REVIEWS OF TOPICAL PROBLEMS

Non-equilibrium thermodynamics and kinetic theory of rarefied gases

V M Zhdanov, V I Roldughin

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Abstract. **The relation between the non-equilibrium thermodynamics and kinetic theory of rarefied gases is discussed. The phenomenological equations of generalized non-equilibrium thermodynamics are formulated using the fundamental relations of kinetic theory. Using the approach developed, the non-equilibrium thermodynamics of a multicomponent gas mixture are formulated for the moment method and Burnett approximation and the boundary conditions including the slip and jump effects are derived for slightly rarefied gases. An application to transport processes in discontinuous systems and gas flows over solid bodies is also made.**

1. Introduction

Non-equilibrium thermodynamics (NT) and kinetic theory (KT) represent two closely related approaches to the description of non-equilibrium processes in real physical media. It is known that NT, being a phenomenological theory, is only

V M Zhdanov Moscow Engineering Physics Institute, Kashirskoe shosse 31, 115409 Moscow, Russia
Tel. (7-095) 323 90 38
V I Roldughin Institute for Physical Chemistry, Russian Academy of Sciences, Leninskiĭ prosp. 31, 117915 Moscow, Russia
Tel. (7-095) 955 46 47
E-mail: roldughin@lmm.phyche.msk.su

capable of establishing the general structure of equations which describe non-equilibrium phenomena, as well as a certain linkage (symmetry relations) between the kinetic coefficients in these equations. The direct calculation of the kinetic coefficients, based on a suitable model of interactions between the particles of the medium, is the province of KT. The role of KT, however, does not end there. Providing the mathematical apparatus for calculating the coefficients of transport and relaxation, the KT developed, for example, for rarefied gases, enables one to gauge the applicability of methods of NT for arbitrary physical media. An especially gratifying object of study in this respect is a rarefied gas which satisfies the condition $l \ll L$ (where l is the mean free path of the particles, and L is the characteristic scale of the problem), for which the well developed solution methods for the kinetic Boltzmann equation (Chapman – Enskog's (ChE) method [1], Grad's method [2]) have provided the basis for verification of both the classical form of NT [3] and its various generalizations [4 – 9].

For a long time, the formal limits on the generalization of NT were those defined in Refs [10, 11], which, on the one hand, proved that the phenomenological expressions for entropy flux and entropy production only coincide with their kinetic counterparts in the first (linear) approximation in the ChE theory, and, on the other hand, proved that the Burnett equations answering the next approximation are incompatible with the conventional form of the Onsager symmetry relations. Strictly speaking, these arguments related to the classical formulation of NT, in which the local entropy of the system only depends on the conventional

thermodynamic variables: density, internal energy (or temperature), and concentration of the components (in the case of a mixture).

At the same time, even Grad on the basis of his method of moments [1, 12] pointed out the workability of the NT methods in a more general situation, when the non-equilibrium state of the gas (and the non-equilibrium entropy) are determined not only by the local values of the thermodynamic variables mentioned above, but also by an arbitrary number of additional variables of state [the moments of the distribution function (DF)]. The same conclusion followed from Refs [13, 14], based on the solution of the linearized Boltzmann equation using the expansion of the DF of particles with respect to velocities over the set of eigenfunctions of the linearized collisions operator [15, 16]. In the latter case it is easy to justify the unification of the Onsager – Casimir phenomenological theories [17, 18] with the kinetic description (see Ref. [19]).

For the first time the idea of such a generalization of NT was put forward in Ref. [20] (Yu Kagan), when the set of independent thermodynamic forces should include not only the terms proportional to the first derivatives of the thermodynamic parameters and velocity (as in the classical formulation of NT [3]), but also the quantities of the appropriate tensor dimension proportional to the derivatives of the fluxes, or, which is the same, to the second derivatives of the initial parameters. This conclusion followed, in particular, from the analysis of the contribution of the viscous transfer of momentum to the rate of diffusion of the mixture, which was calculated in Ref. [20] on the basis of the 13-moment Grad's approximation. This idea was further developed in Refs [21 – 27], which proved the compatibility of the principles of NT with the results obtained using the higher approximations of the ChE method at the level of the linearized Burnett approximation [22 – 26], as well as the linearized Grad's moment equations [7, 27]. Then the expression for entropy production on the right-hand side of the equation of balance of entropy involves additional terms which contain the higher derivatives of the main thermodynamic variables and velocity with respect to coordinates. The set of phenomenological equations in fluxes and forces is extended accordingly [22 – 24, 26].

The so-called extended irreversible thermodynamics (EIT) has been developing independently since it was started in Refs [4, 6]. It also starts with Grad's moment equations [2], but in the non-stationary formulation. Since the relaxation time (the mean time between collisions of the molecules) is usually small, the gas rapidly tends towards the quasi-equilibrium state. In certain situations, however, the characteristic time scale of the problem is comparable with the relaxation time, and this is the specialty of EIT. Still, the basic ideology of EIT remains the same: the expressions for entropy, entropy flux and entropy production are generalized to include additional independent variables of state, which are usually represented by the real physical fluxes: the heat flux and the tensor of viscous stress [4, 7].

In connection with the advances in the statistical theory of open systems, an alternative approach in the KT is being developed, based on the generalized kinetic equation [28 – 30]. Along with the conventional Boltzmann collisions integral, this equation involves an additional dissipative term which accounts for the spatial redistribution of particles and describes the mixing of particles in the phase space. This approach is employed for expressing the set of gas-dynamic equations, which formally does not require the perturbation theory in Knudsen number, because the dissipative terms in these equations arise in association with a rather limited class of DF isotropic with respect to the relative velocity of particles (to which the local Maxwell distribution also belongs). The expressions for entropy flux and entropy production for such a gas also take on a special form. We shall briefly touch upon the implications of this approach as compared with the classical results in Section 2.8.

The methods of NT find many applications in the studies of transport processes in specific media (liquids, gases) in the presence of a flow-confining interfaces. This primarily concerns the so-called NT of discontinuous systems [3], which formulates the general expressions for mass and heat transfer between two volumes separated by a capillary, porous wall or membrane.

On the other hand, as demonstrated for the first time by Waldmann [21, 31 – 33], the methods of NT can be effectively used for analyzing the state of gas near an interface. In both cases the approaches of NT and KT are closely intertwined. For example, formulation of the boundary conditions at the level of the DF, and the use of the kinetic expression for entropy which takes into account the finite thickness of Knudsen layer near the interface [34 – 36] allow one to determine the limits of applicability of Waldmann's phenomenological concepts of boundary-layer entropy production and the equations of balance at the interface. Then the expression for entropy production includes a number of new terms to account for the fluxes of mass and heat localized in the Knudsen layer, and the set of phenomenological equations which link different flows with the relevant thermodynamic forces is extended accordingly [26, 34, 35].

The organic combination of the methods of NT and the results of the rigorous KT in the study of flows of rarefied gases allows not only the explanation of known physical effects but also the prediction of new ones. It will be appropriate to emphasize here that most of these effects cannot be described by straightforward physically plausible reasoning which is often used in the elementary KT. One might agree with the remark made by Kramers [37], who referred to "... those unimprovable speculations of which the kinetic theory of gases affords such ghastly examples".

It is known, for instance, that the Burnett terms in the hydrodynamic equations correspond, as a rule, to corrections of the next order (compared to the first) in Knudsen number ($Kn = l/L$). It is therefore contrary to expectation that the expression for heat flux (for slow gas flows) should involve, along with the conventional term dependent on the temperature gradient, a term proportional to the gradient of pressure which is of the same order as the principal term. An even more surprising consequence of the inclusion of Burnett contributions is the redefinition of the constant of pressure diffusion in the expression for the diffusion flux, which becomes an essentially kinetic quantity [20]. Observe that these results fit naturally into the scheme of generalized NT considered in this review.

Broad opportunities for describing new effects arise in the study of boundary effects in rarefied gases. The inclusion of viscous, thermal and diffusion slipping and the temperature jump on a solid wall has long been known to result in effects of the first order in Knudsen number [34, 36]. The development

of NT of boundary conditions together with the kinetic methods of solution of boundary problems allows a consistent treatment to be given to a number of phenomena observed when a gas flows in channels or around bodies. It is interesting, for example, that the inclusion of Burnett contributions and boundary slipping corrections leads to credible results describing the so-called thermal transpiration of gas in a channel and the associated thermomechanical effect both in the first and in the next order in Knudsen number (slipping effect of the second order). The same applies to such associated effects as diffusion slipping and pressure diffusion of a gas mixture in a channel.

The extended sets of phenomenological equations, which follow from the expression for boundary entropy production, point to the existence of a number of unusual effects — for example, the non-equilibrium surface tension on the impenetrable gas – solid interface, or the inverted temperature profile in the vapor phase between two liquid surfaces. Onsager's reciprocal relations play an important role in the description of new phenomena: they have made it possible to predict the effects of thermal and diffusion polarization of bodies in a homogeneous gas flow, which are reciprocal to the known phenomena of thermophoresis and diffusiophoresis.

Unfortunately, the limited scope of the review has forced us to leave out a whole class of phenomena the analysis of which calls for simultaneous use of the methods of NT and KT. We are referring to the experimentally observed effects for molecular gases in a magnetic field (thermomagnetic rotation of a cylinder in a non-uniformly heated gas — the Scott effect, viscomagnetic thermal and diffusion flows in a flat channel, thermomagnetic creep and thermomagnetic pressure drop). Similarly to the effects mentioned earlier, the theoretical treatment of these phenomena requires, as a rule, simultaneous inclusion of both the Burnett contributions and the boundary corrections. The interested reader may refer to the recently published monograph [38].

These examples seem to prove the importance of generalization of NT and its application jointly with KT to the solution of particular problems. The purpose of this review is to outline the contemporary state of the problem. The kinetic aspect of the theory is based on the linearized Boltzmann kinetic equation, which excludes a number of nonlinear effects [39, 40] but is sufficient for the description of a quite broad scope of phenomena. The results obtained through this approach apply not only to rarefied gases, but also to the kinetics of electrons and ions in plasmas, electrons and phonons in solids. This extends the possible applications of NT methods to different physical media. Note that here we but briefly touch upon the problems of EIT, and do not discuss the attempts at nonlinear generalizations of NT. The reader will find relevant information in the reviews and books [5, 7 – 9].

2. Generalized non-equilibrium thermodynamics

2.1 Kinetic theory and the Onsager principle

Let us recall certain principles of NT in the Onsager formulation [17]. As we know, the Onsager principle postulates linear relaxation of the mean values of extensive thermodynamic variables to their respective equilibrium values. Denoting the deviations of these quantities from their equilibrium values by a_i, we describe the time evolution

of a_i by linear phenomenological equations [3]:

$$\frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_k L_{ik} X_k \,, \tag{2.1}$$

where $J_i = \mathrm{d}a_i/\mathrm{d}t$ is the mean thermodynamic flux, X_i is the thermodynamic force, and the kinetic coefficients L_{ik} satisfy Onsager's reciprocal relations ($L_{ik} = L_{ki}$).

For a system not far from equilibrium, the expression for the deviation ΔS of entropy from its equilibrium value may be represented as a quadratic form with respect to the variables of state:

$$\Delta S = -\frac{1}{2} \sum_i \sum_k g_{ik} a_i a_k \,, \tag{2.2}$$

where g_{ik} is a positive semi-definite matrix of second derivatives. The Onsager's reciprocal relations hold if the thermodynamic forces are defined as [3]

$$X_i = \frac{\partial \Delta S}{\partial a_i} = -\sum_k g_{ik} a_k \,. \tag{2.3}$$

Now expressions $(2.1)-(2.3)$ ignore the fact that the variables of state may be even or odd functions of the velocities of particles. To take this into account, one must introduce two types of variables of state, a_i and b_i, and formulate the generalized Onsager principle in the form [3]

$$\frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_k L_{ik}^{aa} X_k + \sum_k L_{ik}^{ab} Y_k \,,$$

$$\frac{\mathrm{d}b_i}{\mathrm{d}t} = \sum_k L_{ik}^{ba} X_k + \sum_k L_{ik}^{bb} Y_k \,. \tag{2.4}$$

(The corresponding generalized expressions for ΔS and the thermodynamic forces X_i and Y_i are introduced in an obvious way [3].)

The Onsager – Casimir reciprocal relations [17, 18] are then written in the form

$$L_{ik}^{aa} = L_{ki}^{aa} \,, \qquad L_{ik}^{bb} = L_{ki}^{bb} \,, \qquad L_{ik}^{ab} = -L_{ki}^{ba} \,, \tag{2.5}$$

that is, the cross-coefficients are antisymmetrical.

Observe that the time derivative of entropy (2.2) (entropy production) can be represented as

$$\frac{\mathrm{d}\Delta S}{\mathrm{d}t} = -\sum_i \sum_k g_{ik} a_k \frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_i J_i X_i \,, \tag{2.6}$$

and is thus described by a bilinear expression with respect to fluxes and thermodynamic forces which enter the phenomenological equations complying with the Onsager relations (generalization for the case of two types of variables is straightforward).

So, the calculation of entropy production gives the guidelines for the correct calculation of fluxes and the associated thermodynamic forces. Using Eqn (2.1), expression (2.6) can be rewritten as

$$\frac{\mathrm{d}\Delta S}{\mathrm{d}t} = \sum_i \sum_k L_{ik} X_i X_k \geqslant 0 \,, \tag{2.7}$$

where the last inequality actually expresses the second law of thermodynamics for isolated systems. L is a positive definite matrix.

Now let us turn to the kinetic treatment. We assume that the state of the rarefied gas (monatomic for the sake of simplicity) does not deviate far from equilibrium, and so may be described by the DF

$$f = f_0(1 + \phi), \quad f_0 = n_0 \left(\frac{\beta_0}{\pi}\right)^{3/2} \exp(-\beta_0 v^2), \qquad (2.8)$$

where f_0 is the absolute Maxwell distribution of molecules with respect to velocities and ϕ is a small correction ($|\phi| \ll 1$); $\beta_0 = m/2kT_0$; the density n_0 and the temperature T_0 are constant. The correction $\phi(\mathbf{v}, \mathbf{r}, t)$ satisfies the linearized kinetic Boltzmann equation, which in the absence of external forces has the form [39, 40]

$$\frac{\partial \phi}{\partial t} + (\mathbf{v}\nabla_r)\phi = L(\phi),$$

$$L(\phi) = \int (\phi' + \phi_1' - \phi - \phi_1) f_{01} g \sigma(g, \Omega) \, d\Omega \, d\mathbf{v}_1. \qquad (2.9)$$

It will be useful to define the scalar product of functions in Hilbert space as

$$(g, h) = \frac{1}{n_0} \int f_0(\mathbf{v}) g(\mathbf{v}) h(\mathbf{v}) \, d\mathbf{v}. \qquad (2.10)$$

It is easy to show that the following symmetry relation holds for the linearized collisions operator L [40]:

$$(\psi, L\phi) = (L\psi, \phi), \qquad (2.11)$$

which is closely connected with the symmetry of the kernel of collisions operator $K(\mathbf{v}, \mathbf{v}')$. The latter is defined in such a way that [13]

$$-\int K(\mathbf{v}, \mathbf{v}') f_0(\mathbf{v}') \phi(\mathbf{v}') \, d\mathbf{v}' = L(\phi). \qquad (2.12)$$

Another known property of operator L is expressed by the condition [39, 40]

$$(\phi, L\phi) \leqslant 0. \qquad (2.13)$$

The equality sign corresponds to the situation when ϕ is the invariant of collisions. Then the invariants of collisions (mass, momentum, energy of the particles) or linear combinations of them are eigenfunctions of the collisions operator L, corresponding to the eigenvalue $\lambda = 0$; all the rest of the eigenvalues, if they exist, must be negative by virtue of (2.13).

As we know, the entropy of a slightly non-equilibrium gas is given by Ref. [41]

$$S(t) = \int s(\mathbf{r}, t) \, d\mathbf{r} = -k \iint f \ln(f) \, d\mathbf{v} \, d\mathbf{r} + NK, \qquad (2.14)$$

where K is a constant and N is the number of particles in the system.

Since the entropy is at maximum at the state of equilibrium, the deviation of entropy from its equilibrium value S_0 to the second order in ϕ can be represented as (the terms linear in ϕ vanish)

$$\Delta S = S(t) - S_0 = -\frac{k}{2} \iint a^2 \, d\mathbf{v} \, d\mathbf{r}, \qquad (2.15)$$

where $a = f_0^{1/2}\phi$.

The quantity $a(\mathbf{v}, r, t)$ (or ϕ) may be treated as a generalized variable of state which characterizes the deviation of the DF from equilibrium. Since this parameter is a field in the space of velocities, the conventional Onsager relations have to be modified; this procedure is, however, quite straightforward. Observe that the quantity conjugated with the perturbation a ('thermodynamic force') is defined as

$$x = \frac{\delta \Delta S}{\delta a} = -ka. \qquad (2.16)$$

Now we represent ϕ as the sum of even (ϕ_a) and odd (ϕ_b) functions with respect to the velocities of particles. Then

$$\Delta S = -\frac{k}{2} \left(\iint \phi_a^2 f_0 \, d\mathbf{v} \, d\mathbf{r} + \iint \phi_b^2 f_0 \, d\mathbf{v} \, d\mathbf{r} \right),$$

and the thermodynamic forces, associated with a_a and a_b, are

$$x_a = -ka_a, \quad x_b = -ka_b. \qquad (2.17)$$

In accordance with the Onsager – Casimir scheme [3, 19], we may write

$$\frac{\partial a_a}{\partial t} = -k\left(L^{aa}a_a + L^{ab}a_b\right),$$

$$\frac{\partial a_b}{\partial t} = -k\left(L^{ba}a_a + L^{bb}a_b\right), \qquad (2.18)$$

where the operators L^{aa} and L^{bb} must be symmetrical, and L^{ab} and L^{ba} antisymmetrical.

The NT itself does not provide any information regarding the structure of linear operators L. In the case of a rarefied gas their form is easily established using the linearized kinetic equation (2.9) and definition (2.12). As a result, we get

$$L^{aa}a_a = \iint \delta(\mathbf{r} - \mathbf{r}') K(\mathbf{v}, \mathbf{v}') f_0(\mathbf{v}') \, a_a(\mathbf{v}', \mathbf{r}') \, d\mathbf{v}' \, d\mathbf{r}',$$

$$L^{bb}a_b = \iint \delta(\mathbf{r} - \mathbf{r}') K(\mathbf{v}', \mathbf{v}) f_0(\mathbf{v}) \, a_b(\mathbf{v}, \mathbf{r}) \, d\mathbf{v} \, d\mathbf{r}. \qquad (2.19)$$

For the cross-operators L^{aa} and L^{bb} we have

$$L^{ab}a_b = \iint (\mathbf{v}\nabla_r)\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{v} - \mathbf{v}') \, a_b(\mathbf{v}') \, d\mathbf{r}' \, d\mathbf{v}',$$

$$L^{ba}a_a = \iint (\mathbf{v}'\nabla_{r'})\delta(\mathbf{r}' - \mathbf{r})\delta(\mathbf{v}' - \mathbf{v}) \, a_a(\mathbf{v}) \, d\mathbf{r} \, d\mathbf{v}. \qquad (2.20)$$

The symmetry of each of the operators L^{aa} and L^{bb} follows from the symmetry of the kernel of collisions operator $K(\mathbf{v}, \mathbf{v}')$. Operators L^{ab} and L^{ba} are antisymmetrical because their kernels are antisymmetrical

$$\mathbf{v}'\nabla_{r'}\delta(\mathbf{r}' - \mathbf{r})\delta(\mathbf{v}' - \mathbf{v}) = -\mathbf{v}\nabla_r\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{v} - \mathbf{v}').$$

The latter follows from the rule of differentiation of the δ-function: $\nabla_{r'}\delta(\mathbf{r}' - \mathbf{r}) = -\nabla_r\delta(\mathbf{r} - \mathbf{r}')$; the velocity-dependent δ-function then commutes with the differential operator.

These results unite Onsager's phenomenological theory and the kinetic description based on the linearized Boltzmann equation. Observe that this unification does not require any kind of perturbation parameter, the only assumption being that the deviation from equilibrium is small ($|\phi| \ll 1$).

2.2 Expansion in tensor polynomials. Moment equations

The linkage between the results of the kinetic treatment and the conclusions of NT becomes clearer if we use the expansion of the non-equilibrium correction to the DF over the orthogonal set of tensor polynomials in the velocity of molecules

$$\phi = \sum_{n=1}^{\infty} \mathbf{a}^{(n)}(\mathbf{r}, t) \mathbf{P}^{(n)}(\mathbf{v}) . \tag{2.21}$$

The orthogonality of polynomials $\mathbf{P}^{(n)}$ with the weight function f_0 implies that

$$\mathbf{a}^{(n)} = \frac{1}{n_0} \int \mathbf{P}^{(n)} f_0 \phi \, d\mathbf{v} = \left(\mathbf{P}^{(n)}, \phi \right) . \tag{2.22}$$

The polynomials are normalized by the condition $\left(\mathbf{P}^{(n)}, \mathbf{P}^{(n)} \right) = \delta_{nk} \Delta^{(n)}$, where $\Delta^{(n)}$ is the unit projection tensor of the appropriate rank [38] (for scalar polynomials $\Delta^{(0)} = 1$).

The parameters $\mathbf{a}^{(n)}(r, t)$ play the role of variables of state, defining the non-equilibrium state of the system. Using Eqns (2.14), (2.21), for the non-equilibrium entropy $S(t)$ we get

$$S(t) = S_0 - \frac{k}{2} \sum_{n=1}^{\infty} \int \left[\mathbf{a}^{(n)} \right]^2 d\mathbf{r} . \tag{2.23}$$

The quantities conjugated with the non-equilibrium parameters $\mathbf{a}^{(n)}$ are

$$\mathbf{b}^{(n)} = \frac{\delta \Delta S}{\delta \mathbf{a}^{(n)}} = -k \mathbf{a}^{(n)} , \tag{2.24}$$

and the corresponding set of phenomenological equations takes on the form ($R^{nk} = -k L^{nk}$):

$$\frac{\partial \mathbf{a}^{(n)}}{\partial t} = \sum_k L^{nk} \mathbf{b}^{(k)} = -\sum_k R^{nk} \mathbf{a}^{(k)} . \tag{2.25}$$

The equations for coefficients $\mathbf{a}^{(n)}$ (moment equations) can be obtained by multiplying the kinetic equation (2.9) by $f_0 \mathbf{P}^{(n)}$ with subsequent integration with respect to velocities. As a result, we get

$$\frac{\partial \mathbf{a}^{(n)}}{\partial t} + \sum_k \left(\mathbf{P}^{(n)}, \mathbf{v} \mathbf{P}^{(k)} \right) \otimes \nabla_r \mathbf{a}^{(k)} = \sum_k \left(\mathbf{P}^{(n)}, L \mathbf{P}^{(k)} \right) \otimes \mathbf{a}^{(k)} , \tag{2.26}$$

where the symbol $\otimes$ denotes the scalar product of tensors.

Juxtaposition of Eqns (2.25) and (2.26) shows that

$$R^{nk} = \left(\mathbf{P}^{(n)}, \mathbf{v} \mathbf{P}^{(k)} \right) \otimes \nabla_r - \left(\mathbf{P}^{(n)}, L \mathbf{P}^{(k)} \right) \otimes , \tag{2.27}$$

whence it follows that the Onsager – Casimir symmetry relations do hold: the antisymmetry of the first (flow) operator in Eqn (2.27) is ensured by the antisymmetry of the differential operator ∇_r, whereas the symmetry of the second operator in Eqn (2.27) is entailed by the reciprocal relation (2.11) for the linearized collisions operator.

In order to obtain more concrete results from the moment equations (2.26), one has to be more specific in the selection of tensor polynomials $\mathbf{P}^{(n)}$. It is possible, for example, to use the Hermitian tensor polynomials $\mathbf{H}^{(n)}(\mathbf{v})$, as first proposed by Grad [2, 12]. More convenient is the orthonormalized set of eigenfunctions of operator $K(\mathbf{v}, \mathbf{v}')$, which simply are con-

volutions of Hermitian polynomials [12]. Then [13]

$$K(\mathbf{v}, \mathbf{v}') = \sum_{n=1}^{\infty} \lambda_n \mathbf{P}^{(n)}(\mathbf{v}) \mathbf{P}^{(n)}(\mathbf{v}') .$$

Such a definition in polynomials is especially useful in the particular case of 'Maxwell molecules', whose potential of interaction is $U = \alpha / r^4$. Then

$$\sum_k \left(\mathbf{P}^{(n)}, L \mathbf{P}^{(k)} \right) \mathbf{a}^{(k)} = \lambda_n \mathbf{a}^{(n)} . \tag{2.28}$$

The eigenvalues λ_n are real and positive with the exception of $\lambda_0 = 0$. As noted above, the eigenvalue $\lambda_0 = 0$ corresponds to five independent eigenfunctions which are the summation invariants of collisions.

In a spherical-coordinate system, the eigenfunction is represented as the radial function of the absolute velocity multiplied by the spherical function of angular variables [15]. The use of such eigenfunctions is also justified for an arbitrary law of interaction between the molecules [12, 15]. In place of the angular part of the eigenfunctions it is then convenient to use tensor spherical harmonics of the velocity of molecules. As a result, instead of expansion (2.21) we have a two-variable series in polynomials $\mathbf{P}^{mn}(\mathbf{v})$ with two superscripts:

$$\phi = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \mathbf{a}^{mn}(\mathbf{r}, t) \mathbf{P}^{mn}(\mathbf{v}) . \tag{2.29}$$

Then $\mathbf{a}^{mn} = (\mathbf{P}^{mn}, \phi)$, and the polynomials† are [15, 38]

$$\mathbf{P}^{mn}(\mathbf{W}) = (-1)^n \left[\frac{2^{m+n} n! (2m+1)!!}{m! (2m+2n+1)!!} \right]^{1/2}$$
$$\times S_{m+1/2}^{(n)}(W^2) \mathbf{R}^{(m)}(\mathbf{W}) , \tag{2.30}$$

where $\mathbf{W} = \beta_0^{1/2} \mathbf{v}$, and $S_{m+1/2}^{(n)}(W^2)$ are Sonin's polynomials [1]; $\mathbf{R}^{(m)}(\mathbf{W})$ are tensor spherical harmonics. The first few harmonics are written as

$$R^{(0)} = 1 , \quad \mathbf{R}^{(1)} = \mathbf{W} , \quad \mathbf{R}^{(2)} = \overline{\mathbf{W} \mathbf{W}} , \quad \mathbf{R}^{(3)} = \overline{\mathbf{W} \mathbf{W} \mathbf{W}} , \tag{2.31}$$

where $\overline{aaa\ldots}$ denotes the irreducibility of the tensor — in particular,

$$R_{ik}^{(2)} = W_i W_k - \frac{1}{3} \delta_{ik} W^2 ,$$

$$R_{ikl}^{(3)} = W_i W_k W_l - \frac{1}{5} W^2 (\delta_{ik} W_l + \delta_{il} W_k + \delta_{kl} W_i) .$$

The moment equations then take the form

$$\frac{\partial \mathbf{a}^{mn}}{\partial t} + \sum_{m'n'} \left(\mathbf{P}^{mn}, \mathbf{v} \mathbf{P}^{m'n'} \right) \otimes \nabla_r \mathbf{a}^{m'n'}$$
$$= \sum_{m'n'} \left(\mathbf{P}^{mn}, L \mathbf{P}^{m'n'} \right) \otimes \mathbf{a}^{m'n'} . \tag{2.32}$$

It can be proved [38] that for symmetrical irreducible tensors $\mathbf{P}^{mn}$ the flow term on the left-hand side of Eqn (2.32) is a

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† These polynomials up to the normalization coefficient coincide with the irreducible tensor Hermitian polynomials $\mathbf{H}^{mn}(\mathbf{v})$, which are also used in Grad's method of moments [42].

linear combination of derivatives with respect to the coordinates of the coefficients of tensor rank $m + 1$ and $m - 1$.

The right-hand sides of Eqns (2.32) (except the first five which are zero) can be expressed in terms of the so-called 'integral brackets' Λ_{mnk} of the polynomials $\mathbf{P}^{mn}$ [38]. Then equations (2.32) are represented as

$$\frac{\partial \mathbf{a}^{mn}}{\partial t} + \sum_{k=0}^{\infty} \left(\mathbf{A}_{mn}^{m+1,k} \nabla_r \mathbf{a}^{m+1,k} + \mathbf{B}_{mn}^{m-1,k} \overline{\nabla_r \mathbf{a}}^{m-1,k} \right)$$
$$= -\sum_k n_0 \Lambda_{mnk} \mathbf{a}^{mn}, \qquad (2.33)$$

where the operators $\mathbf{A}$ and $\mathbf{B}$ are

$$\mathbf{A}_{mn}^{m+1,k} = \frac{1}{2m+3} \left(\mathbf{P}^{mn} \otimes, \mathbf{v}\mathbf{P}^{m+1,k} \right),$$

$$\mathbf{B}_{mn}^{m-1,k} = \frac{1}{2m+1} \left(\mathbf{P}^{mn} \otimes \mathbf{v}\mathbf{P}^{m-1,k} \right). \qquad (2.34)$$

The first five polynomials $\mathbf{P}^{mn}$ (two scalar and one vector), corresponding to the eigenvalue λ_0, are

$$P^{00} = 1, \quad \mathbf{P}^{10} = \mathbf{W}, \quad P^{01} = \left(\frac{2}{3}\right)^{1/2} \left(W^2 - \frac{3}{2} \right). \quad (2.35)$$

The corresponding expansion coefficients are defined in terms of the thermodynamic (hydrodynamic) variables such as the local density n, velocity u, and temperature T:

$$a^{00} = n_0^{-1} \left[n(\mathbf{r}, t) - n_0 \right] = n_0^{-1} \Delta n(\mathbf{r}, t), \quad \mathbf{a}^{10} = \beta_0^{1/2} \mathbf{u}(\mathbf{r}, t),$$

$$a^{01} = \left(\frac{3}{2}\right)^{1/2} T_0^{-1} \left[T(\mathbf{r}, t) - T_0 \right] = \left(\frac{3}{2}\right)^{1/2} T_0^{-1} \Delta T. \quad (2.36)$$

Equations (2.33) for these coefficients with the right-hand side equal to zero are the conventional conservation laws or hydrodynamic equations:

$$\frac{\partial n}{\partial t} + \nabla n\mathbf{u} = 0, \quad \rho \frac{\partial \mathbf{u}}{\partial t} + \nabla p + \nabla \boldsymbol{\pi} = 0,$$

$$\frac{3}{2} \left(\frac{\mathrm{d}p}{\mathrm{d}t} + p\nabla\mathbf{u} \right) + P_{rs} \frac{\partial u_r}{\partial x_s} + \nabla \mathbf{q} = 0, \quad (2.37)$$

where $P_{rs} = p\delta_{rs} + \pi_{rs}$. Also, $\rho = mn$, $p = nkT$, $\mathrm{d}/\mathrm{d}t = \partial/\partial t + (\mathbf{u}\nabla)$; the tensor of viscous stress $\boldsymbol{\pi}$ and the heat flux $\mathbf{q}$ are

$$\boldsymbol{\pi} = \rho(\mathbf{v}\mathbf{v}, \phi), \quad \mathbf{q} = \frac{\rho}{2} \left(\mathbf{v}\left(v^2 - \frac{5kT}{m} \right), \phi \right), \quad (2.38)$$

and $(\nabla \boldsymbol{\pi})_r = \partial \pi_{rs}/\partial x_s$.

Equations (2.33) for the moments of higher order (with nonzero right-hand side) are of a relaxation character, which is especially clear when we consider the equilibrium state of the gas. Then

$$\frac{\partial \mathbf{a}^{mn}}{\partial t} = -\sum_k n_0 \Lambda_{mnk} \mathbf{a}^{mk}. \quad (2.39)$$

The integral brackets Λ_{mnk} for real potentials of interaction may be represented as linear combinations of the known Chapman–Cowling integrals Ω^{lr} [1]. Another convenient representation of these coefficients is based on the effective

cross-section of collisions

$$\sigma \begin{pmatrix} m\,n \\ m\,k \end{pmatrix},$$

defined for various types of relaxation [38]. Then

$$\Lambda_{mnk} = \langle v_r \rangle \sigma \begin{pmatrix} m\,n \\ m\,k \end{pmatrix}, \quad \langle v_r \rangle = 4 \left(\frac{kT_0}{\pi m} \right)^{1/2}. \quad (2.40)$$

It is easy to see that $n_0 \Lambda_{mnk}$ is of the same order of magnitude as the characteristic frequency of collisions in the gas. Then the set of Eqns (2.39) describes the relaxation of the variables of state $\mathbf{a}^{mn}$ to zero from their initial values with a characteristic time of the order of the mean free time of the particles between collisions. The relaxation equations for coefficients $\mathbf{a}^n(t)$ in the case of 'Maxwell molecules' are especially simple, because condition (2.28) then holds. The solution of Eqn (2.26) for the homogeneous state of the gas in this case is

$$\mathbf{a}^n = \mathbf{a}^n(0) \exp\left(-|\lambda_n|t \right).$$

If $\tau_n = |\lambda_n|^{-1} \ll \tau_L$ (where τ_L is the characteristic time scale of the problem), then the variables of state rather rapidly relax to zero.

2.3 Equation of entropy balance
It is known that the kinetic Boltzmann equation can be used for deriving the equation of balance of entropy [3]

$$\frac{\partial s}{\partial t} + \nabla_r \mathbf{J}^s = \sigma, \quad (2.41)$$

where $s(r, t)$ is the density of entropy, $\mathbf{J}^s$ is the density of total flux of entropy, and σ is the local entropy production due to collisions of molecules in the gas. For the linearized kinetic equation (2.9), Eqn (2.41) is easily derived by multiplying Eqn (2.9) by $(-kf_0\phi)$ and integrating with respect to velocities. Then (up to constants)

$$s(r, t) = -\frac{kn_0}{2}(\phi, \phi), \quad \mathbf{J}^s = -\frac{kn_0}{2}(\phi, \mathbf{v}\phi), \quad (2.42)$$

$$\sigma = -kn_0(\phi, L\phi). \quad (2.43)$$

From condition (2.13) it follows then that

$$\sigma \geqslant 0. \quad (2.44)$$

Substituting into Eqns (2.42), (2.43) the expansions for ϕ (2.29), we get

$$s(r, t) = -\frac{kn_0}{2} \sum_{m,n} (\mathbf{a}^{mn})^2, \quad (2.45)$$

$$\mathbf{J}^s = -\frac{kn_0}{2} \sum_{mn} \sum_{m'n'} \mathbf{a}^{mn} \left(\mathbf{P}^{mn}, \mathbf{v}\mathbf{P}^{m'n'} \right) \mathbf{a}^{m'n'}, \quad (2.46)$$

$$\sigma = -kn_0 \sum_{mn} \sum_{m'n'} \mathbf{a}^{mn} \left(\mathbf{P}^{mn}, L\mathbf{P}^{m'n'} \right) \mathbf{a}^{m'n'}. \quad (2.47)$$

Observe that straightforward linearization of the kinetic expression for the density of entropy $s(r, t) = -k \int f \ln f \, \mathrm{d}\mathbf{v} + nk$ results in Ref. [43]

$$s(r, t) = s_0 - \frac{\mu_0}{T_0}(n - n_0) + \frac{3}{2}\frac{1}{T_0}(p - p_0) - \frac{kn_0}{2}(\phi, \phi), \quad (2.48)$$

where μ_0 is the chemical potential per particle. This expression ensures correct normalization for the quadratic term (2.42) which enters into Eqn (2.41). Such renormalization leads to the equation of entropy balance in which the density of entropy flux $\mathbf{J}^s$ must also be renormalized. We shall return to this matter in a short while; at this point we just observe that the equation of entropy balance in the form (2.41) corresponds to the local formulation of the second law of thermodynamics. For the total entropy $S(t) = \int s(\mathbf{r}, t)\, d\mathbf{r}$ the normalization of (2.48) does not play any role, since $N = N_0$ and $T = T_0$ by virtue of conservation of the total number of particles and energy in a closed system. Integrating Eqn (2.41) over the volume, we get

$$\frac{dS}{dt} + \int_\Omega J^s\, d\Omega = \int_V \sigma\, d\mathbf{r}\,, \tag{2.49}$$

where Ω is the surface surrounding the selected volume V. For an isolated system (which does not exchange thermal energy and matter with the environment), the surface integral on the left-hand side vanishes. Then, making use of Eqn (2.23), we get

$$\frac{dS}{dt} = \int \sum_{n=1}^{\infty} (-k\mathbf{a}^{(n)}) \frac{\partial \mathbf{a}^{(n)}}{\partial t}\, dr = \int_V \sigma\, d\mathbf{r} \geqslant 0\,. \tag{2.50}$$

Given the definitions of flows $\partial \mathbf{a}^{(n)}/\partial t$ and the associated thermodynamic forces (2.24), expression (2.50) is in agreement with the phenomenological expressions (2.6) and (2.7) above. It also fits in with the known conclusion of the Onsager–Casimir theory which states that the antisymmetrical part of matrix R^{nk} [which in our case corresponds to the flow operator in Eqn (2.27)] does not contribute to the increase in entropy in an isolated system [19].

Let us now return to the local entropy balance equation. Differentiating Eqn (2.48) with respect to time, we get

$$\frac{\partial s}{\partial t} = -\frac{\mu_0}{T_0}\frac{\partial n}{\partial t} + \frac{3}{2}\frac{1}{T_0}\frac{\partial p}{\partial t} + \ldots\,,$$

where we have temporarily dropped the derivative of the quadratic term. Making use of the conservation equations (2.48) we find

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x_l}\left[\frac{1}{T_0}\left(-\mu_0 n + \frac{3}{2} p\right)u_l + P_{rl}u_r + q_l\right] + \ldots$$

Using Eqn (2.48) once again, we get

$$\left(-\mu_0 n + \frac{3}{2} p\right)u_l = \left[-\mu_0 n_0 + \frac{3}{2} p_0 + T_0(s - s_0)\right]u_l$$
$$= (T_0 s - p_0)u_l\,.$$

As a result, the complete local equation of entropy balance assumes the conventional form (2.41), with the renormalized expressions for s and $\mathbf{J}^s$ [43]:

$$s = s_0 - \frac{\mu_0}{T_0}(n - n_0) + \frac{3}{2}\frac{1}{T_0}(p - p_0) - \frac{kn_0}{2}\sum_{m,n}(\mathbf{a}^{mn})^2\,, \tag{2.51}$$

$$J_r^s = u_r s + \frac{1}{T_0}\,\pi_{rl}u_l + \frac{1}{T_0}\,q_r$$
$$- \frac{kn_0}{2}\sum_{mn}\sum_{m'n'}\mathbf{a}^{mn}\left(\mathbf{P}^{mn}, v_r\mathbf{P}^{m'n'}\right)\mathbf{a}^{m'n'}\,. \tag{2.52}$$

The expression for the density of entropy production σ retains the form of Eqn (2.43) or (2.47); however, owing to the fact that $(\phi, L\phi) = 0$ for the first five eigenfunctions in Eqn (2.35), the summation in Eqn (2.47) does not involve terms with the coefficients a^{00}, a^{01}, and $\mathbf{a}^{10}$. One may also exclude the corresponding five terms from summation over m and n in the expression for s, combining them with the first three terms. Together they form the Taylor expansion for the local equilibrium entropy $s_{eq}(n, T)$ with respect to the absolute distribution up to the quadratic terms, inclusive.

As a result, the expression for the non-equilibrium density of entropy can be written as [43]

$$s = s_{eq}(n, T) - \frac{kn_0}{2}\sum_{mn}(\mathbf{a}^{mn})^2\,, \tag{2.53}$$

where the summation only involves the terms related to the dissipative fluxes π_{rs}, q_r, etc. A similar expression can be obtained by using the expansion of the DF with respect to the local Maxwell distribution from the outset rather than the absolute (see Section 2.6).

2.4 Extended irreversible thermodynamics

From the arguments developed above it follows that, for small deviations of the state of the gas from equilibrium, the methods of NT for a rather general situation when the non-equilibrium state of the gas (and the non-equilibrium entropy) depends not only on the local values of density, velocity and temperature of the gas (that is, the first five coefficients a^{00}, a^{01}, and $\mathbf{a}^{10}$), but also on an indefinite number of additional variables of state $\mathbf{a}^{(n)}$ or $\mathbf{a}^{mn}$, which satisfy the sets of moment equations (2.26) or (2.33). A finite description of the state of the gas is accomplished by truncating expansions (2.21) or (2.29). Such a definition (for example, truncation based on the assumption that $\mathbf{a}^n = 0$ at $n > k$, or extrapolation from order n to order $n + 1$ [39, 40]) must obviously comply with the basic requirements of NT (Onsager relations, positive entropy production). In this way, the methods of NT provide a tool for checking the correctness of approximate solutions of the kinetic equation [44–46].

The most characteristic example of the finite description is Grad's 13-moment approximation [2], when, in addition to a^{00}, a^{01}, and $\mathbf{a}^{10}$, the coefficients $\mathbf{a}^{20}$ and $\mathbf{a}^{11}$ are retained in expansion (2.29). The corresponding polynomials are written as

$$\mathbf{P}^{20}(\mathbf{W}) = \sqrt{2}\,\overline{\mathbf{WW}}\,, \qquad \mathbf{P}^{11}(\mathbf{W}) = \left(\frac{4}{5}\right)^{1/2}\mathbf{W}\left(W^2 - \frac{5}{2}\right). \tag{2.54}$$

The coefficients $\mathbf{a}^{20}$ and $\mathbf{a}^{11}$ are linear functions of the tensor of viscous stress $\boldsymbol{\pi}$ and the heat flux $\mathbf{q}$:

$$\mathbf{a}^{20} = (2)^{-1/2}\frac{\boldsymbol{\pi}}{p}\,, \qquad \mathbf{a}^{11} = \left(\frac{4}{5}\right)^{1/2}\beta_0^{1/2}\frac{\mathbf{q}}{p}\,. \tag{2.55}$$

Thus, the 13-moment approximation corresponds to the representation of the DF in terms of a finite combination of moments which have concrete physical meaning. The equations in moments (2.33) for $\mathbf{a}^{20}$ and $\mathbf{a}^{11}$ then take the

form [12]

$$\frac{\partial \boldsymbol{\pi}}{\partial t} + 2p\left(\overline{\nabla \mathbf{u}} + \frac{2}{5}\frac{1}{p}\overline{\nabla \mathbf{q}}\right) = -\frac{1}{\tau_\eta}\,\boldsymbol{\pi}\,,$$

$$\frac{\partial \mathbf{q}}{\partial t} + \frac{5}{2}\frac{k}{m}p\left(\nabla T + \frac{2}{5}\frac{T}{p}\nabla \boldsymbol{\pi}\right) = -\frac{1}{\tau_\lambda}\,\mathbf{q}\,. \qquad (2.56)$$

The characteristic collision times τ_η and τ_λ are expressed via the coefficients of viscosity η and heat conductivity λ (calculated in the first Chapman – Cowling approximation†)

$$[\eta]_1 = p\tau_\eta = \frac{kT}{\langle v_r\rangle\sigma\begin{pmatrix}2\;0\\2\;0\end{pmatrix}} = \frac{5}{8}\frac{kT}{\Omega^{(2,2)}}\,,$$

$$[\lambda]_1 = \frac{5}{2}\frac{k}{m}p\tau_\lambda = \frac{5}{2}\frac{k}{m}\frac{kT}{\langle v_r\rangle\sigma\begin{pmatrix}1\;1\\1\;1\end{pmatrix}} = \frac{75}{32}\frac{k^2 T}{m\Omega^{(2,2)}}\,. \quad (2.57)$$

Equations (2.56) can also be obtained using the standard Grad's method of moments, based on the expansion of the DF with respect to the local rather than the absolute Maxwell distribution [12]. As pointed out in the Introduction, the structure of these equations was used in Refs [4 – 8] as a basis in the formulation of the new direction in the phenomenological theory of non-equilibrium processes, EIT. The main idea of EIT is that the fluxes $\boldsymbol{\pi}$ and $\mathbf{q}$ are regarded as independent variables in addition to the conventional thermodynamic variables. Because of this, the expressions for entropy, entropy flux and entropy production carry new terms, and the form of the Gibbs relation used in the classical NT is also changed. As a matter of fact, this is the philosophy of our foregoing discussion, in which all these quantities were considered as functions of an arbitrary number of independent variables of state.

An important argument in favor of Eqns (2.56) is the following: if we neglect the terms $\nabla\boldsymbol{\pi}$ and $\nabla\mathbf{q}$ as small in the second order (see below), then these equations together with the conservation laws (2.37) lead to the conclusion of a finite velocity of propagation of perturbations of temperature (thermal signals) and viscous perturbations [7], thus resolving the paradox of the infinite speed of these signals which is entailed by the conventional linear relations of the classical NT (the Fourier law and Navier – Stokes relation). Generally speaking, the domain of EIT is more closely associated with the analysis of situations where the characteristic time of relaxation for some dissipative process in the medium is commensurate with the characteristic time scale of the problem. It is known, for example, that in the analysis of propagation of ultrasound in a gas the 13-moment approximation fits in somewhat better with the experiment when the ultrasonic frequency is comparable with the mean frequency of collisions between molecules [39]. Even better agreement is achieved by taking into account a greater number of coefficients of expansion (2.29) and the corresponding linearized equations in moments, as was demonstrated rather long ago in the well-known work by Wang Chang and Uhlenbeck [16].

Here we are not going to touch upon other problems within the scope of EIT (for example, the analysis of

fluctuations of dissipative fluxes), referring the reader to the available literature [5 – 9].

2.5 Linear transport relations.
Contribution from space derivatives of fluxes

Apart from the approach adopted in EIT, there is another aspect of generalization of NT (associated with the use of equations in moments), first discussed in Ref. [20]. The characteristic time of collisions between gas molecules is usually small ($\tau \sim 10^{-10}$ s under normal conditions). This means that it takes a relatively short time (a few τ) for a gas even in a spatially inhomogeneous system to achieve the quasi-equilibrium described approximately by Eqns (2.33), in which the time derivatives can be dropped [this, of course, does not apply to the equations for a^{00}, $\mathbf{a}^{10}$, and a^{01} — that is, to the set (2.37)]. As a result, we get a set of coupled steady-state equations each involving the coordinate-derivatives of the moment of the higher order with respect to the order of the principal (leading) moment on the right-hand side of such an equation. If the expansion is limited to a finite number of terms, then it is possible to express any higher-order moment via the moments retained in the expansion, owing to which the set of equations becomes closed [12, 39].

A typical example of such an approach is the above 13-moment approximation. Dropping the time derivatives of flows in Eqn (2.56), we get‡

$$\boldsymbol{\pi} = -2\eta\left[\overline{\nabla\mathbf{u}} + \frac{2}{5}\frac{1}{p}\overline{\nabla\mathbf{q}}\right],\qquad \mathbf{q} = -\lambda\left[\nabla T + \frac{2}{5}\frac{T}{p}\nabla\boldsymbol{\pi}\right]. \qquad (2.58)$$

It is important that relations (2.58) go beyond the limits of the standard linear transport relations derived in the conventional (non-Burnett) approximation by the ChE method and used in the classical NT. This distinction is associated with the appearance of additional terms proportional to the derivatives of heat flux and tensor of viscous stress. Assuming, as is usually done [1, 39], that these terms are infinitesimal in the second order in Knudsen number $\mathrm{Kn} = l/L$ (where l is the mean free path of the molecules, and L is the characteristic length of the problem), we may use the iteration procedure. We substitute the values of $\mathbf{q}$ and $\boldsymbol{\pi}$ obtained in the first approximation into the terms containing the derivatives of fluxes in Eqn (2.58) when the second order terms are dropped [39]. Then

$$\boldsymbol{\pi} = -2\eta\,\overline{\nabla\mathbf{u}} + \frac{4}{5}\frac{\eta\lambda}{p}\,\overline{\nabla\nabla}\,T,\qquad \mathbf{q} = -\lambda\nabla T + \frac{2}{5}\frac{\eta\lambda T}{p}\,\nabla^2\mathbf{u}. \qquad (2.59)$$

Representation (2.59) is known to correspond completely to the results of the linearized Burnett approximation of the ChE method [1].

It should be emphasized that expressions (2.58) are more general than Eqns (2.59). This can be readily seen, for example, in the case of steady viscous gas flow, when from the equation of motion (2.37) it follows that $\nabla\boldsymbol{\pi} = -\nabla p$. The expression for $\mathbf{q}$ in Eqns (2.58) then takes the form

$$\mathbf{q} = -\lambda\left[\nabla T - \frac{2}{5}\frac{T}{p}\nabla p\right], \qquad (2.60)$$

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† The order of approximation using expansion in the Sonin polynomials [1].

‡ The coefficients η and λ correspond to the first Chapman – Cowling approximation; for simplicity hereafter we drop the notation $[\ldots]_1$.

whence it follows that the additional term (heat transfer by pressure gradient, which occurs, for example, in narrow capillary channels) is of the same (first) order of magnitude as the conventional term accounting for heat transfer by gradient of temperature. Formally, the same result follows from Eqns (2.59), since $\eta \nabla^2 \mathbf{u} = \nabla p$; recall, however, that the expression for $\mathbf{q}$ in Eqns (2.59) was obtained under the assumption that the Knudsen number is small.

Even more interesting results come up when the space derivatives of fluxes are taken into account in the case of a gas mixture [20]. Then the set of non-equilibrium parameters, corresponding, for example, to the $(12N + 1)$-moment approximation (where N is the number of components in the mixture), in addition to the conventional variables — the concentrations of particles n_α, the mass-averaged velocity $\mathbf{u}$, and the temperature T — includes the diffusion fluxes $\mathbf{J}_\alpha = \rho_\alpha \mathbf{w}_\alpha$, where $\mathbf{w}_\alpha = \mathbf{u}_\alpha - \mathbf{u}$, $\rho_\alpha = m_\alpha n_\alpha$, the partial tensors of viscous stress $\boldsymbol{\pi}_{\alpha rs}$, and the reduced heat fluxes $\mathbf{h}_\alpha = \mathbf{q}_\alpha - (5/2)p_\alpha \mathbf{w}_\alpha$, where α is the component identifier. The solution of steady-state linearized equations in moments using the iteration procedure in Knudsen number then has the form [20]

$$\sum_{\beta \neq \alpha} \frac{n_\alpha n_\beta k T}{n [D_{\alpha\beta}]_1} (\mathbf{u}_\alpha - \mathbf{u}_\beta) = -\left(\nabla p_\alpha - \frac{\rho_\alpha}{\rho} \nabla p \right)$$

$$+ \left(\eta_\alpha - \frac{\rho_\alpha}{\rho} \eta \right) \nabla^2 \mathbf{u} + \sum_\beta \xi_{\alpha\beta} \left(\frac{\lambda_\alpha}{\rho_\alpha} - \frac{\lambda_\beta}{\rho_\beta} \right) \nabla T,$$

$$\boldsymbol{\pi} = -2\eta \, \overline{\nabla \mathbf{u}} + \frac{4}{5} \sum_\alpha \frac{\eta_\alpha \lambda_\alpha}{p_\alpha} \, \overline{\nabla \nabla} \, T,$$

$$\mathbf{q} - \frac{5}{2} kT \sum_\alpha p_\alpha \mathbf{w}_\alpha = -\lambda \nabla T + T \sum_\beta \sum_\alpha \frac{\lambda_\alpha}{\rho_\alpha} \xi_{\alpha\beta} (\mathbf{u}_\alpha - \mathbf{u}_\beta)$$

$$+ \frac{2}{5} T \sum_\alpha \frac{\eta_\alpha \lambda_\alpha}{p_\alpha} \nabla^2 \mathbf{u}. \qquad (2.61)$$

Here $[D_{\alpha\beta}]_1$ is the coefficient of mutual diffusion of the binary mixture of α- and β-molecules (the first Chapman–Cowling approximation), η_α and λ_α are the partial coefficients of viscosity and heat conductivity, $\eta = \sum_\alpha \eta_\alpha$ and $\lambda = \sum_\alpha \lambda_\alpha$ are same for the gas mixture, and the coefficients $\xi_{\alpha\beta}$ form linear combinations of integrals $\Omega_{\alpha\beta}^{lr}$ [1]. In expressions (2.61) we have dropped a few terms which give small second-order corrections to the kinetic coefficients [20].

Observe that for a steady viscous gas flow, when $\eta \nabla^2 \mathbf{u} = \nabla p$, the first two terms on the right-hand side of the first equation in (2.61) reduce to the form $-\left[\nabla p_\alpha - (\eta_\alpha / \eta) \nabla p \right]$. In this way, the inclusion of derivatives of the tensor of viscous stress at second derivatives of the velocity leads to redefinition of the coefficient of pressure diffusion (coefficient of pressure gradient in the expression for the diffusion flux). For example, for a binary mixture we get

$$\mathbf{J}_{1D} = n y_1 y_2 (\mathbf{u}_1 - \mathbf{u}_2) = -n [D_{12}]_1 \big(\nabla y_1 + [\alpha_p^v]_1 y_1 y_2 \nabla \ln p$$

$$+ [\alpha_T]_1 y_1 y_2 \nabla \ln T \big), \qquad (2.62)$$

where $[\alpha_p^v]_1 = \eta^{-1} \left[(\eta_2 / y_2) - (\eta_1 / y_1) \right]$ is the constant of pressure diffusion in viscous flow [20], and $[\alpha_T]_1$ is the constant of thermal diffusion (the first non-vanishing Chapman–Cowling approximation [1]), $y_\alpha = n_\alpha / n$. Observe that, by contrast with the results of the classical NT and the first (non-Burnett) approximation of the ChE method, $[\alpha_p^v]_1$ is an

essentially kinetic quantity, which depends on the nature of interaction between the molecules [20].

For heat flow in the binary mixture we have

$$\mathbf{h} = \mathbf{q} - \frac{5}{2} p (y_1 \mathbf{w}_1 + y_2 \mathbf{w}_2)$$

$$= -\lambda \nabla T + kT [\alpha_T]_1 \mathbf{J}_{1D} + \frac{2}{5} \sum_{\alpha=1}^{2} \frac{\eta_\alpha \lambda_\alpha}{\eta p_\alpha} \nabla p. \qquad (2.63)$$

Substituting $\mathbf{J}_{1D}$ from Eqn (2.62) into the right-hand side of Eqn (2.63), it is easy to see that the coefficients at $\nabla \ln T$ and ∇y_1 in the cross terms of the expressions for $\mathbf{J}_{1D}$ and $\mathbf{h}$ satisfy the Onsager's reciprocal relations (which is a well known result [3]). At the same time, the set of equations (2.62), (2.63) is not complete, since it does not include the additional thermodynamic fluxes proportional to the pressure gradient. As will become clear from future discussion, a consistent inclusion of the terms of the Burnett approximation gives rise to yet another 'non-physical' flux, the inclusion of which into the set of three vector equations ensures fulfillment of all the necessary symmetry relations (see below).

2.6 Linearization near local equilibrium. Entropy production

The realization of the traditional methods of the KT of gases (the ChE method [1], the Grad's method [2]) is usually associated with the expansion of the DF with respect to the local (not absolute) Maxwell distribution. This approach is more consistent with the local formulation of the laws of NT itself. It will be useful to look at the implications of the method of moments in this case.

We represent the DF as

$$f = f^{(0)}(1 + \Phi), \qquad f^{(0)} = n \left(\frac{m}{2\pi k T} \right)^{3/2} \exp\left(-\frac{m}{2kT} c^2 \right), \qquad (2.64)$$

where $\mathbf{c} = \mathbf{v} - \mathbf{u}$, and n, $\mathbf{u}$, T are functions of $\mathbf{r}$ and t. The linearized kinetic equation for Φ ($|\Phi| \ll 1$) in the absence of external forces is then written as

$$\frac{D\Phi}{Dt} + \frac{D \ln f^{(0)}}{Dt} = L\Phi, \qquad (2.65)$$

where $D/Dt = \partial/\partial t + (\mathbf{v}\nabla)$.

Now we introduce the scalar product of the form (2.10), this time with $f^{(0)}$ in place of f_0:

$$[\Psi, \Phi] = \frac{1}{n} \int \Psi f^{(0)} \Phi \, d\mathbf{v}. \qquad (2.66)$$

By definition, for the local density, velocity and temperature we have

$$[1, \Phi] = 0, \qquad [\mathbf{v}, \Phi] = 0, \qquad [v^2, \Phi] = 0. \qquad (2.67)$$

Further on, without compromising the generality too much, we are going to consider only the slow gas flows, when

$$|u| \ll \left(\frac{kT}{m} \right)^{1/2}. \qquad (2.68)$$

This allows us to use, as before, the variable $\mathbf{v}$ in place of $\mathbf{c}$ in the relevant equations. Observe that if the conditions

$\Delta n/n_0 \ll 1$, $\Delta T/T_0 \ll 1$ hold simultaneously with Eqn (2.68), then $f^{(0)}$ can be approximately expressed as

$$f^{(0)} \cong f_0 \left[1 + \frac{\Delta n}{n_0} + \frac{m}{kT}\mathbf{vu} + \left(\frac{mv^2}{2kT_0} - \frac{3}{2} \right) \frac{\Delta T}{T} \right]. \qquad (2.69)$$

This representation obviously corresponds to the inclusion of the first terms (with the coefficients a^{00}, a^{01}, and $\mathbf{a}^{10}$) in the expansion with respect to the absolute equilibrium (2.29). Since the terms in the expansion are small, the definitions of (Ψ, ϕ) and $[\Psi, \Phi]$ may be regarded as practically the same.

Now let us expand the correction Φ into a double series in the polynomials $\mathbf{P}^{mn}(\mathbf{W})$, where $\mathbf{W} = (m/2kT)^{1/2}\mathbf{v}$. Formally this expansion will coincide with Eqn (2.29); in the definition of $\mathbf{W}$, however, T is generally a function of $\mathbf{r}$ and t. In addition, by virtue of conditions (2.67) we have $a^{00} = a^{01} = \mathbf{a}^{10} = 0$ — that is, the expansion begins with the polynomials (2.54) and the corresponding coefficients $\mathbf{a}^{20}$ and $\mathbf{a}^{11}$.

Although the equation of entropy balance retains its form (2.41), the expression for the entropy density $s(\mathbf{r}, t)$ contains the term s_{eq} which corresponds to the local-equilibrium distribution and depends implicitly on r and t via the density and the temperature, so that

$$s(r, t) = s_{eq}(n, T) - \frac{kn}{2}[\Phi, \Phi]. \qquad (2.70)$$

The relevant expressions for the entropy density flux and entropy production are written as

$$\mathbf{J}^s = \mathbf{u}s + \frac{\mathbf{q}}{T} - \frac{kn}{2}[\Phi, \mathbf{v}\Phi], \qquad (2.71)$$

$$\sigma = -kn[\Phi, L\Phi]. \qquad (2.72)$$

In particular, in the 13-moment approximation the expressions for s and $\mathbf{J}^s$ take on the form [12]

$$s = s_{eq}(n, T) - \frac{1}{2pT}\,\pi\pi - \frac{2m}{5pkT^2}\,\mathbf{qq},$$

$$J_r^s = u_r s + \frac{q_r}{T} - \frac{2}{5pT}\,q_s\pi_{rs} \qquad (2.73)$$

(the expression for entropy production will be discussed below).

It is interesting that the entropy density flux $\mathbf{J}^s$ (2.73) contains, along with the conventional terms, a contribution which is manifested when both the viscous stress π and the heat flux $\mathbf{q}$ are present in the gas, as pointed out by Grad himself [12]. We shall see that this circumstance may play an important role in the NT of boundary conditions.

Now let us turn to the equations in moments. Given that the gas, as noted above, rapidly evolves towards quasi-equilibrium, we shall confine our treatment to the steady state. Dropping the partial time derivatives in the kinetic equation (2.65), we represent it in the form

$$(\mathbf{v}\nabla)\ln f^{(0)} + (\mathbf{v}\nabla)\Phi = L\Phi, \qquad (2.74)$$

where

$$\nabla \ln f^{(0)} = \nabla \ln p + \left(\beta v^2 - \frac{5}{2} \right)\nabla \ln T + 2\beta(\mathbf{v}\nabla)\mathbf{u}. \qquad (2.75)$$

Multiplying both sides of Eqn (2.74) by $f^{(0)}\mathbf{P}^{mn}$ and integrating with respect to velocities, we come to the set of equations in moments of the form

$$[\mathbf{P}^{mn}, (\mathbf{v}\nabla)\ln f^{(0)}] + \sum_{m'n'}[\mathbf{P}^{mn}, \mathbf{v}\mathbf{P}^{m'n'}]\nabla \mathbf{a}^{m'n'}$$

$$= -\sum_k n\Lambda_{mnk}\mathbf{a}^{mk}. \qquad (2.76)$$

Equations (2.76) for the first five polynomials P^{00}, $\mathbf{P}^{10}$, and P^{01} (with the right-hand side equal to zero) express the conservation laws, which for the steady slow gas motions under consideration are

$$\nabla\mathbf{u} = 0, \qquad \nabla p + \nabla\pi = 0, \qquad \nabla\mathbf{q} = 0. \qquad (2.77)$$

Now we calculate the local entropy production σ, substituting the expansion for Φ and replacing the collisions integral by the left-hand side of Eqn (2.75). As a result, we get

$$T\sigma = -kT\sum_{mn} n\mathbf{a}^{mn}\left\{ [\mathbf{P}^{mn}, (\mathbf{v}\nabla)\ln f^{(0)}] \right.$$

$$\left. + \sum_{m'n'}[\mathbf{P}^{mn}, \mathbf{v}\mathbf{P}^{m'n'}]\nabla\mathbf{a}^{m'n'} \right\}, \qquad (2.78)$$

or, making use of Eqns (2.75) and (2.33),

$$T\sigma = -\frac{1}{T}\mathbf{q}\nabla T - \pi \otimes \overline{\nabla\mathbf{u}}$$

$$- p\sum_{mn}\mathbf{a}^{mn}\sum_{k=0}^{\infty}\left(\mathbf{A}_{mn}^{m+1, k}\nabla\mathbf{a}^{m+1, k} + \mathbf{B}_{mn}^{m-1, k}\,\overline{\nabla\mathbf{a}}^{m-1, k} \right). \qquad (2.79)$$

The first two terms on the right-hand side of Eqn (2.79) correspond to the conventional representation of entropy production as a bilinear combination of the fluxes $\mathbf{q}$ and π, and the corresponding thermodynamic forces which are found within the framework of classical NT for vector and tensor phenomena [3]. The new circumstance is that the same fluxes ($\mathbf{a}^{11} \sim \mathbf{q}$ and $\mathbf{a}^{20} \sim \pi$) appear, together with the associated additional forces, in the subsequent terms in Eqn (2.79).

By way of illustration, let us consider the 20-moment approximation, when the expansion for Φ includes, along with the polynomials $\mathbf{P}^{11}$ and $\mathbf{P}^{20}$, the tensor polynomial of the third rank $\mathbf{P}^{30} = (4/3)^{1/2}\,\overline{\mathbf{WWW}}$ with the corresponding coefficient $\mathbf{a}^{30}$. This polynomial is connected with the moment of the third-order DF $\mathbf{S} = m\int \overline{\mathbf{vv}}f\,d\mathbf{v}$, and so $\mathbf{a}^{30} = (1/3)^{1/2}\beta^{1/2}\mathbf{S}/p$. In this approximation the production of entropy (2.79) is [27]

$$T\sigma = -\mathbf{q}\left(\frac{\nabla T}{T} + \frac{2}{5p}\,\nabla\pi \right)$$

$$- \pi\left(\overline{\nabla\mathbf{u}} + \frac{2}{5}\frac{1}{p}\,\overline{\nabla\mathbf{q}} + \frac{1}{2p}\,\nabla\mathbf{S} \right) - \frac{1}{2Tp}\,\mathbf{S}\,\overline{\nabla\pi}, \qquad (2.80)$$

where

$$\overline{(\nabla\pi)}_{ijk} = \left(\frac{\partial\pi_{ik}}{\partial x_j} + \frac{\partial\pi_{jk}}{\partial x_i} + \frac{\partial\pi_{ij}}{\partial x_k} \right)$$

$$- \frac{2}{5}\left(\frac{\partial\pi_{il}}{\partial x_l}\,\delta_{jk} + \frac{\partial\pi_{jl}}{\partial x_l}\,\delta_{ik} + \frac{\partial\pi_{kl}}{\partial x_l}\,\delta_{ij} \right).$$

The linear phenomenological equations, corresponding to representation (2.80), are written as

$$\mathbf{q} = -\Lambda_{11}\left[\frac{\nabla T}{T} + \frac{2}{5p}\,\nabla\pi\right],$$

$$\pi = -\Lambda_{22}\left[\overline{\nabla\mathbf{u}} + \frac{2}{5p}\,\overline{\nabla\mathbf{q}} + \frac{1}{2p}\,\nabla\mathbf{S}\right], \qquad (2.81)$$

$$\mathbf{S} = -\Lambda_{33}\,\frac{\overline{\nabla\pi}}{p}\,.$$

In the 13-moment approximation ($\mathbf{S} = 0$) expressions (2.81) are in complete agreement with relations (2.58), which follow from the solution of the equations in moments (2.33) or (2.76). Then $\Lambda_{11} = \lambda T$, $\Lambda_{22} = 2\eta$. Comparison with the known solution for the 20-moment approximation [12, 27] also gives $\Lambda_{33} = (2/3)(kT/m)\eta$.

Observe that the complication of the form of the thermodynamic forces in the first two equations in (2.81), which now include the derivatives of fluxes, does not call for revision of the values of coefficients Λ_{11} and Λ_{22}, which are still determined by the values of the conventional heat conductivity and viscosity.

Recall that the heat flux $\mathbf{q}$ can be represented in the form (2.60):

$$\mathbf{q} = -\lambda\left(\nabla T - \frac{2T}{5p}\,\nabla p\right). \qquad (2.60')$$

In the well-known monograph [47], the discussion of the general equation of heat transport leads to the conclusion that the heat flux must only depend on the temperature gradient, and must not depend on the gradient of pressure, the argument being that (Ref. [47], p. 274) "should $\mathbf{q}$ include a term proportional to ∇p, then the expression for the change of entropy (entropy production — *Authors*) would carry a term containing [...] the product $\nabla p\nabla T$. Since the latter may be either positive or negative, the time derivative of the entropy would not be strictly positive, which is impossible". It is easy to see, however, that if $\mathbf{q}$ is represented in the form (2.60'), then the corresponding part of the entropy production in Eqn (2.80) is

$$T\sigma = \lambda T\left(\frac{\nabla T}{T} - \frac{2T}{5p}\,\nabla p\right)^2,$$

and is always positive because $\lambda > 0$. The same applies to all other fluxes in Eqns (2.81), because entropy production can always be represented as a sum of quadratic forms of the generalized thermodynamic forces which appear in Eqns (2.81), and will be positive as long as the coefficients η and λ are positive, which is confirmed by experiments and concrete calculations.

The set of equations (2.81) does not include the cross terms, whose coefficients would be expected to comply with the Onsager relations. The reason is that the set (2.81) corresponds to the minimum number of polynomials of the same tensor dimension (first, second and third order). As we have seen, the cross terms will appear even in this approximation if we consider a gas mixture, because the diffusion velocity and the heat flux form a set of vector equations (corresponding to the first-order tensor). It is easy to prove that the set of linear phenomenological equations with cross terms can be written for a pure gas as well, if one uses a greater number of coefficients in the expansion and the corresponding 'non-physical' fluxes. If, for example, for the formal expressions of the fluxes $\mathbf{J}^{mn}$ we select the coefficients $n\mathbf{a}^{mn}$, and for the thermodynamic forces $\mathbf{F}^{mn}$ the expressions

$$-k\left[(\mathbf{P}^{mn}(\mathbf{v}\nabla)\ln f^{(0)}) + \sum_{m'n'}(\mathbf{P}^{mn},\mathbf{v}\mathbf{P}^{m'n'})\nabla\mathbf{a}^{m'n'}\right],$$

then the set of linear phenomenological equations of different tensor dimension which link the thermodynamic fluxes and forces will be expressed as

$$\mathbf{J}^{1n} = \sum_{k} L_{nk}^{(1)}\mathbf{F}^{1k},$$

$$\mathbf{J}^{2n} = \sum_{k} L_{nk}^{(2)}\mathbf{F}^{2k}, \qquad (2.82)$$

$$\dots\dots\dots\dots\dots$$

$$\mathbf{J}^{mn} = \sum_{k} L_{nk}^{(m)}\mathbf{F}^{mn},$$

where the kinetic cross-coefficients must satisfy the Onsager relations $L_{nk}^{(m)} = L_{kn}^{(m)}$.

The linear relations (2.82) have the same structure as the direct solution of the equations for the coefficients $n\mathbf{a}^{mm}$ (2.76). Moreover, the matrix of phenomenological coefficients $L_{nk}^{(m)}$ corresponds to the reciprocal matrix Λ_{mnk}^{-1}. Since the matrix of coefficients Λ_{mnk} is symmetrical [by virtue of Eqn (2.11)], the reciprocal matrix of coefficients $L_{nk}^{(m)}$ is also symmetrical, which proves the fulfillment of the Onsager relations.

From the linear relations (2.82), whose right-hand sides contain the derivatives of the fluxes, one may go over to the linear relations between fluxes and forces, in which the thermodynamic forces are expressed in terms of the first and higher-order derivatives of the conventional thermodynamic variables and velocity. For this purpose it is sufficient to employ the standard iteration procedure using a small parameter (the Knudsen number), or decompose the fluxes into components corresponding to the contributions of the first and subsequent orders of magnitude [22–24, 26]. More obvious is the straightforward approximate solution of the linearized kinetic equation using the ChE method. The results of the Burnett approximation in the ChE method and their conformity with the inferences of NT are discussed in the next section.

2.7 The Chapman–Enskog method and non-equilibrium thermodynamics

According to the ChE method, the solution of the linearized equation (2.74) is sought in the form

$$\Phi = \sum_{n=1}^{\infty} \Phi_n = \Phi_1 + \Phi_2 + \dots,$$

where Φ_n is found by the method of successive approximations [1]:

$$\sum_{k=0}^{n-1} D^{(k)}\Phi_{n-k-1} = -(\mathbf{v}\nabla)\Phi_{n-1} + L(\Phi_n). \qquad (2.83)$$

The structure of operator $D^{(k)}$ is determined by the transformation of the first term on the left-hand side of Eqn (2.74) with due account for the level of approximation used for the

conservation equations (2.37) (equations of Euler, Navier – Stokes, etc.).

Let us consider the expression for entropy production (2.72). Using Eqn (2.83), we rewrite it in the form

$$\sigma = -k \sum_{n=1}^{\infty} \left[\Phi_n, \left[\sum_{k=0}^{n-1} D^{(k)} \Phi_{n-k-1} + (\mathbf{v}\nabla)\Phi_{n-1} \right] \right]. \quad (2.84)$$

Now we use the expressions for Φ in the first and the second (Burnett) approximations [1]:

$$\Phi_1 = \Phi_t (\mathbf{v}\nabla) \ln T + \Phi_p \overline{\mathbf{vv}} \otimes \overline{\nabla \mathbf{u}}, \quad (2.85)$$

where Φ_t and Φ_p are found from the solution of the integral equations

$$\mathbf{v} \left(\beta v^2 - \frac{5}{2} \right) = L(\mathbf{v}\Phi_t), \quad 2\beta \overline{\mathbf{vv}} = L(\overline{\mathbf{vv}} \Phi_p), \quad (2.86)$$

and

$$\Phi_2 = \mathbf{\Phi}_{\mathrm{B}}^T \otimes \frac{\overline{\nabla\nabla} T}{T} + \mathbf{v}\mathbf{\Phi}_{\mathrm{B}}^u \otimes \overline{\nabla\nabla\mathbf{u}} + \mathbf{v}\Phi_{\mathrm{B}}^v \nabla^2 \mathbf{u}, \quad (2.87)$$

where $\mathbf{\Phi}_{\mathrm{B}}^T$, $\mathbf{\Phi}_{\mathrm{B}}^u$, and Φ_{B}^v are found from equations of the form

$$\Phi_t \mathbf{vv} + \frac{T}{p} \left(\frac{2}{3} \beta v^2 - 1 \right) \lambda \delta = L(\mathbf{\Phi}_{\mathrm{B}}^T),$$

$$\Phi_p \overline{\mathbf{vvv}} = L(\mathbf{v}\mathbf{\Phi}_{\mathrm{B}}^u), \quad \left(\Phi_p \frac{v^2}{5} + \frac{\eta}{p} \right) \mathbf{v} = L(\mathbf{v}\Phi_{\mathrm{B}}^v). \quad (2.88)$$

Using the known expressions for $D^{(0)}\Phi_0$ and $D^{(1)}\Phi_0$ [1], it is easy to get [22 – 24]

$$T\sigma = - \left[(\mathbf{q}^{(1)}\nabla) \ln T + \boldsymbol{\pi}^{(1)} \otimes \overline{\nabla\mathbf{u}} + \mathbf{J}^T \otimes \frac{\overline{\nabla\nabla} T}{T} \right.$$
$$\left. + \mathbf{J}^u \otimes \overline{\nabla\nabla u} + \mathbf{J}^v \nabla^2 \mathbf{u} \right], \quad (2.89)$$

where $\mathbf{q}^{(1)}$ and $\boldsymbol{\pi}^{(1)}$ are given by Eqn (2.38), and

$$\mathbf{J}^T = kT[\Phi_t \overline{\mathbf{vv}}, \Phi], \quad \mathbf{J}^u = kT[\Phi_p \overline{\mathbf{vvv}}, \Phi],$$

$$\mathbf{J}^v = kT \left[\left(\Phi_p \frac{v^2}{5} + \frac{\eta}{kT} \right) \mathbf{v}, \Phi \right]. \quad (2.90)$$

The tensor dimensions of the flows $\mathbf{J}^T$, $\mathbf{J}^u$, and $\mathbf{J}^v$ are obvious.

The system of linear phenomenological equations, corresponding to representation (2.89), breaks down into three subsystems of different tensor dimensions [24, 26]

$$\mathbf{q} = -\Lambda_{11} \nabla \ln T - \Lambda_{12} \nabla^2 \mathbf{u},$$
$$\mathbf{J}^v = -\Lambda_{21} \nabla \ln T - \Lambda_{22} \nabla^2 \mathbf{u}; \quad (2.91)$$

$$\boldsymbol{\pi} = -\lambda_{11} \overline{\nabla\mathbf{u}} - \lambda_{12} \frac{\overline{\nabla\nabla} T}{T},$$

$$\mathbf{J}^T = -\lambda_{21} \overline{\nabla\mathbf{u}} - \lambda_{22} \frac{\overline{\nabla\nabla} T}{T}; \quad (2.92)$$

$$\mathbf{J}^u = -L_{11} \overline{\nabla\nabla\mathbf{u}}. \quad (2.93)$$

The concrete form of the kinetic coefficients is found by substituting the expression for $\Phi = \Phi_1 + \Phi_2$ into Eqns (2.90). The Onsager symmetry relations for the coefficients $\Lambda_{12} = \Lambda_{21}$ and $\lambda_{12} = \lambda_{21}$ follow from the symmetry condition

for the linearized collisions operator. Moreover, it is easy to prove that $\lambda_{12} = 2\Lambda_{12}$: for example,

$$\lambda_{12} = -\frac{1}{10} m \left[\overline{\mathbf{vv}} \otimes \mathbf{\Phi}_{\mathrm{B}}^T \right] = -\frac{2}{15} kT[v^4 \Phi_p, \Phi_t] = 2\Lambda_{12}.$$

In this way, four coefficients out of nine in Eqns (2.91) – (2.93) are equal to each other. This is confirmed by comparison with the results of the 13-moment approximation (2.59). Then

$$\Lambda_{11} = [\lambda]_1 T, \quad \Lambda_{12} = -\frac{2}{5} \frac{T}{p} [\eta]_1 [\lambda]_1,$$

$$\lambda_{11} = 2[\eta]_1, \quad \lambda_{12} = -\frac{4}{5} \frac{T}{p} [\eta]_1 [\lambda]_1. \quad (2.94)$$

An improved estimate using a greater number of polynomials gives $\Lambda_{12} = [\Lambda_{12}]_1 (1 + \varepsilon)$ [33], where $\varepsilon = -0.205$ for the model representing the molecules as rigid elastic spheres, and $\varepsilon = -0.10$ for the Lenard – Jones potential.

Observe that, as opposed to the set of phenomenological equations (2.81) considered earlier and obtained in the 20-moment approximation, the system (2.91) – (2.93), based on the consistent Burnett approximation, includes a number of non-physical fluxes $\mathbf{J}^v$, $\mathbf{J}^T$, and $\mathbf{J}^u$. Their presence in the subsystems of equations of the same tensor dimension is required for the fulfillment of the Onsager symmetry relations. A similar situation is encountered when the equations in moments are used, if one includes some moments of the higher order.

The results above are readily generalized for the multi-component gas mixture [26]. Then the expression for entropy production is

$$\sigma T = - \left[\mathbf{h}\nabla \ln T + \boldsymbol{\pi} \otimes \overline{\nabla\mathbf{u}} + p \sum_{\beta=1}^{N-1} (\mathbf{w}_\beta - \mathbf{w}_N)\mathbf{d}_\beta \right.$$

$$+ \mathbf{J}^T \otimes \frac{\overline{\nabla\nabla} T}{T} + \mathbf{J}^u \otimes \overline{\nabla\nabla\mathbf{u}} + \mathbf{J}^v \nabla^2 \mathbf{u}$$

$$\left. + \sum_{\beta=1}^{N-1} (\mathbf{J}_\beta^D - \mathbf{J}_N^D)\nabla \mathbf{d}_\beta \right]. \quad (2.95)$$

As for the case of single-component gas, the system of phenomenological equations based on the entropy production in the form (2.95) exhibits some new 'non-physical' fluxes, the number of which increases accordingly. Apart from the conventional symmetry relations, characteristic of the vector fluxes in the mixture, the system displays new links between the coefficients in each subsystem of equations, which ensure the fulfillment of the Onsager relations. The form of these equations and linkages between the coefficients can easily be found from the expression for entropy production (2.95).

2.8 Unified description of kinetic and hydrodynamic processes (Klimontovich method)

As pointed out in the introduction, an alternative approach in the KT was recently proposed by Yu Klimontovich. According to Klimontovich [28 – 30], this approach is justified by the fact that in the traditional treatments the transition from a kinetic to a gas-dynamic description is associated with the tacit replacement of the fine structure of the continuous medium on the kinetic level by the more coarsely defined structure in gas dynamics. Accordingly, the conventional Knudsen number used as the small perturbation parameter

in the traditional theory, replaced in the new approach by the so-called 'physical Knudsen parameter', defined as the ratio of the size of a 'point' of continuous medium to the characteristic length of the problem. Then the kinetic and gas-dynamic processes can be described on the basis of a unified kinetic equation, obtained by 'averaging' (smoothing) the dynamic equations over the physically infinitesimal volume using the appropriate non-equilibrium Gibbs ensemble. The important feature of this equation is the presence of an additional 'collisions integral', which accounts for the redistribution of particles in ordinary space rather than in the phase space of velocities. In the absence of external forces this integral can be represented as [29]

$$I_R = \nabla(D\,\nabla f)\,,$$

where D is the coefficient of self-diffusion. The inclusion of self-diffusion results in the redefinition of the entropy flux, which is now represented as the sum of convection and diffusion parts,

$$\mathbf{J}^s_{\mathrm{conv}} = (\rho\,\mathbf{u} - D\,\nabla\rho)\bar{s}\,, \qquad \mathbf{J}^s_{\mathrm{dif}} = -\rho D\,\nabla\bar{s}\,, \qquad (2.96)$$

where $\bar{s} = s/\rho$.

For the local Maxwell distribution the heat flux is given by Ref. [29]

$$\mathbf{q} = -\rho D T \nabla\bar{s}\,. \qquad (2.97)$$

The part of entropy production σ associated with the Boltzmann collisions integral then vanishes, but the entropy production due to the additional 'dissipative integral' I_R remains.

Using the expression for the density of entropy $\rho\,\bar{s}$ at local equilibrium, from Eqn (2.97) we get

$$\mathbf{q} = \frac{k}{m}\,TD\,\nabla\rho - \frac{3}{2}\frac{k}{m}\,\rho\chi\nabla T\,. \qquad (2.98)$$

Equation (2.98) actually assumes that $\chi = D$, where χ is the coefficient of temperature conduction.

The important feature of this approach is that the closed set of dissipative gas-dynamic equations in ρ, $\mathbf{u}$, and T formally follows from the kinetic equation without using the perturbation theory in Knudsen number. The entropy production is nonzero even when the state of the gas is determined by the local equilibrium.

It is interesting that the expression for heat flux (2.98) can be reduced to the same form as expression (2.60), which corresponds to the 13-moment approximation or the Burnett approximation. Indeed, using the equation of state $\rho = mp/kT$, we get in place of Eqn (2.98) ($\chi = D$)

$$\mathbf{q} = -\lambda\nabla T + D\,\nabla p\,, \qquad (2.99)$$

where $\lambda = (5k/2m)\rho\chi$ is the heat conductivity of the gas. It is easy to see that Eqn (2.99) coincides with Eqn (2.60).

3. Non-equilibrium thermodynamics of boundary conditions

3.1 General remarks
Inclusion of the Burnett terms into equations of transport ensures a more consistent description of the effects of rarefaction of the gas, which are manifest not only in the second but also in the first order in the expansion in Knudsen number (heat flux due to the gradient of pressure, and pressure diffusion in viscous flow). These may be referred to as bulk effects, since formally they do not depend on the gas-confining surfaces. Equally important effects associated with the rarefaction of the gas are observed near an interface (for example, near the wall of the vessel [39–41]). It is known well that the values of macroscopic parameters for inhomogeneous rarefied gases (velocity, temperature, concentration, etc.) in the immediate vicinity of the streamlined body differ from the corresponding values which characterize the state of the surface. This difference is due to the finite mean free path of the molecules and may be accounted for by introducing certain effective boundary conditions defined as various apparent discontinuities in the macroscopic parameters at the boundary of the condensed phase. This means in fact that the 'sticking' boundary conditions are replaced with 'slipping' boundary conditions [39, 41]. It should be noted that the effects of slipping are rather general and are important not only for gases, but also for condensed media [49, 50].

Considerable progress in the consistent formulation of boundary conditions for slightly rarefied gases was associated with the development of the approximate methods of solution of boundary problems based on the linearized Boltzmann equation [39, 40]. The bulk solutions (obtained by the ChE or Grad's methods) still hold outside of the so-called Knudsen layer (the boundary layer of gas a few mean free paths thick). The behavior of the DF within the Knudsen layer constitutes a separate problem which defies the standard methods of perturbation theory; so this problem is usually treated on the basis of simplified kinetic equations with model collision integrals. A review of the existing methods and results can be found, for example, in the monographs [39, 40]. We should also mention the cycle of works by Sone [51–56], who performed a detailed analysis of the boundary conditions with appropriate corrections for the finite thickness of the Knudsen layer up to the second order terms.

At the same time, the straightforward solution of the Boltzmann equation is not always necessary for deriving the overall structure of the boundary conditions and getting reasonably accurate values of the kinetic coefficients (slipping coefficients). One of the possible approaches consists in using the conservation laws (conservation of the fluxes of momentum or energy in the gas) and the assumption that the DF of the molecules incident on the wall remains the same as in the bulk, without being changed in the Knudsen layer. This approach was used for the first time by Maxwell [57] for the calculation of the viscous and thermal slipping associated with the motion of nonuniformly heated gas near a solid surface. Grad derived more comprehensive conditions of slipping using the 13-moment approximation for the bulk DF [2, 12]. Grad's scheme was later applied to the flows of mixed and polyatomic gases [58, 59]. Unfortunately, neglecting the change in DF in the Knudsen layer results in the loss of certain effects in the boundary conditions. The results can be improved by using the modified Maxwell method (known as the approximate Loyalka method [60, 61]), which is practically equivalent to the simplest selection of the test function in the variation technique, often used in the solution of boundary problems [40, 62, 63].

As in the foregoing discussion of the bulk effects, our main task consists in outlining the applicability of the methods of

NT and demonstrating the linkage between the methods of NT and KT in the formulation of boundary conditions. The practicality of NT in solving certain boundary problems (Couette flow, Poiseuille flow) was first discussed in Refs [64, 65]. Unfortunately, purely technical mistakes in the calculation of slipping coefficients cast doubts on the applicability of NT to boundary problems [66, 67]; further analysis [68, 69], however, proved the complete compatibility of the methods of KT and NT in this respect.

A general scheme for using the NT for formulating the boundary conditions for hydrodynamic equations in the case of slow gas motion was proposed by Waldmann [21, 31 – 33]. In his original work [31] he introduced the production of entropy ΔS_w on the interface, defined as the difference between the total entropy fluxes in the gas and in the condensed phase integrated over the boundary surface. With due account for the conservation of mass, momentum and energy across the interface, and the invariance of ΔS_w with respect to Galileo's transformation, Waldmann reduced the expression for ΔS_w to a bilinear combination of thermodynamic fluxes and forces. The fluxes are the temperature jump, the slipping velocity, and the singular heat flux in the boundary layer, whereas the forces are the off-diagonal part of the stress tensor, as well as the tangential and the normal gradients of temperature.

Later it was discovered that to ensure fulfillment of the Onsager relations it is necessary to include the contribution of the Burnett terms in the entropy flux (and into the surface entropy production)†. The resulting system of phenomenological equations for the case of a non-isothermal plane Poiseuille flow was subsequently verified by the kinetic methods in Refs [70 – 72].

Waldmann's method was subsequently employed for formulating the boundary conditions on the interface between liquid phases [73], multicomponent mixtures [74 – 77], and gases with internal degrees of freedom [78 – 80]. The methods of NT were also used for describing phase transitions [81 – 83].

A considerable disadvantage of Waldmann's method is that in the formulation of the boundary conditions it actually neglects the finite thickness of the Knudsen layer and the flux of mass localized in this layer. As noted already in Refs [84, 85], such an omission leads to the loss of terms in the boundary conditions which are of the same order of magnitude as the terms obtained within the method itself. The scheme for deriving the boundary conditions with due account for the finite thickness of the layer can be developed without too much effort; the structure of the expressions will then be somewhat different, and there will be a number of new relations between the kinetic coefficients [26, 34 – 36]. Such a generalization will be discussed in the sections to follow. To begin with, like in the first part of our review, we shall discuss the linkage between the microscopic (in terms of the DF) and macroscopic (hydrodynamic) descriptions.

3.2 Microscopic boundary conditions
Our formulation of the microscopic boundary conditions by the methods of NT is based on the entropy production ΔS_σ

† Unfortunately, this circumstance was overlooked in the analysis of surface effects in slightly rarefied gases in the well-known monograph [41] (p. 74), which reproduces the erroneous result of Waldmann's original paper [31].

due to the collisions of molecules with streamlined surfaces. The production of entropy ΔS_σ is found by integrating the steady-state equation of balance (2.41) with respect to the infinitesimally thin surface element. Using the Gauss theorem, it is easy to find that the local entropy production per unit area of the surface is

$$\Delta S_\sigma = J^s - J_s^s , \qquad (3.1)$$

where $J^s = (\mathbf{J}^s \mathbf{n})$, $\mathbf{n}$ is the outward normal to the surface, and $\mathbf{J}_s^s$ is the density of entropy flux in the condensed phase. For the density of entropy flux directed from the condensed phase across the interface (in the absence of mass transport), we have

$$J_s^s = \frac{\mathbf{n}\mathbf{J}_q^s}{T_0} , \qquad (3.2)$$

where $\mathbf{J}_q^s$ is the heat flux, and T_0 is the surface temperature. Now we represent the DF of the gas molecules as $f = f_{0w}(1 + \phi)$, where f_{0w} is the absolute Maxwell distribution in equilibrium with the surface, and ϕ is a correction. Using the classical expression (2.42) for the flux of entropy in the gas, and assuming that (in the absence of chemical reactions on the surface) the heat flux in the condensed phase is equal to the energy density flux in the gas, after some straightforward algebra we come to the following expression for entropy production due to collisions of molecules with the surface [43, 45]:

$$\Delta S_\sigma = -k \int (\mathbf{v}\mathbf{n}) f_{0w} \frac{\phi^2}{2} \, \mathrm{d}\mathbf{v} . \qquad (3.3)$$

We represent ϕ as $\phi = \phi^+ + \phi^-$, where ϕ^+ is the non-equilibrium addition to the DF of the molecules escaping from the surface of the walls, and ϕ^- is the addition to the DF of the molecules incident on the walls. Then Eqn (3.3) can be rewritten as

$$\Delta S_\sigma = -k \int f_{0w}(\mathbf{v}\mathbf{n}) \frac{(\phi^+)^2}{2} \, \mathrm{d}\mathbf{v} - k \int f_{0w}(\mathbf{v}\mathbf{n}) \frac{(\phi^-)^2}{2} \, \mathrm{d}\mathbf{v} . \quad (3.4)$$

Regarding $(\mathbf{v}\mathbf{n}) f_{0w} \phi^+$ and $(\mathbf{v}\mathbf{n}) f_{0w} \phi^-$ as thermodynamic fluxes, and ϕ^+ and ϕ^- as thermodynamic forces, we may write the phenomenological equations of NT in the following form [45]:

$$(\mathbf{v}\mathbf{n}) f_{0w} \phi^+ = \int_{(\mathbf{v}\mathbf{n})>0} \chi_{11}(\mathbf{v}' \to \mathbf{v}) \phi^+(\mathbf{v}') \, \mathrm{d}\mathbf{v}'$$
$$+ \int_{(\mathbf{v}\mathbf{n})<0} \chi_{12}(\mathbf{v}' \to \mathbf{v}) \phi^-(\mathbf{v}') \, \mathrm{d}\mathbf{v}' ,$$

$$(\mathbf{v}\mathbf{n}) f_{0w} \phi^- = \int_{(\mathbf{v}\mathbf{n})>0} \chi_{21}(\mathbf{v}' \to \mathbf{v}) \phi^+(\mathbf{v}') \, \mathrm{d}\mathbf{v}'$$
$$+ \int_{(\mathbf{v}\mathbf{n})<0} \chi_{22}(\mathbf{v}' \to \mathbf{v}) \phi^-(\mathbf{v}') \, \mathrm{d}\mathbf{v}' . \qquad (3.5)$$

The Onsager relations are then reduced to the equation

$$\chi_{21}(\mathbf{v}' \to \mathbf{v}) = \chi_{12}(\mathbf{v}' \to \mathbf{v}) . \qquad (3.6)$$

Since the operators χ_{ij} are somehow connected with the operator of scattering of molecules by the surface, it would be

interesting to ascertain the property of the operator corresponding to Eqn (3.6). Traditionally, the boundary conditions are written as [35]

$$(\mathbf{vn})f_{0w}\phi^+ = \int_{(\mathbf{vn})<0} R(\mathbf{v}' \to \mathbf{v})|v_n'|f_{0w}\phi^-(\mathbf{v}')\,\mathrm{d}\mathbf{v}', \quad (3.7)$$

where $R(\mathbf{v}' \to \mathbf{v})$ is the scattering operator. Juxtaposition of Eqns (3.7) and (3.5) yields

$$\chi_{12}(\mathbf{v}' \to \mathbf{v}) = R(\mathbf{v}' \to \mathbf{v})|v_n'|f_{0w}(\mathbf{v}'), \quad \chi_{11} = 0. \quad (3.8)$$

Using the principle of reversibility of the microscopic motion, and considering the motion of molecules inverse to the transition $\mathbf{v}' \to \mathbf{v}$, we may write the boundary condition for the DF of the reverse motion:

$$(\mathbf{vn})f_{0w}\phi_T^- = \int_{(\mathbf{vn})<0} R(\mathbf{v}' \to \mathbf{v})|v_n'|f_{0w}\phi_T^+(\mathbf{v}')\,\mathrm{d}\mathbf{v}'. \quad (3.9)$$

Since $\phi_T^-(\mathbf{v}) = \phi^-(-\mathbf{v})$ and $\phi_T^+(\mathbf{v}) = \phi^+(-\mathbf{v})$, from comparison of Eqns (3.9) and (3.5) we find

$$\chi_{21}(\mathbf{v}' \to \mathbf{v}) = R(-\mathbf{v}' \to -\mathbf{v})|v_n'|f_{0w}(\mathbf{v}'), \quad \chi_{22} = 0. \quad (3.10)$$

As follows from Eqns (3.10) and (3.6),

$$|v_n'|f_{0w}(\mathbf{v}')R(\mathbf{v}' \to \mathbf{v}) = |v_n'|f_{0w}(\mathbf{v}')R(-\mathbf{v}' \to -\mathbf{v}), \quad (3.11)$$

which means that the Onsager relations (3.6) are equivalent to the reciprocal relation for the scattering operator obtained earlier in a different way [86].

Methods of NT offer the simplest among all the existing proofs [38] of the reciprocal relation (3.11).

The boundary conditions (3.5) are sufficient for getting a closed solution of the Boltzmann kinetic equation. In particular, one can construct a solution corresponding to the hydrodynamic approximation. This solution, in turn, can be found from the hydrodynamic transport equations supplemented by the appropriate boundary conditions. Obviously enough, the boundary conditions for these equations should be contained in the boundary conditions (3.5). In other words, it is possible to make a transition from the microscopic boundary conditions to the hydrodynamic ones.

The feasibility of such a transition was thoroughly studied by Waldmann [43, 78, 87–90]. He gave a detailed analysis of the symmetry properties, their linkage with the structure of the solution of the Boltzmann equation, and obtained solutions for a number of particular problems (Couette flow and heat transport between parallel plates). The boundary conditions for the moments of the DF are derived on the basis of the microscopic boundary condition [89]. It must be admitted, however, that in spite of certain advances in the solution of particular problems, Waldmann [89, 90] failed to set up a reliable bridge from the microscopic approach to the hydrodynamic boundary conditions. This is mainly because the same DF was used both for the bulk and for the boundary (Knudsen) layers. This fault was corrected in the works [34–36], where the microscopic entropy production on the interface was used for formulating the hydrodynamic boundary conditions, whereas the structure of boundary conditions was found to be related to the structure of the bulk DF.

This approach will be used in the next section for deriving the microscopic boundary conditions.

3.3 Equations of balance on the interface

In accordance with Refs [34, 35], we introduce a correction into the DF to account for an abrupt change in the parameters of the gas at the boundary (within the Knudsen layer), and write the DF in the form

$$f = f^{(0)}(1 + \Phi + \varphi), \quad (3.12)$$

where Φ is the bulk (for example, ChE) correction to the local Maxwell DF $f^{(0)}$, and φ is the Knudsen correction which vanishes outside the kinetic boundary layer.

Function $f^{(0)}$ in Eqn (3.12) is definite for the values of density, velocity and temperature corresponding to the bulk solution which holds outside the Knudsen layer (let us call these the hydrodynamic parameters). The extrapolated values of these parameters on the streamlined surface may differ from the actual values and from the values at equilibrium with the wall, which is naturally interpreted as the existence of jumps of density, velocity and temperature at the boundary [39].

The correction φ obviously satisfies the homogeneous equation which follows from Eqn (2.74)

$$(\mathbf{v}\nabla)\varphi = L(\varphi) \quad (3.13)$$

and the boundary conditions, which in the absence of chemical reactions on the surface may be written in the form [39, 40]

$$(\mathbf{vn})f(\mathbf{v}, \mathbf{x}_0) = \int_{(\mathbf{v}'\mathbf{n})<0} R(\mathbf{v}' \to \mathbf{v})|\mathbf{v}'\mathbf{n}|f(\mathbf{v}', \mathbf{x}_0)\,\mathrm{d}\mathbf{v}',$$

$$(\mathbf{vn}) > 0. \quad (3.14)$$

Here $\mathbf{x}_0$ is the coordinate on the surface belonging to the surface element δS.

Assuming that the motion is slow, and the jumps of density and temperature across the boundary are small, we have

$$f(\mathbf{v}) = f_{0w}(\mathbf{v})\left[1 + \frac{\delta p(0)}{p_0} + \frac{\delta T(0)}{T_0}\left(\beta v^2 - \frac{5}{2}\right)\right.$$

$$\left. + \frac{m(\mathbf{vu}(0))}{kT_0} + \Phi(0) + \varphi(0)\right], \quad (3.15)$$

where $\delta p(0)$ and $\delta T(0)$ are the jumps of thermodynamic parameters across the boundary with respect to the values p_0 and T_0 at equilibrium with the wall.

Let us consider the problem of gas flowing past a slightly curved surface. We define the orthogonal system of coordinates with the origin at $\mathbf{x}_0$, the x axis directed along the inward normal, and the y and z axes directed along the surface. The length element in such a system will be defined as

$$\mathrm{d}l^2 = \mathrm{d}x^2 + h_y^2\,\mathrm{d}y^2 + h_z^2\,\mathrm{d}z^2, \quad (3.16)$$

where h_y and h_z are the metric coefficients.

Expressing the left-hand side of Eqn (3.13) in these coordinates, multiplying both sides of Eqn (3.13) by $h_y h_z$, and integrating with respect to x from 0 to ∞, we find

$$v_x\varphi(0) = -\frac{1}{h_y(0)h_z(0)}\int_0^\infty h_y h_z L(\varphi)\,\mathrm{d}x + \mathrm{div}_\tau\,\hat{\mathbf{j}}_\tau^\varphi, \quad (3.17)$$

where we have used the definition of two-dimensional divergence of flux

$$\text{div}_\tau \hat{\mathbf{j}}_\tau = \frac{1}{h_y(0)h_z(0)} \left\{ \frac{\partial}{\partial y} \left[h_z(0)\hat{j}_y \right] + \frac{\partial}{\partial z} \left[h_y(0)\hat{j}_z \right] \right\} \quad (3.18)$$

and introduced the two-dimensional flux

$$\hat{\mathbf{j}}_\tau^\varphi = h_z^{-1}(0)\mathbf{e}_y \int_0^\infty h_z v_y \varphi \, dx + h_y^{-1}(0)\mathbf{e}_z \int_0^\infty h_y v_z \varphi \, dx . \quad (3.19)$$

Now we use Eqns (3.17)–(3.19) for expressing the equations of balance of mass, momentum and energy on the interface. With this purpose we integrate Eqn (3.17) over the half-space $v_x > 0$. Using Eqn (3.14) and the property of the scattering operator

$$\int_{v_x > 0} R(\mathbf{v}' \to \mathbf{v}) \, d\mathbf{v} = 1 ,$$

it is easy to find that

$$\int v_x f_{0w} \left[\frac{\delta p(0)}{p_0} + \frac{\delta T(0)}{T_0} \left(\beta v^2 - \frac{5}{2} \right) \right.$$
$$\left. + \frac{m\mathbf{v}\mathbf{u}(0)}{kT_0} + \Phi(0) + \varphi(0) \right] d\mathbf{v} = 0 , \quad (3.20)$$

where the integration is carried out over the entire space of velocities. Since $\Phi(0)$ does not contribute to the macroscopic velocity of the gas, we have

$$nu_x(0) + \int v_x f_{0w} \varphi(0) \, d\mathbf{v} = 0 . \quad (3.21)$$

Making use of the known property of the collisions integral $(1, L(\varphi)) = 0$, with the aid of Eqn (3.17) we find

$$nu_x(0) = -\text{div}_\tau \hat{\mathbf{j}}_\tau^n , \quad (3.22)$$

where

$$\hat{\mathbf{j}}_\tau^n = h_z^{-1}(0)\mathbf{e}_y \int_0^\infty h_z n \, u_y^{\text{Kn}} \, dx + h_y^{-1}(0)\mathbf{e}_z \int_0^\infty h_y n \, u_z^{\text{Kn}} \, dx ,$$

$$\mathbf{u}^{\text{Kn}} = \frac{1}{n} \int \mathbf{v} f_{0w} \varphi \, d\mathbf{v} . \quad (3.23)$$

The quantity $\hat{\mathbf{j}}^n$ is the density of flux of the number of particles localized in the Knudsen layer. Equation (3.22) formally implies that the normal component of the hydrodynamic velocity $u_x(0)$ does not vanish on the interface. This also follows directly from Eqn (3.21), which corresponds to the zero velocity of the gas as defined from the complete DF (the impermeability of the surface).

The equations of balance of momentum and energy on the interface are obtained by multiplying Eqn (3.17) by $m\mathbf{v}$ and $mv^2/2$, respectively, and integrating over the half-space of velocities. The further procedure is similar to that described above. Then for the density of flux of energy we get

$$Q_x(0) - Q_x^f = -\text{div}_\tau \hat{\mathbf{j}}_\tau^q , \quad (3.24)$$

where $Q_x = q_x + P_{xj}u_j$ is the hydrodynamic energy density flux, and Q_x^f is the same defined for the complete DF, or, which is the same, the energy density flux in the streamlined solid. The quantity $\hat{\mathbf{j}}_\tau^q$ is the energy density flux localized in the Knudsen layer. Its definition is similar to Eqn (3.23), with nu_i^{Kn} replaced by

$$Q_i^{\text{Kn}} = \int \frac{mv^2}{2} v_i f_{0w} \varphi \, dv \quad (i = y, z) .$$

For the flux of momentum, owing to its tensor character, we get a more cumbersome equation of balance, which for the thin Knudsen layer can be represented in the form of two relations:

$$P_{xx}(0) - P_{xx}^f = -\text{div}_\tau \hat{\mathbf{j}}_{x\tau}^p + \hat{j}_{\tau\tau'}^p K_{\tau\tau'} \delta_{\tau\tau'} ,$$

$$P_{x\tau}(0) - P_{x\tau}^f = -\text{div}_{\tau'} \hat{\mathbf{j}}_{\tau'\tau}^p + \hat{j}_{x\mu}^p K_{\mu\mu} \delta_{\mu\tau} , \quad (3.25)$$

where $\text{div}_\tau \hat{\mathbf{j}}_{\tau j}^p$ is the divergence of the tensor, and K_{ij} is the tensor of curvature of the surface

$$K_{yy} = \frac{1}{h_y(0)} \frac{\partial}{\partial x} h_y(0) , \qquad K_{zz} = \frac{1}{h_z(0)} \frac{\partial}{\partial x} h_z(0) . \quad (3.26)$$

The first equation in (3.25) may be interpreted as the generalized Laplace equation, where the tensor of Knudsen stress acts as the surface tension.

The above relations indicate that the normal components of hydrodynamic fluxes exhibit discontinuities on the interface. A purely phenomenological description of these discontinuities was first given in Ref. [31] for the density of fluxes of energy and momentum, and in Refs [84, 85] for the flux of mass.

Formally, the phenomenological boundary equations of balance for the fluxes of mass, energy and momentum do not differ from those obtained above using the microscopic approach. From this one might be tempted to conclude that the microscopic approach is supererogatory. But this is not the case. The phenomenological approach [31] assumes that the thickness of Knudsen layer is zero. This assumption itself brings an error into the boundary conditions. Also, it is not quite clear to which portion of the boundary layer (whose thickness is of the order of l) one should refer the macroscopic fluxes on the boundary: to the solid surface, to the outer boundary of the Knudsen layer, or to some effective slipping plane in between. All this adds uncertainty to the physical meaning of the boundary fluxes, and introduces an uncontrollable error into the calculation of physical characteristics when the phenomenological boundary conditions are used.

It is only the microscopic approach that can ascribe a clear physical meaning to the boundary fluxes and formulate the boundary conditions directly on the surface of the solid.

To obtain the suite of boundary conditions supplementary to the equations of balance, including the conditions for fluxes tangential to the circumfused surface, we shall use the methods of NT. We start with the expression (3.1) for entropy production on the interface. The approaches to the formulation of boundary conditions proposed by different authors rely on different methods of calculation of the flux of entropy in the gas. We begin with the method developed in Refs [21, 31–33].

3.4 Phenomenological formulation of macroscopic boundary conditions (Waldmann's method)

The form of expression for the flux of entropy in the gas eventually defines the structure of the resulting boundary conditions. The structure of boundary conditions is also affected by the form of the equations of balance on the interface. Formally, the equations of balance were expressed by Waldmann in his first paper on the NT of boundary conditions [31] based on the phenomenological model. These equations of balance, however, did not account for the transport of mass in the boundary layer, and lacked a consistent definition of the interfacial fluxes of momentum and energy.

Waldmann [31] initially calculated the flow of entropy in the gas in the hydrodynamic approximation. The resulting boundary conditions looked quite sensible, but, as revealed by straightforward calculations, they did not comply with the Onsager relations even in the first approximation in Knudsen number, corresponding to the method selected for calculating the flow of entropy.

To remove this obstacle, Waldmann and colleagues [21, 32, 33] proposed using the Burnett equations of transport (2.58) in the 13-moment approximation for calculating the flux of entropy. These transport equations comport with the entropy flux in the gas from Eqn (2.73),

$$\mathbf{J}^s = +\frac{\mathbf{q}}{T} - \frac{2}{5}\frac{\mathbf{q}\boldsymbol{\pi}}{pT}\,.$$

Using the equations of balance and this expression for the flux of entropy, one can reduce the production of entropy on the interface to the form

$$\Delta S_w = \int \Delta S_\sigma \, \mathrm{d}\Sigma$$

$$= \int \mathrm{d}\Sigma \left[\frac{1}{2}(J_{qn}^s + q_n)\left(\frac{1}{T_0} - \frac{1}{T(0)} + \frac{2}{5pT_0}\,\sigma_{nn}\right)\right.$$

$$+ \frac{\boldsymbol{\sigma}_{\tau n}}{T_0}\left(\mathbf{u}_\tau + \frac{2}{5p}\,\mathbf{q}_\tau\right) + \frac{\hat{\mathbf{j}}_\tau^n}{n}\frac{1}{T_0}\frac{\partial}{\partial\tau}(p + \sigma_{nn})$$

$$\left. - \frac{1}{2}\hat{\mathbf{j}}_\tau^q\frac{\partial}{\partial\tau}\left(\frac{1}{T_0} + \frac{1}{T(0)} - \frac{2}{5pT_0}\,\sigma_{nn}\right)\right]\,. \qquad (3.27)$$

Now we define the fluxes as

$$I_0 = \frac{1}{T_0} - \frac{1}{T(0)} + \frac{2}{5pT_0}\,\sigma_{nn}\,, \qquad \mathbf{I}_1 = \frac{1}{T_0}\left(\mathbf{u}_\tau + \frac{2}{5p}\,\mathbf{q}_\tau\right),$$

$$\mathbf{I}_2 = \hat{\mathbf{j}}_\tau^q = \hat{\mathbf{j}}_\tau^e - \frac{5}{2}\frac{p}{n}\hat{\mathbf{j}}_\tau^n\,, \qquad \mathbf{I}_3 = \frac{\hat{\mathbf{j}}_\tau^n}{n}\,. \qquad (3.28)$$

Then the forces are

$$X_0 = \frac{1}{2}\left(J_{qn}^s + q_n\right), \qquad \mathbf{X}_2 = \frac{1}{2}\frac{\partial}{\partial\tau}\left(\frac{1}{T_0} + \frac{1}{T(0)} - \frac{2}{5pT_0}\,\sigma_{nn}\right),$$

$$\mathbf{X}_1 = \boldsymbol{\sigma}_{n\tau}\,, \qquad \mathbf{X}_3 = \frac{1}{T_0}\frac{\partial}{\partial\tau}\,\pi_{nn}\,. \qquad (3.29)$$

The phenomenological equations (boundary conditions) are

$$I_0 = L_{00}X_0\,, \qquad (3.30)$$

$$\mathbf{I}_k = \sum_{i=1}^{3} L_{ki}\mathbf{X}_i\,, \qquad k = 1, 2, 3\,, \qquad (3.31)$$

and, according to the Onsager principle, $L_{ik} = L_{ki}$.

The phenomenological equations in this form were expressed in Refs [84, 85] using the Waldmann method. They differ from those obtained in Refs [21, 32] by the additional flow $\mathbf{j}_\tau^n$ and force $\partial\pi_{nn}/\partial\tau$. The absence of these terms in the Waldmann boundary conditions is due to the neglect of mass transport in the boundary layer.

Equation (3.30) describes the temperature jump caused by the heat flux normal to the surface. The first equation in (3.31) is related to isothermal ($\mathbf{X}_1$), thermal ($\mathbf{X}_2$) and baric ($\mathbf{X}_3$) slipping. The other two equations describe heat transport in the Knudsen layer and establish the relationship between these fluxes and the effects of slipping of different natures.

Initially [31], Waldmann obtained the boundary conditions not only without the third thermodynamic force, but also without the term $(2/5p)\mathbf{q}_\tau$ in the first flux. It is easy to see that the Onsager relations do not hold for such truncated equations, because the term $(2/5p)\mathbf{q}_\tau$ gives a definitive contribution to the magnitude of the coefficient of thermal slipping K_{TS} [note that $L_{12} + 2\lambda/5p = (\eta/\rho)K_{TS}$]: it contributes $3/2$, whereas the term with L_{12} adds -0.33 [68].

There is yet another contradiction associated with Waldmann's method: in order to obtain the first-order boundary conditions of slipping one has to use the Burnett transport equations. Furthermore, the boundary conditions (3.31) predict some second-order slipping effects — for example, slipping associated with temperature stress — but the values of the relevant kinetic coefficients are incorrect, as shown by straightforward calculations. These contradictions can be avoided by using the kinetic approach to the formulation of boundary conditions by the methods of NT, proposed in Refs [34, 35].

3.5 Kinetic formulation of macroscopic boundary conditions

The calculation of ΔS_σ, as proposed in Refs [34, 35], is based on the kinetic expression for the flux of entropy in the gas taken directly on the surface of the solid. Substituting the complete DF $f = f^{(0)}(1 + \Phi + \varphi)$ into the expression for $\mathbf{J}^s$ (2.71), and with due account for the form of $f^{(0)}$, it is easy to find that

$$\Delta S_\sigma = (\mathbf{Q}^f\mathbf{n})\left[\frac{1}{T_0} - \frac{1}{T(0)}\right] - \frac{1}{T(0)}\,u_i(0)n_k\left[P_{ik}^f - p(0)\delta_{ik}\right]$$

$$- \frac{k}{2}\int(\mathbf{vn})f^{(0)}(\Phi + \varphi)^2\,\mathrm{d}v\,. \qquad (3.32)$$

Recall that Q^f and P_{ik}^f have been defined for the complete DF which includes the Knudsen correction, and $p(0) = n(0)kT(0)$; $n(0)$, $\mathbf{u}(0)$ and $T(0)$ are the extrapolated values of the hydrodynamic parameters on the wall.

It is convenient to split the second term in Eqn (3.32) into parts corresponding to the components of $\mathbf{u}$ and P_{ik}^f normal and tangential to the surface. Furthermore, to transform the last term in Eqn (3.32) we must use the known expression for the bulk DF $\Phi(0)$. The structure of the Knudsen DF in each particular case can be found through its connection with $\Phi(0)$ via the boundary condition (3.14) with due account for Eqn (3.15). The analysis reveals (see, for example, Ref. [34]) that the inclusion of terms of the order of φ^2 in Eqn (3.32) will only result in the renormalization of the kinetic coefficients in the relevant phenomenological equations, without loss of the symmetry properties for the cross coefficients. This allows us to drop the terms of the order of φ^2 in Eqn (3.32), and write

the final expression for ΔS_σ as

$$\Delta S_\sigma = (\mathbf{Q}^f \mathbf{n}) \left[\frac{1}{T_0} - \frac{1}{T(0)} \right] - \frac{1}{T(0)} (\mathbf{u}(0)\mathbf{n}) \left[P_{nn}^f - p(0) \right]$$

$$- \frac{1}{T(0)} \, \pi_{n\tau}^f \mathbf{u}_\tau(0) - \frac{k}{2} \int (\mathbf{v}\mathbf{n}) f^{(0)} (\Phi^2 + 2\Phi\varphi) \, d\mathbf{v}, \quad (3.33)$$

where $\mathbf{u}_\tau(0)$ is the tangential component of the hydrodynamic velocity of the gas, which is actually equivalent to the velocity of slipping at the wall, and $\pi_{n\tau}^f$ is the off-diagonal part of the tensor P_{ik}^f.

Now let us demonstrate how Eqn (3.33) can be used for obtaining a number of phenomenological relations between fluxes and forces on the interface, which serve as some kind of boundary conditions for the hydrodynamic equations and define the contribution to the total transport of mass, momentum and energy from the fluxes localized in the Knudsen layer. For this purpose it will be useful to consider a number of particular typical cases.

3.6 Boundary conditions for tangential fluxes. Examples of fluxes

Let us illustrate the formulation of boundary conditions for the case of flow of simple gas along a flat surface in the presence of inhomogeneous temperature and velocity distributions (the Kramers problem). Given that the temperature gradient $\nabla_\tau T$ is constant, and the transverse gradient of the longitudinal velocity is $\mathbf{u}_\tau' = d\mathbf{u}_\tau/dx$ (with x axis normal to the surface, and vector τ aligned with the surface), the bulk correction is

$$\Phi = v_x \mathbf{v}_\tau \Phi_p \mathbf{u}_\tau' + \Phi_t \mathbf{v}_\tau \nabla_\tau \ln T. \quad (3.34)$$

The correction (3.34) corresponds to the following entropy production:

$$\Delta S = \frac{1}{T} \, \mathbf{u}_\tau(0) \eta \, \mathbf{u}_\tau' + \left[v_x^2 v_\tau^2 \Phi_p \Phi_t \right] \frac{d\mathbf{u}_\tau}{dx} \, \nabla_\tau \ln T$$

$$- \left[v_x^2 \mathbf{v}_\tau \varphi(0) \Phi_p \right] \mathbf{u}_\tau' + \left[v_x \mathbf{v}_\tau \Phi_t \varphi(0) \right] \nabla_\tau \ln T. \quad (3.35)$$

Now let us transform the last two terms in Eqn (3.35). Using Eqn (2.86) and the symmetry property of the collisions operator (2.11), we get

$$\left[v_x \mathbf{v}_\tau \Phi_t \varphi(0) \right] = - \int_0^\infty \left[\mathbf{v}_\tau \Phi_t L(\varphi) \right] dx$$

$$= \int_0^\infty \left[\varphi L(\mathbf{v}_\tau \Phi_t) \right] dx = \int_0^\infty \left[\varphi \mathbf{v}_\tau \left(c^2 - \frac{5}{2} \right) \right] dx = \frac{\hat{\mathbf{j}}_\tau^q}{kT}, \quad (3.36)$$

where $\hat{\mathbf{j}}_\tau^q$ is the heat flux localized in the Knudsen layer.

Using a procedure similar to Eqn (3.36), we can demonstrate that

$$\left[v_x^2 \mathbf{v}_\tau \Phi_p \varphi(0) \right] = 0.$$

As a result, the production of entropy takes on the form

$$\Delta S = \left[\frac{\eta \mathbf{u}_\tau(0)}{kT_0} - a_B \nabla_\tau \ln T \right] \mathbf{u}_\tau' - \frac{\hat{\mathbf{j}}_\tau^q}{kT_0} \, \nabla_\tau \ln T, \quad (3.37)$$

where $a_B = - \left[v_x^2 v_\tau^2 \Phi_p \Phi_t \right]$. This expression for entropy production corresponds to the following phenomenological

equations

$$\frac{\eta \mathbf{u}_\tau(0)}{kT_0} - a_B \nabla_\tau \ln T = \Lambda_{11} \mathbf{u}_\tau' + \Lambda_{12} \nabla_\tau \ln T,$$

$$\frac{\hat{\mathbf{j}}_\tau^q}{kT} = \Lambda_{21} \mathbf{u}_\tau' + \Lambda_{22} \nabla_\tau \ln T, \quad (3.38)$$

where the kinetic coefficients satisfy the Onsager relations $\Lambda_{12} = \Lambda_{21}$. The values of the kinetic coefficients in Eqn (3.38) were calculated by many authors (see Refs [39, 40, 70, 71, 91]). Observe first of all that the calculation of the Burnett coefficient a_B using Φ_p and Φ_t in the first Chapman – Cowling approximation [1] yields

$$a_B = \frac{3}{2} \frac{\eta^2}{mp}.$$

For the rest of the coefficients we shall quote the results obtained by the variation method for the Maxwell model of specular-diffuse reflection of molecules from the wall [70, 71]:

$$\Lambda_{11} = \frac{l\eta}{kT} C_m = \frac{l\eta}{kT} \frac{\sqrt{\pi}}{2} \frac{2-\varepsilon}{\varepsilon} \left(1 + \frac{4-\pi}{2\pi} \varepsilon \right),$$

$$\Lambda_{12} + a_B = \frac{\eta^2}{mp} K_{TS} = \frac{\eta^2}{mp} \frac{3}{4} (1 + 0.5\varepsilon), \quad (3.39)$$

$$\Lambda_{21} = -\frac{\eta^2}{mp} \frac{3}{4} (1 - 0.5\varepsilon), \quad \Lambda_{22} = \frac{l}{k} \lambda C_q = \frac{l}{k} \lambda \frac{9}{10\sqrt{\pi}} \varepsilon,$$

where ε is the coefficient of accommodation of momentum, $l = \eta/\beta^{1/2} p$ is the mean free path, and C_m, K_{TS} and C_q are the coefficients of isothermal and thermal slipping and the Knudsen heat flux. This common notation will be used in our subsequent discussion. It is easy to see that $\Lambda_{12} = \Lambda_{21}$.

The set of equations (3.38) is equivalent to the first two equations in (3.31) obtained by the phenomenological Waldmann method. We ought to point out, however, the following fundamental differences between these two systems.

Firstly, Eqns (3.38) are obtained in the first approximation of the ChE theory, whereas the derivation of Eqns (3.31) required the Burnett transport equations. In this way, the kinetic approach establishes a direct correspondence between the structure (approximation) of the bulk DF and the relevant boundary condition, whereas the phenomenological method does not. Moreover, the required accuracy of calculation of the flux of entropy in Waldmann's method is not known in advance. As indicated above, this leads, for example, to the formulation of incorrect first-order boundary conditions [41] using the formally sound physical reasoning and the hydrodynamic approximation for the flux of entropy. In other words, in the purely phenomenological approach, the accuracy of the entropy calculation has to be adjusted in accordance with the presupposed boundary conditions, which makes the use of methods of NT meaningless.

Secondly, the Onsager relations for Eqn (3.38) hold exactly, whereas the kinetic coefficients L_{12} and L_{21} for Eqn (3.31) are only approximately equal. This is because the coefficient $(2/5)\lambda/p$ in the Waldmann equations and its counterpart $(kT/\eta)a_B$ in Eqn (3.38) are not the same. They only coincide when Φ_t and Φ_p in the expression for a_B are taken in the first Chapman – Cowling approximation. Although in this case the coefficients L_{12} and L_{21} differ little,

this difference is of fundamental importance since it shows that the phenomenological coefficients are not quite consistent with the rigorous relations of the KT and NT. This incongruity increases upon transition to higher-order approximations.

Now let us consider an example of the boundary conditions for the Burnett approximation in the case of gas flow when there is a tangential temperature gradient, and the first and the second derivatives of velocity are nonzero: $\mathbf{u}'_\tau = d\mathbf{u}_\tau/dx$ and $\mathbf{u}''_\tau = d^2\mathbf{u}_\tau/dx^2$. The bulk correction then has the form

$$\Phi = \mathbf{v}_\tau \Phi_t \nabla_\tau \ln T + v_x \mathbf{v}_\tau \Phi_p \mathbf{u}'_\tau + \left(\mathbf{\Phi}^u_{Bxx\tau} + \mathbf{v}_\tau \Phi^v_B\right)\mathbf{u}''_\tau. \quad (3.40)$$

The calculation of entropy production using procedure (3.36) yields

$$\Delta S = \mathbf{u}'_\tau \left[\frac{\eta}{kT_0}\mathbf{u}_\tau(0) - a_B \nabla_\tau \ln T - c_B \mathbf{u}''_\tau\right]$$
$$+ \frac{1}{kT}\hat{\mathbf{j}}^q_\tau \nabla_\tau \ln T + \frac{\eta}{nkT_0}\hat{\mathbf{j}}^n_\tau \mathbf{u}''_\tau, \quad (3.41)$$

where we have used the notation

$$c_B = -\left[\mathbf{v}_\tau \Phi^v_B + \mathbf{\Phi}^u_{Bxx\tau}, v_x^2 \mathbf{v}_\tau \Phi_p\right]. \quad (3.42)$$

The set of phenomenological equations, corresponding to the production of entropy (3.41), may be written in the form

$$\left[\frac{\eta}{kT_0}\mathbf{u}_\tau(0) - a_B \nabla_\tau \ln T - c_B \mathbf{u}''_\tau\right]$$
$$= \Lambda_{11}\mathbf{u}'_\tau + \Lambda_{12}\nabla_\tau \ln T + \Lambda_{13}\mathbf{u}''_\tau,$$
$$\frac{\hat{\mathbf{j}}^q_\tau}{kT_0} = \Lambda_{21}\mathbf{u}'_\tau + \Lambda_{22}\nabla_\tau \ln T + \Lambda_{23}\mathbf{u}''_\tau, \quad (3.43)$$
$$\frac{\eta\hat{\mathbf{j}}^n_\tau}{nkT_0} = \Lambda_{31}\mathbf{u}'_\tau + \Lambda_{32}\nabla_\tau \ln T + \Lambda_{33}\mathbf{u}''_\tau.$$

The kinetic coefficients in Eqns (3.43), supplementary to those in Eqns (3.39) and calculated by the variation technique, are as follows [70]:

$$c_B = -\frac{3}{2}\frac{\eta l^2}{kT}, \qquad \Lambda_{13} = \Lambda_{31} = \frac{18 - 5\varepsilon}{24}\frac{\eta l^2}{kT},$$
$$\Lambda_{32} = \Lambda_{23} = -\frac{\eta^2}{\rho}lC_v = -\frac{\eta^2}{mp}l\frac{7}{4\sqrt{\pi}}\varepsilon, \quad (3.44)$$
$$\Lambda_{33} = -\frac{\eta l^3}{kT}\frac{3}{4\sqrt{\pi}}\varepsilon.$$

Formally, the systems of phenomenological equations (3.31) and (3.43) coincide: each term in Eqns (3.43) has a corresponding term in Eqns (3.31). The coefficients in the two sets, however, are essentially different. Because of this, for example, the relation $L_{13} = L_{31}$ does not hold. While the difference between L_{12} and L_{21} was small, the coefficients L_{13} and L_{31} may differ severalfold. This is because c_B differs severalfold from the respective coefficient in Eqns (3.31). One may conclude therefore that the phenomenological Waldmann method becomes inadequate even in the Burnett approximation.

The set of equations (3.43) allows us to close completely the hydrodynamic transport equations in the first approxima-

tion in Knudsen number (recall that $\eta\mathbf{u}'' = \nabla p$). Let us illustrate this point using the example of the flow of a simple gas in a flat channel of width d in the presence of gradients of temperature ∇T and pressure ∇p. When the Knudsen number $\mathrm{Kn} = l/d$ is small, the velocity profile $\mathbf{u}_H(x)$ (where x is the coordinate across the channel) corresponds to the Poiseuille flow. It differs from the conventional hydrodynamic flow by the slipping on the walls and by the boundary-layer profiles in the fluxes of mass and heat. The bulk velocity and heat flux are given by [71]

$$\mathbf{u}_H(x) = \frac{\nabla p}{2\eta}\left[x^2 - \left(\frac{d}{2}\right)^2\right] + \mathbf{u}_\tau(0),$$
$$\mathbf{q}_H = -\lambda\nabla T + \frac{2}{5}\frac{\lambda T}{p}\nabla p, \quad (3.45)$$

where the last term in the first equation is the velocity of slipping on the wall, and in the second is the Burnett bulk heat flux [see Eqn (2.60)].

The flows of mass and heat averaged across the channel, with due account for the fluxes in the two boundary (Knudsen) layers, are given by

$$\langle\mathbf{u}\rangle = \langle\mathbf{u}_H(x)\rangle + \frac{2}{n}\hat{\mathbf{j}}^n_\tau, \qquad \langle\mathbf{q}\rangle = \langle\mathbf{q}_H\rangle + 2\hat{\mathbf{j}}^q_\tau.$$

Using Eqns (3.45) and (3.43), it will be convenient to represent $\langle\mathbf{u}\rangle$ and $\langle\mathbf{q}\rangle$ in a form characteristic of the discontinuous systems (see Section 4):

$$\langle\mathbf{u}\rangle = -\Lambda_{mm}\frac{\nabla p}{T} - \Lambda_{mq}\frac{\nabla T}{T^2},$$
$$\langle\mathbf{q}\rangle = -\Lambda_{qm}\frac{\nabla p}{T} - \Lambda_{qq}\frac{\nabla T}{T^2}, \quad (3.46)$$

where

$$\Lambda_{mm} = \frac{d^2 T}{12\eta}\left[1 + 6C_m\mathrm{Kn} + 5\varepsilon\mathrm{Kn}^2 - \frac{18\varepsilon}{\sqrt{\pi}}\mathrm{Kn}^3\right],$$
$$\Lambda_{mq} = -K_{TS}\frac{\eta T}{\rho}\left[1 - \frac{14}{3\sqrt{\pi}(1 + 0.5\varepsilon)}\mathrm{Kn}\right],$$
$$\Lambda_{qm} = \frac{2}{5}\frac{\lambda T^2}{p}\left[1 - \frac{1}{2}(1 - 0.5\varepsilon) - \frac{7}{3\sqrt{\pi}}\mathrm{Kn}\right], \quad (3.47)$$
$$\Lambda_{qq} = -\lambda T^2\left[1 - \frac{9\varepsilon}{5\sqrt{\pi}}\mathrm{Kn}\right].$$

Here $\mathrm{Kn} = \beta^{1/2}(\eta/pd)$ and $\lambda = (15/4)(k/m)\eta$.

Each of the coefficients in the Onsager matrix contains a series in Knudsen number up to second-order terms inclusive (recall that $\eta \sim \mathrm{Kn}$ and $\lambda \sim \mathrm{Kn}$). The most obvious is the structure of Λ_{mm}. In this case the parabolic profile is defined by the term $(-d^2/12\eta)\nabla p$, while the slipping effects associated with the first and the second derivatives of the hydrodynamic velocity (isothermal slipping of the first and the second order, respectively), are of the order of Kn and Kn^2. In addition, there is a contribution to $\langle\mathbf{u}\rangle$ due to the distortions of the flow velocity profile in the Knudsen layer. Also, there are two terms of different order, which are associated with $\mathbf{u}'_H$ and $\mathbf{u}''_H$ and whose contribution is of the order of Kn^2 and Kn^3 with respect to the bulk flow.

For the heat flow, associated with the temperature gradient, the contribution from the Knudsen terms is of the order of Kn with respect to the bulk term, which describes heat transport by the conventional mechanism of heat conduction. This contribution is determined by the boundary-layer distortion of the heat flux profile, which remains constant in the bulk.

An interesting situation is observed in relation to the reciprocal phenomena: mass transport by the temperature gradient, and isothermal heat transport by the pressure gradient. It is easy to see that the cross coefficients satisfy the Onsager relations ($\Lambda_{mq} = \Lambda_{qm}$). The nature of the individual contributions to each of these coefficients, however, is different. For example, in the first order in Kn in the expression for $\langle \mathbf{u} \rangle$, the leading term is associated with the coefficient $K_{TS} = (3/4)(1 + 0.5\varepsilon)$, which describes thermal slipping. The correction of the order of Kn is determined by the distortion of the velocity profile in the boundary layer.

Concerning the isothermal heat flow, the fulfillment of the Onsager relations in the first order in Knudsen number is ensured by the inclusion of two terms, namely, the bulk (Burnett) flow $\sim (2/5)(\lambda T \nabla p/p)$, and the Knudsen heat flow associated with $\mathbf{u}'_H$, whose contribution is of the same order as that of the bulk term. The next-order term in Kn is due to the Knudsen-layer distortion of the isothermal bulk flux of heat, which is nonuniform in the cross-section.

The set of equations (3.43) also exemplifies the structure of boundary conditions which may be obtained using other Burnett and super-Burnett corrections to the DF. The form of the boundary conditions in the Burnett approximation has been considered in detail in Ref. [35] for a simple gas, and in Refs [26, 71, 92, 93] for a mixture of gases. Let us name the specialities of the Burnett boundary conditions supplementary to those defined in Eqns (3.43). The Burnett boundary conditions exhibit terms of two types. For example, in addition to the second derivative of the velocity $\mathrm{d}^2 \mathbf{u}_\tau/\mathrm{d}x^2$, there are thermodynamic forces expressed in terms of other partial derivatives of the velocity. The suite of thermodynamic forces also includes the second derivatives of the temperature of the gas, which serve a dual purpose: on the one hand, they reflect the structure of the bulk DF of the Burnett approximation, and on the other hand they reflect the change in the Knudsen DF along the surface [these terms are associated with the second term on the right-hand side of Eqn (3.17)]. The additional terms reflect slipping effects of a new type — in particular, the second-order slipping coefficients start to exhibit a dependence on the coefficients of accommodation of energy, while the boundary heat fluxes start to depend on the coefficients of accommodation of momentum, and so on.

Some of these effects cannot, in principle, be predicted within the framework of the phenomenological approach. This is because such an approach allows the inclusion into the boundary conditions only a finite number of the integral characteristics of the boundary layer which enter the equations of balance. Non-physical fluxes in the Knudsen layer cannot, in principle, arise in the boundary conditions of purely phenomenological origin. At the same time, in the kinetic approach they naturally [via the term $k/2 \int \Phi(0)\varphi(0)(\mathbf{vn})f^{(0)}\,\mathrm{d}\mathbf{v}$] appear in the boundary-layer entropy production, and hence in the boundary conditions. Again we arrive at the conclusion that Waldmann's phenomenological method fails for effects which go beyond the limits of the hydrodynamic approximation.

3.7 Boundary conditions for fluxes normal to the surface

Let us discuss the specific features of the boundary conditions obtained from the kinetic entropy production, using the example of fluxes normal to the surface. Neglecting the last term in Eqn (3.32), directly related to the structure of Φ, we may write the expression for entropy production as

$$\Delta S_\sigma = -\frac{Q_n^f}{T_0}\frac{T(0) - T_0}{T_0} - \frac{1}{T_0}u_n(0)\left[P_{nn}^f - p(0)\right], \quad (3.48)$$

where $u_n(0)$ is the projection of the hydrodynamic velocity onto the outward normal of the surface. This entropy production corresponds to a pair of phenomenological equations for the boundary jumps of temperature and normal components of the stress tensor of the form

$$\frac{T(0) - T_0}{T_0} = L_{00}\frac{Q_n^f}{T_0} + L_{01}\frac{u_n(0)}{T_0},$$

$$P_{nn}^f - p(0) = L_{10}\frac{Q_n^f}{T_0} + L_{11}\frac{u_n(0)}{T_0}. \quad (3.49)$$

By contrast to the purely phenomenological equations [31 – 33, 84, 85], from Eqns (3.49) it follows that the temperature jump depends not only on the flow of heat across the interface, but also on the new thermodynamic force $u_n(0)$, which, as demonstrated above, may be nonzero even for impermeable surfaces. Relations similar to Eqns (3.49) have earlier been obtained for the cases when phase transitions (like evaporation or condensation [94]) take place on the interface. The second equation in (3.49) describes the effect of the difference between the gas pressure and the normal stress applied to the streamlined surface. It is analogous to the vapor pressure jump in case of evaporation from the surface. This effect may be interpreted as the existence of a certain non-equilibrium surface tension in the non-equilibrium gas. In the case of a temperature gradient normal to the surface, this effect is associated with the temperature profile in the Knudsen layer. In general, it is closely related to the Knudsen stresses which develop in non-equilibrium gases close to the interfaces. As demonstrated in Ref. [35], the non-equilibrium surface tension is manifested similarly to the classical interface tension caused by surface stresses [95].

Observe that in Waldmann's method, even though it takes into account the transport of mass in the Knudsen layer, the boundary conditions do not include the second equation in (3.49), notwithstanding the fact that this system has been obtained in the lowest approximation of the kinetic method. When the higher terms in the production of entropy are included, the divergence between the kinetic and phenomenological results increases [35]. Thus, the phenomenological approach fails not only in supplying the correct values of the kinetic coefficients, but also in the formulation of the boundary conditions themselves.

The reason for the inadequacy of the phenomenological approach is clear from the analysis carried out in Section 2. As we go beyond the hydrodynamic approximation, the equations of NT, including the boundary conditions, must involve non-physical fluxes. It is not possible to justify the introduction of non-physical fluxes within the framework of purely phenomenological approach, because the non-equilibrium DF carries much more information than any finite set of transport equations. Knowing the connection between information and entropy, we may argue that the phenomen-

ological approach, based on the hydrodynamic transport equations, is dealing with incomplete information (entropy), and therefore the resulting boundary conditions are also incomplete. In the kinetic approach there is no such loss of information (entropy), which permits the correct boundary conditions in the required approximation to be obtained.

3.8 Boundary conditions on a liquid – vapor interface

This approach can be employed for formulating the boundary conditions for a liquid – vapor interface. In case of flat stationary surfaces the boundary conditions were obtained by Waldmann's method in Refs [81, 82] in a form close to Eqns (3.49). As compared with solid surfaces, however, liquid surfaces have additional degrees of freedom associated with their complex motion. Because of this, additional fluxes and forces come up in the calculations of entropy production on the liquid surface. They may be of scalar, vector, or tensor dimension. Thermodynamic forces are expressed by combining the ∇ operators and the velocity of motion of the liquid surface. These additional forces have a quite definite physical meaning. The DF of molecules inelastically scattered by (or escaping from) a non-uniformly moving surface is different from the Maxwell distribution. This difference will affect the transport of mass, momentum and energy in the boundary layers, and eventually modify the hydrodynamic boundary conditions. The boundary conditions for liquid surfaces have been considered in sufficient detail in Ref. [96] using the phenomenological approach, and in Ref. [97] on the basis of kinetic entropy production. The interested reader may refer to these publications. Here we shall discuss just one remarkable effect associated with the jumps of vapor temperature and pressure on the surface of evaporation.

We are speaking of the effect of inversion of the temperature profile predicted in Ref. [98]: in the vapor phase between two liquid surfaces the slope of the temperature profile may be opposite to that predetermined by the difference in the temperatures of liquids. This effect was discussed in detail in the context of both KT [99 – 102] and NT [103, 104], and was found to be in agreement with the second law of thermodynamics. We shall need the phenomenological equations on the surface of evaporation, which have the form [104]

$$T(0) - T_0 = -l_{11}Q_n - l_{12}u_n(0),$$

$$\frac{T_0\big[p(0) - p_0\big]}{\rho_0} = -l_{21}Q_n - l_{22}u_n(0), \tag{3.50}$$

where p_0 is the equilibrium vapor pressure over the flat liquid surface; T_0 is the temperature of the surface; $T(0)$ and $p(0)$ are the extrapolated values of temperature and pressure on the liquid surface, Q_n is the heat flow across the surface, and $\rho_0 u_n(0)$ is the rate of evaporation. The minus signs in Eqns (3.50) emphasize that the coefficients l_{ij} are positive.

We denote the temperature corresponding to the equilibrium between liquid and vapor at pressure $p(0)$ by T_p. Then, using the Clapeyron – Clausius equation, we may write

$$\frac{T_0\big[p(0) - p_0\big]}{\rho_0} = (T_p - T_0)L, \tag{3.51}$$

where L is the heat of vaporization.

Now let us consider the following situation. Let there be a flat gap filled with vapor between two liquid volumes. The liquids are kept at temperatures T_1 and T_2 (Fig. 1). We want to find the vapor temperature profile in the gap. Assume that the temperatures of the liquids T_1 and T_2 are actually maintained some distance away from the interfaces, whereas the temperatures of the interfaces T_{01} and T_{02} are found from the self-consistent solution of the problem. For the sake of definiteness, let $T_1 > T_2$; then the liquid evaporates from surface 1 and condenses on surface 2. We also assume that the rate of evaporation and the free path length (compared to H) are small. Then it is obvious that the vapor pressure in the gap in the first approximation is constant. This implies that T_p is also constant, and the heat flow is zero. Using Eqns (3.50) and (3.51), for the temperatures of liquid surfaces we find:

$$T_{01} = T_p + \frac{l_{22}}{L}u_n, \qquad T_{02} = T_p - \frac{l_{22}}{L}u_n. \tag{3.52}$$

Using the first equation in (3.50), applied to the surfaces at $x = 0$ and $x = H$, we get

$$T(0) = -\frac{l_{12} - l_{22}}{L}u_n + T_p,$$

$$T(H) = \frac{l_{12} - l_{22}}{L}u_n + T_p. \tag{3.53}$$

From Eqn (3.53) we see that at $L > l_{22}/l_{12}$ the slope of the temperature profile in the vapor phase is opposite to that predetermined by the existing temperature difference.
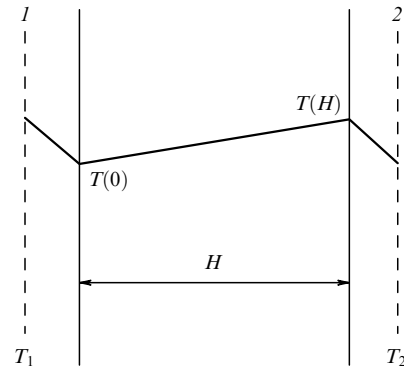

Figure 1. Temperature profile formed in the problem of evaporation when $T_1 > T_2$.

The kinetic coefficients l_{ij} have been calculated by different authors. For example, the values obtained in Ref. [94] for the case of complete accommodation are

$$l_{12} = T_0\,\frac{1}{\rho_0\sqrt{2RT_0}}\,\frac{1}{8}\,\sqrt{\pi}\left(1 + \frac{16}{5\pi}\right),$$

$$l_{22} = RT_0^2\,\frac{1}{\rho_0\sqrt{2RT_0}}\,\frac{1}{2}\,\sqrt{\pi}\left(\frac{9}{8} + \frac{4}{\pi}\right). \tag{3.54}$$

The inverse profile occurs at $L > 4.73RT_0$. Since we always have $L > 10RT_0$, the inverse profile must be observed for all liquids.

From the arguments developed above it also follows that the inverse temperature profile should be formed near a single surface of evaporation.

4. Non-equilibrium thermodynamics and the kinetic theory of discontinuous systems

4.1 Phenomenological relations

The methods of NT are widely used for so-called discontinuous systems, usually consisting of two volumes separated by a capillary, porous wall or membrane [3]. Assume that the system is filled with a gas mixture of N components, and that the temperature, pressure, and concentrations of components in the two volumes are different. The change in the parameters of the mixture in each volume is described by the equations of balance of matter and energy, which are expressed with due account for the transport of mass and heat through the connecting channel. The relevant fluxes, averaged over the cross section of the channel, are expressed in the quasi-stationary approximations, corresponding to the conventional steady-state expressions with slowly changing values of parameters in the volumes (that is, at the inlet and outlet of the channel). The side walls of the channel are adiabatically insulated and impermeable, so that the transport only occurs along the channel.

According to the classical NT of discontinuous systems [3], the linear phenomenological expressions for the fluxes can be obtained by averaging the local fluxes of mass and energy over the cross section of the channel, which are in turn found from the conventional expressions for entropy production in the gas mixture. The averaging procedure only leads to the redefinition of phenomenological coefficients, which still satisfy the Onsager relations. The KT, based on the linearized Boltzmann equation, not only validates such linear relations between fluxes and thermodynamic forces, but also establishes the explicit form of the kinetic coefficients in the Onsager matrix. The methods of calculation of these coefficients for specific boundary conditions on the walls of the channel have been considered for arbitrary Knudsen numbers ($\mathrm{Kn} = 1/a$, where a is the characteristic transverse dimension of the channel) and channels of different geometry in many publications [44, 71, 105–113]. As a rule, the treatment was based on the model expressions for the linearized collisions integral. At the same time, it is possible to obtain rather general relations for the fluxes of mass and heat in the channel on the basis of the kinetic equation with the exact collisions integral. This approach was pursued in Refs [72, 92, 93, 114, 115]. The analysis based, among other things, on the kinetic expression for entropy production in the channel, allows a considerable extension of the system of linear phenomenological equations for the fluxes. It also becomes possible to separate the contributions associated with the Burnett terms and the transport of mass and heat localized in the Knudsen layer [72, 92, 93]. As in our previous discussion, the methods of KT will considerably enrich the content and substance of the results obtained through the purely phenomenological approach within the framework of NT.

Let us recall some relations of the NT of discontinuous systems using the example of a binary gas mixture. The phenomenological expression for entropy production in a unit volume of the channel is then written as [3, 44]

$$\langle \Delta S \rangle = -\langle u_m \rangle \frac{\nabla_z p}{T} - \langle h \rangle \frac{\nabla_z T}{T^2} - \frac{p}{T}\big(\langle u_1 \rangle - \langle u_2 \rangle\big)\nabla_z y_1 . \quad (4.1)$$

Here $\langle u_\alpha \rangle$ is the macroscopic velocity of component α,

$$n\langle u_m \rangle = \sum_{\alpha=1}^{2} n_\alpha \langle u_\alpha \rangle$$

is the average molar flow rate of the mixture,

$$\langle h \rangle = \langle q \rangle - \frac{5}{2}\sum_{\alpha=1}^{2} p_\alpha \langle w_\alpha \rangle$$

is the reduced heat flow. By $\nabla_z p$, $\nabla_z T$ and $\nabla_z y_1$ we denote the gradients of pressure, temperature and relative concentration of component 1 along the channel (z axis); angle brackets $\langle \ldots \rangle$ denote averaging over the cross section of the channel. Observe that the difference in the velocities of components actually determines the diffusion flow of component 1 in the frame where $\langle u_m \rangle = 0$, since $J_{1D} = n_1\big(\langle u_1 \rangle - \langle u_m \rangle\big) = n y_1 y_2\big(\langle u_1 \rangle - \langle u_2 \rangle\big)$.

The production of entropy ΔS has the form of a bilinear combination of fluxes and thermodynamic forces. The relevant linear phenomenological relations are

$$\begin{matrix} \langle u_m \rangle \\ \langle u_1 \rangle - \langle u_2 \rangle \\ \langle h \rangle \end{matrix} = -\begin{pmatrix} \Lambda_{mm} & \Lambda_{m1} & \Lambda_{mq} \\ \Lambda_{1m} & \Lambda_{11} & \Lambda_{1q} \\ \Lambda_{qm} & \Lambda_{q1} & \Lambda_{qq} \end{pmatrix}\begin{pmatrix} T^{-1}\nabla_z p \\ pT^{-1}\nabla_z y_1 \\ T^{-2}\nabla_z T \end{pmatrix}. \quad (4.2)$$

The coefficients Λ_{ik} satisfy the Onsager reciprocal relations, $\Lambda_{ik} = \Lambda_{ki}$.

In hydrodynamics and in the KT of gas mixtures it is more convenient to use the mass-averaged velocity $\langle u \rangle = \sum_\alpha (\rho_\alpha/\rho)\langle u_\alpha \rangle$. It is easy to see that $\langle u \rangle$ and $\langle u_m \rangle$ for a binary mixture are linked by

$$\langle u \rangle = \langle u_m \rangle + \frac{m_1 - m_2}{\rho} J_{1D}. \quad (4.3)$$

Then in place of the system (4.2) we have [116–118]

$$\begin{matrix} \langle u_m \rangle \\ \langle u_1 \rangle - \langle u_2 \rangle \\ \langle h \rangle \end{matrix} = -\begin{pmatrix} \lambda_{mm} & \lambda_{m1} & \lambda_{mq} \\ \lambda_{1m} & \lambda_{11} & \lambda_{1q} \\ \lambda_{qm} & \lambda_{q1} & \lambda_{qq} \end{pmatrix}\begin{pmatrix} T^{-1}\nabla_z p \\ pT^{-1}\nabla_z d_{1z} \\ T^{-2}\nabla_z T \end{pmatrix}, \quad (4.4)$$

where $d_{1z} = \nabla_z y_1 + (y_1 - \rho_1/\rho)\nabla_z \ln p$, and the coefficients in the Onsager matrix satisfy the symmetry relation.

Now let us turn to the kinetic analysis of the problem.

4.2 Kinetic expressions for averaged fluxes in the channel

Consider the flow of a multicomponent gas mixture in a round cylindrical capillary of radius R under the action of the gradients of pressure $(k = p^{-1}\nabla_z p)$, temperature $(\tau = T^{-1}\nabla_z T)$ and concentration $(s_\alpha = \nabla_z y_\alpha)$. We assume that p, T, and y_α change little over the characteristic mean free path length of the molecules, and so $|kl| \ll 1$, $|\tau l| \ll 1$, $|s_\alpha l| \ll 1$.

For slow flows of mixture in the channel, the DF of molecules of kind α is sought in the form

$$f_\alpha(\mathbf{v}_\alpha, r) = f_\alpha^{(0)}\big[1 + \Phi_\alpha(\mathbf{v}_\alpha, \mathbf{x}_\perp)\big],$$

$$f_\alpha^{(0)} = f_{\alpha 0}\left[1 + kz + \left(\beta_\alpha v_\alpha^2 - \frac{5}{2}\right)\tau z + y_\alpha^{-1}s_\alpha z\right]. \quad (4.5)$$

Here $\mathbf{x}_\perp$ is the two-dimensional radius vector in the transverse cross section of the channel, and the subscript 0 corresponds to the absolute Maxwell distribution.

The non-equilibrium correction Φ_α satisfies the system of linearized equations of the form [93, 107]

$$\mathbf{v}_{\alpha\perp}\frac{\partial \Phi_\alpha}{\partial \mathbf{x}_\perp} + v_{\alpha z}\left(\beta_\alpha v_\alpha^2 - \frac{5}{2}\right)\tau = \sum_\beta L_{\alpha\beta}(\Phi_\alpha, \Phi_\beta)\,, \qquad (4.6)$$

which must be supplemented by the boundary conditions on the wall of the channel [107, 119]:

$$\Phi_\alpha(\mathbf{x}_\alpha^F, \mathbf{v}_\alpha) = A\Phi_\alpha(\mathbf{x}_\perp^F, \mathbf{v}_\alpha)\,, \qquad \mathbf{v}_{\alpha\perp}\mathbf{n}_\perp(\mathbf{x}_\perp^F) > 0\,, \qquad \mathbf{x}_\perp^F \in \mathrm{d}F\,. \tag{4.7}$$

Here A is the generalized boundary operator satisfying the reciprocal relation, $\mathbf{n}_\perp(\mathbf{x}_\perp^F)$ is the unit normal at point $\mathbf{x}_\perp^F$ of the channel surface, and $\mathrm{d}F$ is an infinitesimal surface element.

We make use of the known integral relations of the ChE method, which arise in the solution of the problem of diffusion and heat conduction in an infinite space [48, 116]:

$$\frac{n}{n_\alpha}\left(\delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho}\right)v_{\alpha z} = \sum_\beta L_{\alpha\beta}(v_z\Phi_d^\gamma)\,,$$

$$\left(\beta_\alpha v_\alpha^2 - \frac{5}{2}\right)v_{\alpha z} = \sum_\beta L_{\alpha\beta}(v_z\Phi_t)\,. \tag{4.8}$$

It is easy to see that the diffusion velocity $\langle w_\alpha \rangle = \langle u_\alpha \rangle - \langle u \rangle$ and the reduced heat flow $\langle h \rangle$, averaged over the cross-section of the channel s, are given by

$$\langle w_{\gamma z}\rangle = \frac{1}{s}\int_s \mathrm{d}s\left[\int \frac{1}{n}\sum_\beta \frac{n}{n_\beta}\left(\delta_{\beta\gamma} - \frac{\rho_\beta}{\rho}\right)v_{\beta z}f_{\beta 0}\Phi_\beta \,\mathrm{d}\mathbf{v}_\beta\right]\,,$$

$$\langle h_z\rangle = \frac{kT}{s}\int_s \mathrm{d}s\left[\int \sum_\alpha \left(\beta_\alpha v_\alpha^2 - \frac{5}{2}\right)v_{\alpha z}f_{\alpha 0}\Phi_\alpha \,\mathrm{d}\mathbf{v}_\alpha\right]\,. \tag{4.9}$$

Using Eqns (4.8) and the symmetry property of the linearized collisions operator $([\Phi, L\Psi] = [\Psi, L\Phi])$, we may rewrite Eqns (4.9) as

$$\langle w_{\gamma z}\rangle = \frac{1}{ns}\int_s \left[\Phi, L(v_z\Phi_d^\gamma)\right]\mathrm{d}s = \frac{1}{ns}\int_s \left[\Phi_d^\gamma, L(v_z\Phi)\right]\mathrm{d}s\,,$$

$$\langle h_z\rangle = \frac{kT}{ns}\int_s \left[\Phi, L(v_z\Phi_t)\right]\mathrm{d}s = \frac{kT}{ns}\int_s \left[\Phi_t, L(v_z\Phi)\right]\mathrm{d}s\,, \quad (4.10)$$

where we have used the notations

$$[\Phi, \Psi] = \sum_\alpha \int f_{\alpha 0}\Phi_\alpha \Psi_\alpha \,\mathrm{d}\mathbf{v}_\alpha\,, \qquad L(v_z\Psi_\alpha) = \sum_\beta L_{\alpha\beta}(v_z\Psi_\alpha)\,. \tag{4.11}$$

Replacing $L(\Phi)$ in the integrands with the left-hand side of the kinetic equation (4.6), and integrating with respect to velocities and the cross-section of the channel, we get [93]

$$\langle w_{\alpha z}\rangle = -\sum_\beta D_{\alpha\beta}d_{\beta z} - D_{T\alpha}\nabla_z\ln T + \frac{2}{nR}M_d^\alpha(R)\,,$$

$$\langle h_z\rangle = -\lambda'\nabla_z T - kT\sum_\beta D_{T\beta}nd_{\beta z} + \frac{2kT}{R}M_q(R)\,. \quad (4.12)$$

Here λ' is the coefficient of heat conductivity,

$$\lambda' = -k\left[v_z\Phi_t, v_z\left(\beta v^2 - \frac{5}{2}\right)\right]\,, \tag{4.13}$$

and $D_{\alpha\beta}$ and $D_{T\alpha}$ coincide with the definitions of the coefficients of multicomponent diffusion and thermal diffusion [48]. The right-hand side of Eqns (4.12) also carries the moments of the DF on the wall of the channel, which turn out to be the functionals of the known solutions $\Phi_{d\alpha}^\gamma$ and $\Phi_{t\alpha}$:

$$M_d^\alpha(R) = \left[v_z\Phi_d^\alpha, v_r\Phi(R)\right]\,, \qquad M_q(R) = \left[v_z\Phi_t, v_r\Phi(R)\right]\,. \tag{4.14}$$

Observe that the expressions for the diffusion velocity and heat flow (4.12) do not formally contain the terms related to the Burnett contributions. At the same time, as follows from the results quoted in Section 2.5 of this review, these terms (the heat flow due to the gradient of pressure, and pressure diffusion in viscous flow) must certainly appear in the relevant expressions. The problem is easily resolved if we recall that the bulk (Burnett) contributions are contained in the values of the moments of the DF on the channel walls. Appropriate calculations (see Refs [72, 93]) give

$$\langle w_{\alpha z}\rangle = -\sum_\beta D_{\alpha\beta}d_{\beta z} - D_{T\alpha}\nabla_z\ln T - \frac{b_\alpha}{\eta}\nabla_z p + \frac{\hat{j}_{w\alpha}}{n_\alpha}\,,$$

$$\langle h_z\rangle = -\lambda'\nabla_z T - p\sum_\beta D_{T\beta}(d_{\beta z} + K_{T\beta}\nabla_z\ln T)$$

$$- a_{\mathrm{B}}\frac{kT}{\eta}\nabla_z p + \hat{j}_q\,. \tag{4.15}$$

Here we have introduced the thermal diffusion relations, so that

$$\sum_\beta D_{\alpha\beta}K_{T\beta} = D_{T\alpha}\,, \qquad \sum_\alpha K_{T\alpha} = 0$$

and the total coefficient of heat conductivity of the mixture is

$$\lambda = \lambda' - nk\sum_\alpha K_{T\alpha}D_{T\alpha}\,.$$

The coefficients b_α and a_{B} are given by the expressions below, and correspond to the Burnett approximation because they can be expressed in terms of $\Phi_{\mathrm{B}\alpha}$ [93]:

$$b_\alpha = -\langle v_z\Phi_d^\alpha, v_r^2 v_z\Phi_p\rangle = -\frac{1}{2}\frac{n_\alpha}{n}\int v_{\alpha z}f_{\alpha 0}\Phi_{\mathrm{B}\alpha}\,\mathrm{d}\mathbf{v}_\alpha\,,$$

$$a_{\mathrm{B}} = -\langle v_z\Phi_t, v_r^2 v_z\Phi_p\rangle = -\frac{1}{2}\left\langle v_z\left(\beta v^2 - \frac{5}{2}\right), v_z\Phi_{\mathrm{B}}\right\rangle\,. \tag{4.16}$$

The moments of the Knudsen DF $j_{w\alpha}$ and j_q correspond to the diffusion and heat fluxes localized in the Knudsen layer (see similar expressions in Section 3.6), and can be written as [93]

$$\frac{\hat{j}_{w\alpha}}{n_\alpha} = \frac{2}{nR}\left[v_z\Phi_d^\alpha, v_r\varphi(R)\right]$$

$$= \frac{1}{s}\int_s \mathrm{d}s\int \frac{1}{n}\sum_\beta \frac{n}{n_\beta}\left(\delta_{\beta\alpha} - \frac{\rho_\beta}{\rho}\right)v_{\beta z}f_{\beta 0}\varphi_\beta \,\mathrm{d}\mathbf{v}_\beta\,,$$

$$\frac{\hat{j}_q}{kT} = \frac{2}{R}\left[v_z\Phi_t, v_r\varphi(R)\right]$$

$$= \frac{1}{s}\int_s \mathrm{d}s\int \sum_\beta \left(\beta_\beta^2 - \frac{5}{2}\right)v_{\beta z}f_{\beta 0}\varphi_\beta \,\mathrm{d}\mathbf{v}_\beta\,. \tag{4.17}$$

Here we do not reproduce the detailed derivation of the expression for the mass-averaged velocity of the mixture $\langle u_z \rangle$ averaged over the cross-section of the channel. The final result may be written as [72, 93]

$$\langle u_z \rangle = -\frac{R^2}{8\eta}\nabla_z p + u_h(R) + \frac{\hat{j}_m}{\rho}, \tag{4.18}$$

where

$$\frac{\hat{j}_m}{\rho} = \frac{kT}{\eta}\frac{1}{R}\left[v_z\Phi_B, v_r\varphi(R)\right] = \frac{1}{s}\int_s \mathrm{d}s \int \sum_\alpha \frac{m_\alpha}{\rho}v_{\alpha z}f_{\alpha 0}\varphi_\alpha \,\mathrm{d}\mathbf{v}_\alpha. \tag{4.19}$$

Observe that the Burnett coefficients a_B and b_α can be calculated with the aid of Eqn (4.16) on the basis of the known solutions in the first approximation of the ChE method. A complete definition of the cross-section-averaged values of velocity and heat fluxes requires finding the slipping velocity $u_h(R)$ and the fluxes localized in the Knudsen layer. The latter can be calculated using the well-developed methods for solution of the linearized equation for boundary problems [40].

We have quoted some results of such calculations in the previous section for the case of a gas flow in a flat channel [see Eqns (3.46) and (3.47)]. Let us consider another characteristic example related to the calculation of the diffusion flow averaged over the cross-section of the channel for small Knudsen numbers. Using Eqns (4.15), we write the expression for $J_{1D} = ny_1y_2\left(\langle w_1 \rangle - \langle w_2 \rangle\right)$ for a binary gas mixture in the form

$$J_{1D} = -n[D_{12}]_1\left[\nabla_z y_1 + \left(y_1 - \frac{\rho_1}{\rho}\right)\nabla_z \ln p\right.$$
$$\left. + [\alpha_T]_1 y_1 y_2 \nabla_z \ln T\right] - (b_2 - b_1)\frac{1}{\eta}\nabla_z p + (y_2 j_{w1} - y_1 j_{w2}). \tag{4.20}$$

The term in square brackets corresponds to the conventional result of the first approximation of the ChE method [1, 48]. Straightforward calculation of the higher-order (Burnett and Knudsen) terms reveals that their contribution in the first approximation in Knudsen number is comparable with the pressure diffusion term which appears in square brackets in Eqn (4.20). Calculating b_α on the basis of the expression for $\Phi_{d\alpha}^B$ which corresponds to the inclusion of only one term in the expansion in the Sonin polynomials [1, 48], we get [92]

$$b_2 - b_1 = \frac{nm_1m_2}{\rho kT}[D_{12}]_1\left(y_1\frac{\eta_2}{\eta} - y_2\frac{\eta_1}{\eta}\right), \tag{4.21}$$

where η_α is the partial coefficient of viscosity, and $[D_{12}]_1$ is the coefficient of mutual diffusion, both calculated in the first Chapman–Cowling approximation.

It is easy to see that result (4.21) leads to the redefinition of the coefficient of pressure diffusion, and the expression for J_{1D} coincides with Eqn (2.62) obtained in Grad's 13-moment approximation [20].

The fluxes localized in the Knudsen layer were calculated in Refs [71, 120] using the approximate Loyalka method [60, 61], which corresponds to the simplest approximation of the variation technique [119]. Adding the contributions from these fluxes in the first approximation in Knudsen number, we come to the following final expression for the averaged

diffusion flow in the channel:

$$J_{1D} = -n[D_{12}]_1\left[\nabla_z y_1 + \bar{\alpha}_p y_1 y_2 \nabla_z \ln p + [\alpha_T]_1 y_1 y_2 \nabla_z \ln T\right], \tag{4.22}$$

where the constant of pressure diffusion, calculated for the model of purely diffuse scattering by the wall ($\varepsilon_\alpha = 1$), is [92, 120]

$$\bar{\alpha}_p = \frac{1}{2}\left(\alpha_p^B + \frac{m_2^{1/2} - m_1^{1/2}}{m_1^{1/2}y_1 + m_2^{1/2}y_2}\right).$$

Observe that Eqn (4.22) holds for arbitrary geometry of the channel cross-section. The dependence on the geometry (flat channel, cylindrical capillary) shows up in the next order in Knudsen number [71].

The comparison of J_{1D} with the phenomenological relation (4.2) reveals, in particular, that $\Lambda_{m1} = Tp^{-1}D_{12}\alpha_p$. This coefficient is symmetrical to the coefficient Λ_{1m}, which defines the contribution of the concentration gradient to the average molar flow $n\langle u_m \rangle$. For small Knudsen numbers the isothermal flow $n\langle u_m \rangle$ can be represented as [109]

$$n\langle u_m \rangle = n\langle u_v \rangle + n\sigma_{12}D_{12}\left(\nabla_z y_1 + \alpha_p^v y_1 y_2 \nabla_z \ln p\right),$$

where $\langle u_v \rangle$ is the averaged viscous flow of the mixture, and σ_{12} is the coefficient of diffusion slipping [121].

The symmetry condition $\Lambda_{1m} = \Lambda_{m1}$ then gives $\sigma_{12} = -\bar{\alpha}_p$. Straightforward calculations [108–113, 119, 120] confirm that this condition is satisfied. Observe that while the calculation of σ_{12} is mainly associated with the solution of the kinetic problem for the Knudsen layer, the calculation of $\bar{\alpha}_p$ requires simultaneously taking into account both the Burnett and Knudsen contributions. We encountered a similar situation when checking the fulfillment of the condition $\Lambda_{mq} = \Lambda_{qm}$ for the flow of simple gas in the channel.

4.3 Reciprocity theorem and symmetry relations
The symmetry of coefficients in the Onsager matrix in the expressions for complete flows (4.2) and (4.4) can be proved either from the general statistical concepts of NT, or at the purely kinetic level, if we take advantage of the symmetry of the kernel of collisions operator and the kernel of the boundary operator A. For the case of simple gas flow, the symmetry of coefficients Λ_{ik} or λ_{ik} was proved in Refs [45, 70–72, 107, 115].

In hydrodynamics and electrodynamics there are general relations known as reciprocity theorems [122, 123], which follow directly from the fundamental equations and can be successfully used in concrete calculations. The use of the reciprocal relations in the KT of gases can also considerably simplify the calculations in solving particular problems. Furthermore, the reciprocal relations allow certain conclusions to be made concerning the symmetry properties of the kinetic coefficients [122, 124, 125]. Proofs based on the reciprocity theorems do not rely on the concepts of NT, and therefore may be regarded as indirect confirmation of Onsager's reciprocal relations.

The reciprocal relations in the KT were first formulated and used by Waldmann [126–128]. For the problem of the flow of a simple gas in a capillary they were obtained in Ref. [129], and in Refs [130–133] they were used in the proof of the symmetry of kinetic coefficients in the problem of external gas flows past solid bodies. Here we are going to consider the flow

of a multicomponent mixture in a capillary connecting two vessels under the action of drops of pressure Δp and temperature ΔT.

We shall seek the DF of the molecules of gas components in the form (2.8), $f_\alpha = f_{\alpha 0}(1 + \phi_\alpha)$, where $f_{\alpha 0}$ is the absolute Maxwell distribution, and ϕ_α is the correction. Consider two steady flows, one caused by the temperature difference between the vessels (the corresponding correction denoted by $\phi_{\alpha T}$), and the other by the pressure drop ($\phi_{\alpha p}$). Functions $\phi_{\alpha T}$ and $\phi_{\alpha p}$ satisfy the steady-state equations [cf. Eqn (2.9)]

$$\mathbf{v}_\alpha \frac{\partial \phi_{\alpha T}}{\partial \mathbf{r}} = L(\phi_T), \qquad \mathbf{v}_\beta \frac{\partial \phi_{\beta p}}{\partial \mathbf{r}} = L(\phi_p). \qquad (4.23)$$

Multiplying the first equation in (4.23) by $\phi_{\alpha p}I$, and the second by $\phi_{\beta T}I$, where I is the operator of inversion in the space of velocities $[I\phi(\mathbf{v}) = \phi(-\mathbf{v})]$, we carry out integration with the weight functions $f_{\alpha 0}$ and $f_{\beta 0}$, and summation over the components of the mixture. Subtracting the second of the resulting equations from the first, we get

$$\frac{\partial}{\partial \mathbf{r}} [\phi_p I \mathbf{v} \phi_T] = 0, \qquad (4.24)$$

where we have taken advantage of the fact that the collisions operator is symmetrical and invariant with respect to the action of operator I.

Integrating Eqn (4.24) over the volume of the gas and using the Gauss theorem, we find

$$\int_{\Sigma_g} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_g + \int_{\Sigma_w} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_w = 0, \qquad (4.25)$$

where integration is carried out over the surfaces passing through the gas in the first term, and over the walls of the capillary and partly of the vessels in the second (Fig. 2).
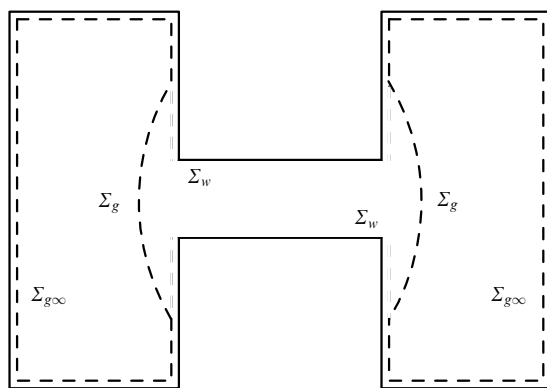

Figure 2. To the proof of the reciprocity theorem.

Before employing Eqn (4.25) for a particular task, let us demonstrate that the second integral is equal to zero. With this purpose we move the surfaces Σ_g directly to the walls of the vessels; then we get

$$\int_{\Sigma_{g\infty}} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_{g\infty} + \int_{\Sigma_w} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_w = 0. \quad (4.26)$$

The surfaces $\Sigma_{w\infty}$ are located far from the outlet of the capillary, so we may assume that their temperature is constant. There is no transport of mass and heat across

these surfaces. Let us assume that the Maxwell distributions $f_{\alpha 0}$ correspond to the temperature T_0 of the left-hand vessel. Then, as demonstrated in Ref. [115], the equation

$$[\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T]\Big|_{\Sigma_{w\infty}} = 0 \qquad (4.27)$$

holds for any point on the surface of this vessel.

Obviously, a relation similar to Eqn (4.27) can be obtained for the second vessel as well, whose temperature is $T = T_0 + \Delta T$. This follows from the general considerations of 'symmetry' of the vessels, and from the fact that the renormalization of the functions $f_{\alpha 0}$ to the temperature of the second vessel gives corrections to $\phi_{\alpha T}$ and $\phi_{\alpha p}$ of the form $(\beta v_\alpha^2 - 3/2)\Delta T/T_0$. Since the flows of heat and mass across the surface of the vessel walls are zero, this renormalization does not affect the left-hand side of Eqn (4.27).

As a result, from Eqn (4.27) we get

$$\int_{\Sigma_w} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_w = 0, \qquad (4.28)$$

which for the flow in question was obtained in a more complicated way in Ref. [129].

In this way, Eqn (4.25), which expresses the reciprocity theorem, becomes

$$\int_{\Sigma_g} [\phi_p I \mathbf{v} \mathbf{n}_\perp \phi_T] \, \mathrm{d}\Sigma_g = 0. \qquad (4.29)$$

If the surfaces Σ_g are moved away from the outlet of the capillary, the functions $f_\alpha = f_{\alpha 0}(1 + \phi_{\alpha T})$ and $f_\alpha = f_{\alpha 0}(1 + \phi_{\alpha p})$ rather rapidly (faster than $1/R$, where R is the distance to the outlet of the capillary) tend to the equilibrium distributions, corresponding to the given values of temperature and pressure in the vessels. In other words, on the surfaces Σ_g the values of $\phi_{\alpha p}$ and $\phi_{\alpha T}$ are either equal to zero (for the vessel where $f_{\alpha 0}$ corresponds to T_0 and p_0), or $\phi_{\alpha p} = \Delta p/p_0$ and $\phi_{\alpha T} = (\beta v_\alpha^2 - 5/2)\Delta T/T_0$ (for the vessel with elevated pressure Δp or temperature ΔT). Taking advantage of this circumstance, one can easily calculate the integrals in Eqn (4.29) and obtain the equation

$$\left(\langle u_{mT} \rangle \frac{\Delta p}{T_0} - \langle h_p \rangle \frac{\Delta T}{T_0^2} \right) \Sigma_0 = 0, \qquad (4.30)$$

where $\langle u_{mT} \rangle$ and $\langle h_p \rangle$ are the mean molar velocity caused by the gradient of temperature and the heat flow caused by the gradient of pressure, averaged over the cross-section of the capillary Σ_0.

Using Eqn (4.2), we may write

$$\langle u_{mT} \rangle = \Lambda_{mq} \frac{1}{T^2} \frac{\Delta T}{H}, \qquad \langle h_p \rangle = \Lambda_{qm} \frac{1}{T} \frac{\Delta p}{H},$$

where H is the length of the capillary. Substituting these expressions into Eqn (4.30) and taking into account that the temperature and pressure drops are independent parameters, we prove the symmetry of the kinetic coefficients, $\Lambda_{qm} = \Lambda_{mq}$.

5. Non-equilibrium thermodynamics and problems of flows around bodies

5.1 General remarks
The methods of NT and KT are also widely used in the study of flows of rarefied gases near convex bodies [39, 40, 91, 134,

135]. Here we are going to consider only the slow gas motions, which have been attracting much interest in recent decades in connection with the active development of aerosol technologies [135 – 137].

The pivotal problem of gas flows near condensed bodies is recognized as the calculation of viscous drag. The results more or less accurately reproducing the well-known Stokes formula [40] have been obtained for small Knudsen and Reynolds numbers, corresponding to the so-called creeping regime, using the hydrodynamic approach with due account for slipping, as well as numerical and variation techniques. Similar approaches have been used for solving quite a number of related problems, including the problem of motion of drops in native vapor [138, 139], the calculation of kinetic thermal effects [132, 140 – 144], and the calculation of the rate of thermophoresis and diffusiophoresis of aerosol particles [91, 134 – 137, 145]. Direct application of the methods of NT to the analysis of motion of particles in rarefied gases allowed the prediction of the effects of thermal [91] and diffusion [145] polarization of particles moving in uniform gases and gas mixtures, as well as their linkage with the effects of thermophoresis and diffusiophoresis. Also demonstrated was the symmetry of the tensor of mobility of particles implied by Onsager's reciprocal relations [130, 131].

Until now, the technique considered best developed for studying disperse systems has been the method based on the dusty gas model. It was initially used for analyzing the diffusion of gases in porous media and capillaries at arbitrary Knudsen numbers [118, 134]. The expressions for flows obtained with this method are directly related to the NT of discontinuous systems. The efficiency of this method was later demonstrated for the description of air-disperse systems [135], in particular, in the analysis of thermophoresis of aerosol particles [146, 147], as well as electrokinetic [148] and diffusion phenomena [149]. Here we shall discuss a different approach to the study of disperse systems with the methods of NT, proposed originally in Ref. [150]. By contrast to Refs [147 – 149], where the treatment is based on an ensemble of a large number of particles, we analyze the motion of individual particles in a gas (mixture of gases) nonuniform in temperature (or concentration). In this case it is not necessary to use the integral phenomenological relations for discontinuous systems. The analysis is based on the local phenomenological equations, which allow the establishment of new links between various non-equilibrium effects.

This approach was also generalized for the motion of a sphere in a gas mixture [145]. In Refs [124, 151] it was used for expressing the general phenomenological equations of motion of particles of arbitrary shape in nonuniform multicomponent fluids capable of conducting an electric current. The feasibility of the generalization of this method for the flows which requires taking into account the higher derivatives of microscopic parameters of the gas was demonstrated in Ref. [151].

5.2 Non-equilibrium thermodynamics of the motion of particles in an nonuniform gas

Consider the motion of particle of arbitrary shape in a multicomponent gas mixture, characterized by the constant external gradients of temperature $\nabla_\infty T$ and concentration $\nabla_\infty C_i$. Assume also that the particle is moving at a constant velocity $\mathbf{u}_\infty$ relative to the mean mass velocity of the mixture under the action of an external force $\mathbf{F}$.

We calculate the entropy production ΔS_p associated with the presence of a foreign particle in the nonuniform gas. The equation of entropy balance, which holds both for the gas and for the particle in the gas, can be written in the form

$$\mathrm{div}(\mathbf{u}s + \mathbf{J}^{s\prime}) = \sigma \,.$$

Here $\mathbf{J}^{s\prime}$ is the flux of entropy in the frame anchored to the center of mass of the moving gas. Now we integrate this equation over the volume of the gas which contains the particle. On the right-hand side we get the total entropy production ΔS_V. Using the Gauss theorem, the left-hand side is transformed into an integral over the surface enclosing this volume. For such a surface it is convenient to take a cylinder of large enough radius, with the center of symmetry coinciding with the center of mass of the particle and the axis directed along the external gradients of temperature and concentration (z axis). If the radius of the cylinder is much greater than its height, integration over the surface of the cylinder is reduced to the integration over its ends, that is,

$$\Delta S_V = 2\pi \int_0^\infty (u_z s + J_z^{s\prime})r\,\mathrm{d}r \Big|_{z=-H}^{z=H} \,. \tag{5.1}$$

Let us point to two important circumstances. Firstly, expression (5.1) only involves the entropy flux in the gas. This implies that, although we do not know the structure of the flux and the entropy production near the surface of the particle, we can still calculate the production of entropy associated with the presence of the particle, using the asymptotic form of the entropy flux in the gas far from the particle. Secondly, in Eqn (5.1) we may place the ends of the cylinder as far from the particle as to be able to use the purely hydrodynamic expressions for the entropy flux, because the kinetic corrections are of the order of l/H and can be disregarded.

The total entropy flux in the gas mixture can be represented in the form [3]

$$J_z^s = u_z s + J_z^{s\prime} = \frac{u_r(p\delta_{rz} + \pi_{rz})}{T_0} + \frac{q_z}{T} + \sum \frac{J_{iz}(\mu_i - \mu_N)}{T_0} \,, \tag{5.2}$$

where μ_i is the chemical potential of the ith component, the number of which is N.

The distributions of temperature, pressure and concentrations far from the particle can be found from the general solutions of the stationary Navier – Stokes equations for velocity and pressure, and the Laplace equations for temperature and concentrations. As we know, the general solutions can be written in the form [122]

$$p = p_0 + \sum_{n=-2}^{-\infty} p_n \,,$$

$$\mathbf{u} = \mathbf{u}_0 + \sum_{n=-2}^{-\infty} \left(\mathrm{rot}[\mathbf{r}\boldsymbol{\chi}_n] + \nabla\beta_n + \frac{n+3}{2\eta^2(n+1)(2n+3)}\, r^2\nabla p_n \right.$$

$$\left. - \frac{n}{\eta(n+1)(2n+3)}\, \mathbf{r}p_n \right) ,$$

$$T = T_0 + \sum_{n=-2}^{-\infty} T_n + (\nabla T\mathbf{r}) \,, \qquad C_j = C_{j0} + \sum_{n=-2}^{-\infty} C_{jn} + (\nabla C_j\mathbf{r}) \,.$$
$$\tag{5.3}$$

Here p_n, χ_n, β_n, T_n, and C_{jn} are spherical harmonics of order n. The values $n \leqslant -2$ assume that the perturbations brought by

the particle into the given external distribution decrease with distance $r \to \infty$.

We introduce a special notation for the harmonics with $n = -2$:

$$T_{-2} = \frac{(\mathbf{A}\mathbf{r})}{r^3}, \qquad C_{j-2} = \frac{(\mathbf{B}_j\mathbf{r})}{r^3}, \qquad p_{-2} = \frac{(\mathbf{f}\mathbf{r})}{r^3}, \qquad (5.4)$$

where $\mathbf{A}$ and $\mathbf{B}$ may be referred to as the temperature and concentration dipole moments of the particle.

Further, we use the kinetic expressions for $\boldsymbol{\pi}$, $\mathbf{J}_i$ and $\mathbf{q}$, corresponding to the first approximation in the ChE method

$$\boldsymbol{\pi} = -\eta\,\overline{\nabla\mathbf{u}}, \qquad \mathbf{q} = -\lambda\nabla T - T\sum_{j=1}^{N-1}\chi_j^c\,\nabla C_j,$$

$$\mathbf{J}_i = \rho_i(\mathbf{u}_i - \mathbf{u}) = -\frac{\rho_i D_i^T}{T}\nabla T - \rho\sum_{j=1}^{N-1}D_{ij}\nabla C_j, \qquad (5.5)$$

where λ, D_{ij}, D_i^T, and χ_j^c are, respectively, the coefficients of heat conductivity, mutual diffusion, thermal diffusion, and the Dufour effect. We have dropped the terms relating to pressure diffusion because the calculations indicate that in the absence of external pressure gradient their contribution is zero.

Substituting Eqns (5.5) into (5.1), we get the following expression for entropy production:

$$\Delta S = \frac{q_H \delta T}{T_0^2} + \sum_{i=1}^{N-1}\frac{J_{iH}\delta(\mu_i - \mu_N)}{T_0} + \frac{\mathbf{F}\mathbf{u}_m}{T_0} + \frac{\mathbf{P}\nabla T}{T_0}$$

$$+ \sum_{j=1}^{N-1}\frac{\mathbf{Q}_j\nabla C_j}{T_0}. \qquad (5.6)$$

Here we have introduced the notation for the molar velocity of the gas mixture $\mathbf{u}_m$, and used the relation $\mathbf{F} = -4\pi\mathbf{f}$; q_H and J_{iH} are the total amount of heat and mass of the components carried across the planes $z = \pm H$. Vectors $\mathbf{P}$ and $\mathbf{Q}$ have the form

$$\mathbf{P} = 4\pi\left[\frac{\lambda\mathbf{A}}{T_0} + \sum_k\sum_j\frac{\partial(\mu_k - \mu_N)}{\partial C_j}\,\mathbf{B}_j\,\frac{\rho_k D^T}{T_0}\right],$$

$$\mathbf{Q}_i = 4\pi\left[-\rho_0\sum_k\sum_i D_{ki}\frac{\partial(\mu_k - \mu_N)}{\partial C_j}\,\mathbf{B}_j + T_0\chi_i^c\mathbf{A}\right]. \quad (5.7)$$

The first two terms in Eqn (5.6) describe the production of entropy in the absence of the particle, while the remaining three are associated with the presence of the particle in the inhomogeneous mixture. The term with $\mathbf{F}\mathbf{u}_m$ is the classical expression for the dissipation of energy when the particle moves in a viscous medium. The two other terms are due to the distortion of the fields of temperature and concentrations by the particle.

The structure of the expression for entropy production (5.6) and the Curie principle allow us to write the following phenomenological equations of motion for a single particle in an inhomogeneous medium:

$$\mathbf{u}_m = \Lambda_{00}\mathbf{F} + \sum_{j=1}^{N-1}\Lambda_{0j}\nabla C_j + \Lambda_{0N}\nabla T,$$

$$\mathbf{Q}_i = \Lambda_{i0}\mathbf{F} + \sum_{j=1}^{N-1}\Lambda_{ij}\nabla C_j + \Lambda_{iN}\nabla T,$$

$$\mathbf{P} = \Lambda_{N0}\mathbf{F} + \sum_{j=1}^{N-1}\Lambda_{Nj}\nabla C_j + \Lambda_{NN}\nabla T. \qquad (5.8)$$

The form of the phenomenological equations (5.8) is somewhat unusual. The generalized forces are represented here by the conventional parameters of nonlinear thermodynamics: the gradients of pressure, concentration, and the common mechanical force. At the same time, the fluxes are represented by dipole moments, which are hardly flows as such. It is true that here, unlike the classical electric dipole moment, they all display a non-equilibrium nature. We believe that it is hardly possible to obtain the phenomenological equations (5.8) from 'general considerations'. This statement is corroborated by the fact that the effect of thermal polarization, which is thermodynamically reciprocal to thermophoresis (this has been known for over a century) and is described by the second equation in (5.8), has only recently been predicted and observed experimentally.

Since we are considering the motion of bodies of arbitrary geometry, the coefficients Λ_{ij} in Eqns (5.8) are tensors. The Onsager relations for them are $\Lambda_{ml} = \Lambda_{lm}^T$, where T denotes the transpose. Let us analyze the physical meaning of these coefficients. The coefficient Λ_{00} is obviously related to the tensor of mobility of particles in a viscous medium, and expresses the well-known Stokes law. Other coefficients in the first equation in (5.8) define the effects of diffusiophoresis and thermophoresis. Via the Onsager relations, these effects are linked with the effects of diffusion and thermal polarization, described by the second and third equations. Observe that, irrespective of the shape of the particles, the principal role in these equations belongs to the 'dipole moments', whereas the finer structure of the flow of gas mixture and the distributions of concentration and temperature described by the higher multipoles retreat backstage.

The proposed procedure for constructing the phenomenological equations of motion of particles in nonuniform media can easily be extended to the cases of a conductive gas mixture and a particle rotated by a torque [151]. In Refs [130, 131] the situation when the mean temperature of the gas is different from the mean temperature of the particle is considered — that is, there is an exchange of heat between the particle and the surrounding gas. The relevant thermodynamic flows and forces are scalar quantities. They can be rather easily included into the set of equations (5.8).

5.3 Arbitrary distribution of gas velocity

Another possible extension of the set of equations (5.8) is associated with the inclusion of inhomogeneous gradients of temperature and concentration, and the coordinate-dependent gas velocity — that is, with the inclusion of thermodynamic forces of the form $\nabla\mathbf{u}$, $\nabla\nabla\mathbf{u}$, $\nabla\nabla T$, etc. We shall analyze this situation using the example of nonuniform gas flow around a particle at rest.

Consider the simplest flow which requires inclusion of the higher derivatives of the macroscopic characteristics of the gas into the phenomenological equations. Specifically, let the initial distribution of the velocity of gas flow in the neighborhood of the point where we place the particle be described by an arbitrary function $\mathbf{u}(\mathbf{r})$, which is sufficiently smooth to be expanded in a Taylor series:

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}(0) + \mathbf{r} \otimes \nabla\mathbf{u} + \frac{1}{2}\,\mathbf{r}\mathbf{r} \otimes \nabla\nabla\mathbf{u} + \ldots \qquad (5.9)$$

Now we place a solid particle of arbitrary shape at the origin of coordinates. This will perturb the flow field, which becomes

$$\mathbf{U}(\mathbf{r}) = \mathbf{u}(\mathbf{r}) + \mathbf{u}'(\mathbf{r}), \quad (5.10)$$

where $\mathbf{u}'(\mathbf{r})$ is the perturbation caused by the particle, decreasing with the distance.

For describing the general structure of perturbations of velocity and pressure we may use the solutions of Eqn (5.3).

It is obvious that there will be additional entropy production associated with the presence of the particle. This entropy production can be calculated using the procedure developed above. Skipping the algebra [151], we quote the final result:

$$\Delta S_p = u_\mu(0) \int_{S_b} \Pi^t_{\mu\nu} n_\nu \, dS_b + \sum_{k=0}^{\infty} \frac{1}{k!} \nabla^k u_\mu \otimes \int_{S_b} \mathbf{r}^k \Pi^t_{\mu\nu} n_\nu \, dS_b,$$

$$(5.11)$$

where $\mathbf{n}$ is the vector normal to the surface of the particle over which the integration is performed, and Π^t is the hydrodynamic stress tensor defined for the total velocity $\mathbf{U}(\mathbf{r})$.

Observe that $\int_{S_b} \Pi^t_{\mu\nu} n_\nu \, dS_b$ is the force F_μ acting on the particle from the side of the gas. Denoting the moments by $\mathbf{F}^k_\mu$

$$\mathbf{F}^k_\mu = \frac{1}{k!} \int_{S_b} \mathbf{r}^k \Pi^t_{\mu\nu} n_\nu \, dS_b, \quad (5.12)$$

we can use the production of entropy (5.11) for writing the following set of phenomenological equations:

$$\mathbf{F}_\mu = \widetilde{\Lambda}_{00} u_\mu(0) + \sum_{n=1}^{\infty} \widetilde{\Lambda}_{0n} \otimes \nabla^n u_\mu,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$(5.13)$$

$$\mathbf{F}^k_\mu = \widetilde{\Lambda}_{k0} u_\mu(0) + \sum_{n=1}^{\infty} \widetilde{\Lambda}_{kn} \otimes \nabla^n u_\mu,$$

for which the Onsager relation is $\widetilde{\Lambda}_{ml} = \widetilde{\Lambda}^T_{lm}$.

Note the analogy between the phenomenological equations (5.13) and the equations obtained in the higher approximations of the KT (Section 2). In both cases the generalized thermodynamic forces are represented by the higher derivatives of the macroscopic gas velocity. These are associated with the non-physical fluxes, which in this case are certain moments of the stress tensor. The analogy may be more profound, but its substance is not yet clear. As a matter of fact, the transport of foreign particles in a gas may be described within the framework of a unified kinetic approach, which treats the particles as a component of the gas mixture. The most vivid example is the description of thermophoresis and diffusiophoresis of aerosol particles in the dusty gas model [134, 146]. In this context, the phenomenological equations (5.13) may represent a particular case of the set (1.91) in the unified (yet to be developed) KT of a gas with suspended particles.

It is also possible that we do not yet fully understand the role of non-physical fluxes in the KT — at first sight they do not carry any additional information, whereas the phenomenological equations (5.13) have more substance. The first equation in (5.13) is the generalization of the Faxen relation [123, 149] for the particle circumfused by a gas with an arbitrary field of velocities. Such fluxes are encountered rather often, and for solving particular problems it is necessary to calculate the force upon the particle from the side of the gas. The magnitude of this force is determined by the values of the coefficients $\widetilde{\Lambda}_{0k}$. A straightforward calculation of these coefficients even for bodies of simple shape is a rather difficult task. These coefficients, however, can be calculated with the aid of the Onsager relations $\widetilde{\Lambda}_{0k} = \widetilde{\Lambda}^T_{k0}$. To find these, as we can readily see from Eqns (5.11), (5.12), one must calculate the moments $\mathbf{F}^k$ for the motion of a particle in a homogeneous gas (or for a homogeneous gas flow around the particle). Simple calculations in the hydrodynamic approximation give $\Lambda_{20} = \pi\eta R^2$ for a sphere, which coincides with the value of Λ_{02} obtained earlier for this case by Faxen [123]. The scheme described above shows clearly enough how the equations (5.8) are generalized for the case of arbitrary fields of temperature and concentrations.

6. Conclusion

The above analysis of the linkage between NT and KT, and the numerous examples, prove convincingly that the methods of NT can be successfully employed for solving a broad scope of problems of the dynamics of rarefied gases. This linkage arises when we go beyond the limits of the canonical methods of NT, and use additional variables of state along with the conventional thermodynamic variables, which allows us to extend the suite of thermodynamic fluxes and forces in the description of non-equilibrium systems. This is the origin and the impetus of the EIT [5, 8], and the closely related extended hydrodynamics [154, 155], which holds for the range of finite (not small) frequencies and wave vectors, when the $(\mathbf{k}, \omega)$-dependence of the transport coefficients in the set of hydrodynamic equations becomes significant. The obstacles in the way of EIT have been discussed in recent publications [8, 9, 156].

Another aspect of the generalization of EIT is associated with the possible use of its methods for analyzing the slow motions of rarefied gases for both internal and external flows, for arbitrary rarefaction of the gas (intermediate Knudsen numbers). Of fundamental importance here is the fact that the kinetic results, obtained using the linearized equations in Grad's moments or the linearized Burnett approximation in the ChE method, fit naturally into the scheme of NT, extending the set of phenomenological equations by introducing the higher moments of the DF and additional terms which contain the higher derivatives of the principal thermodynamic variables and velocity with respect to coordinates.

The results presented in this review also point to the efficiency of the NT methods for solving the boundary problems of the dynamics of rarefied gases. Using the equations of balance on the interface and the expression for the boundary entropy production, one can obtain a number of important expressions (including the symmetry relations for the kinetic cross coefficients), and considerably reduce the amount of calculation compared with the straightforward kinetic analysis of the problem. NT and KT in this case work efficiently together, giving a more detailed analysis of the transport processes in discontinuous systems and in flows around bodies.

The arguments developed above prove the necessity of further investigating the capabilities of NT for solving various problems related to the study of non-equilibrium phenomena not only in gases, but also in other physical media. The

analysis of the linkage between NT and KT is also of interest from the standpoint of the statistical theory of open systems, based on the generalized kinetic equation and the accordingly modified equations of gas dynamics [28 – 30]. We believe that the discussion of these problems will give new stimulus for the development of all aspects of NT as applied to the study of non-equilibrium phenomena.

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