \cdot \nabla \theta - \rho (\partial \alpha_{\theta} / \partial t)
$$
  
 
$$
\times (\partial \theta / \partial t),
$$

which is received from the equation of the internal energy transfer. It allows by the help of expression (34) to find the speed of heat propagation in the inert gases:

$$
w=\sqrt{\lambda/(\rho\alpha_{\theta})}=2a_0.
$$

As we see, in the inert gases the speed of heat propagation is twice more than adiabatic sound speed.

# 4. Conclusion

The joint analysis of the general aspects of the kinetic and phenomenological theories shows that at application of the moments method the dependence of the distribution function on time and coordinates should be implemented by the state parameters of non-equilibrium gas. At replacement of the reference system the distribution function saves not only the numerical value, but also form of the functional dependence on its arguments. If to outline the set of simplifying operations resulting in the Navier–Stokes–Fourier equations, it is found that the total time derivative of absolute temperature must be certainly entered to the number of state parameters. In view of it for the distribution function the expression which as the first approximation by nonequilibrium variables updates the Chapman and Enskog result is received. The updated equations allow us to overcome the paradox of head conduction.

The existence of the locally non-equilibrium component of the internal energy is confirmed by the empiric data about the dispersion of the sound speed. The obtained results agree with the researches of Green and Lindsay (in detail see, for instance, [6]), Zarubin and Kuvyrkin [4], in which the concept of thermodynamic temperature  $\Theta$  as function depended on absolute temperature  $\theta$  and its change speed  $\dot{\theta}$  are entered. If the thermodynamic temperature was defined by the equation  $3R\Theta/2 = u$ , by the expressions (25), (28), (32), (33) as basis we receive

$$
\Theta = \theta + 2\alpha_\theta \dot{\theta}/(3R).
$$

In the spatially uniform non-stationary conditions the thermodynamic temperature of the isolated volume of gas remains constant, and absolute temperature changes according to the exponential law, relaxing to the equilibrium value  $\theta = \Theta$ .

We mark that in the phenomenological thermodynamics the absolute temperature is considered as the extent of heat content and is entered in the determinism principle (15) as primary concept. As the difference of the extent of heat content is inherent in points of the medium in any non-equilibrium condition, the fact of the existence of absolute temperature is not subject to doubt.

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