Y.A. HUMENYUK

Institute for Condensed Matter Physics, Nat. Acad. of Sci. of Ukraine
(1, Svientsitskii Str., Lviv 79011, Ukraine; e-mail: josyp@ph.icmp.lviv.ua)

UDC 536.12; 536.71;
533.21; 536.633.2;
536.757

THERMODYNAMIC QUANTITIES OF A LOW-DENSITY GAS IN THE WEAKLY NONEQUILIBRIUM HEAT-CONDUCTION STEADY STATE

A low-density gas in the heat-conduction steady state is considered. Within the theory of continuous media, corrections to the pressure and the internal energy are obtained, which are related to the local temperature gradients of several orders. Corresponding expressions are derived for the compressibilities along and across the heat flux as well as for heat capacities. The expression for the nonequilibrium entropy is shown to obey the second law of thermodynamics. The free energy calculated is found out not to satisfy properties of a thermodynamic potential.

Keywords: heat flux, temperature gradients, equation of state, nonequilibrium entropy, steady-state thermodynamics.

1. Introduction

The weakly nonequilibrium steady state of the many-particle system with a steady heat flux is one of the widely studied states, which goes beyond the scope of equilibrium thermodynamics. Due to the proximity to the equilibrium state, it can be interpreted in terms of a perturbation and investigated by the methods developed for equilibrium states and weak deviations from them. In most cases, the heat-conduction states have been studied owing to the very phenomenon of heat conduction. It is a subject of investigations in linear irreversible thermodynamics [1, 2], kinetic theory [3–5], and linear response theory, see [5, 6]. However, such macroscopic quantities as the pressure, internal energy, or entropy are also of importance. One can even consider the problem more widely in the context of the construction of thermodynamics for these steady states. The approaches proposed can be conditionally divided onto phenomenological or thermodynamic ones, as well as those making use of methods of kinetic theory or statistical mechanics. Below, we survey the most known approaches.

From the historical viewpoint, it is worth to mention the works by Leontovich [7, 8], in which the definitions of thermodynamic quantities in nonequilibrium states are discussed. Specifically, he considered the free energy and the entropy of thermally uniform and thermally nonuniform nonequilibrium systems. These quantities were introduced on the grounds of equilibrium thermodynamics adapted for a spatially nonuniform system making use of an external fictitious field, which imitated the spatial nonuniformity of the corresponding nonequilibrium states [7, 8]. Exactly this fictitious field (being absent in reality) is, to the great extent, the deficiency of this approach.

1.1. Extended thermodynamics

Constructions of thermodynamics for nonequilibrium or steady systems (including heat-conduction ones) are treated in many works as establishing the basic thermodynamic equality (the Gibbs equation), which has to contain differential contributions due to ad-

---

ditional variables of description. This conception is known as "extended thermodynamics". The idea of extension was introduced by Grad for the hydrodynamic description in his works [9, 10] on the Boltzmann kinetic equation. In addition to the densities of mass, momentum, and energy of a nonequilibrium gas, he introduced additionally a stress tensor and a heat flux assigned to make the description to be more detailed. This idea is used to describe various systems on the (extended) thermodynamic level, where the heat flux is interpreted, for instance, as an additional degree of freedom (see [11–13]).

A version of this approach developed for steady-state systems by Jou and co-workers [11, 14, 15] is usually referred to as extended irreversible thermodynamics (EIT). The starting point is the entropy density, which depends on the internal energy density, specific volume, and heat flux supplemented by the Gibbs equation for its differential. Equilibrium thermodynamic relations are directly extended to the steady-state case and give expressions for the nonequilibrium temperature [16], scalar pressure [17, 18], and other related quantities. The questions of the definition of a temperature for nonequilibrium situations were discussed in Ref. [19] in detail. The EIT approach is also applied to ultrarelativistic particles [17], electrical conductive systems [20], *etc.* Some non-trivial conclusions such as a dependence of the nonequilibrium temperature on the heat flux, breaking of the energy equipartition law, and the anisotropy of the pressure tensor cause alertness.

There were attempts to validate the idea of extended thermodynamics, by using the kinetic-theoretical scheme [21] of the Grad method [9,10] and with the aid of nonequilibrium statistical ensembles [17,22–27]. The corresponding ensemble distributions were sought by means of the information theory, making use of the information entropy maximization subject to additional constraints. The exponential form of the obtained distributions contains momentum and energy fluxes, which cause difficulties with their normalization conditions. To avoid them, in the subsequent analysis, the distributions are expanded in the contributions from the fluxes, which are considered to be small (see e.g. [17, 28]). Many authors believe that the information theory is applicable to steady states. There are studies of a linear harmonic chain [29], low-density gas [17, 28], dense fluid [22, 28], *etc.* A formal comparison of two realizations of the ensemble approach is given in Ref. [30].

The EIT formulation contains an internal difficulty lying in that the entropy density has not been proved to have the potential properties. Its differential includes the specific volume as a thermodynamic configurational variable, which does not describe the spatial anisotropy of the steady state. Nevertheless, the calculations give an anisotropic form of the pressure tensor, which requires one to consider the spatial anisotropy of a specific volume.

1.2. Phenomenologies

Oono and Paniconi [31] started to construct a panoramic scheme of steady-state thermodynamics in a phenomenological approach. They discussed such basic ingredients as the variables of a steady state, transitions between the states, key thermodynamic principles, stability, and probability of fluctuations under steady conditions. In fact, they thought over a general structure of steady-state thermodynamics. Since the authors developed the framework in a close analogy with equilibrium thermodynamics, their arguments seem insufficient and controversial. The formulation was given in general terms for an arbitrary system without any application to physically unambiguous situations like the heat-conduction state or a system under stationary shear.

Another phenomenological attempt to develop thermodynamics of nonequilibrium steady states was made by Sasa and Tasaki [32] within the idea to define the thermodynamic quantities "operationally". The heat-conduction steady-state pressure was defined by the contact of the steady-state system with the equilibrium one at a fixed pressure. The steady-state chemical potential was also introduced by the contact with an equilibrium system realized by a specially devised porous wall. The authors proposed an implicit expression for the steady-state free energy and discussed its formal properties such as additivity, extensivity, and concavity. The minimal-work principle was analyzed, an expression for steady-state fluctuation probability was obtained, and new nonequilibrium phenomena were anticipated. The phenomenology was formulated in general and illustrated for the heat-conduction, shear, and electrical systems.

No explicit expression for the steady-state pressure, internal energy, or entropy was proposed.

1.3. Fluctuation theorems

Efforts have been made to support some of the mentioned phenomenological constructions in the case of heat-conduction steady states, by using the approach of fluctuation theorems [33–35], which is based on the language of probabilities of trajectories in the phase space. Each trajectory realizes microscopically a thermodynamic transition of the system between two macroscopic steady states. The driven Langevin system, the Hamiltonian particle system, and the discrete Markovian process have been considered to perform generalizations of the following conceptions to the nonequilibrium steady case: entropy [36–38], the Clausius relation, the second law of thermodynamics, and the basic thermodynamic equality [36, 37, 39, 40]. Moreover, the connection [33] between nonequilibrium work and free energy difference [41, 42], entropy production, and a generalization of the Clausius relation to the case of several thermal baths [40, 43], have been analyzed. Almost all of these works deal with weak deviations from the equilibrium.

However, they presented only formal results, which suffer from the excessive generality. These formalisms have not been applied to specific or simple systems like a low-density gas under nonequilibrium stationary conditions.

1.4. Kinetic theory

Within kinetic theory, the heat-conduction steady state of a low-density gas has been studied on the basis of the Boltzmann kinetic equation [3, 4, 44]. Thermodynamic quantities such as entropy and the pressure tensor were calculated [45], by using the one-particle distribution function obtained up to the second order in gradients of the Chapman–Enskog method [3, 4]. The pressure tensor obtained is diagonal, but anisotropic with different values along and across the heat flux, as in the EIT. A violation of the energy equipartition law is found out. The solution for the distribution function and the thermodynamic results are shown [46] to differ from the EIT counterpart obtained from the entropy maximization principle. Similar studies were carried out for a two-dimensional hard-disk gas [47] verified by molecular dynamics [48]. The results for the steady distribution function are applied to the analysis [48,49] of the weak contact through a microscopic window between the gas under nonequilibrium conditions with a steady heat flux and the equilibrium gas.

1.5. Computer simulations

Heat-conduction steady systems were investigated by computer simulations. In Ref. [50], the one-dimensional binary gas mixture of point particles was considered, by using a self-consistent version of the moment method for the Bhatnagar–Gross–Krook kinetic model, as well as by molecular dynamics. However, thermodynamic properties were less studied. The temperature profile along the system was analyzed for deviations from the Fourier law for the heat conduction. Moreover, profiles for higher moments were given, and the thermal conductivity coefficient in the domain of high total numbers of particles was presented.

By molecular dynamics, Morriss and co-workers studied [51] the low-density hard-disk system in a narrow linear channel, which is in contact with two thermostats of fixed “temperatures” on both ends [52]. In the model, hard disks collide with the thermostat walls according to deterministic rules [52–54]. The temperature profile, local entropy density, entropy production rate, and heat flux through the system were obtained [51]. These results were shown to be consistent with the Boltzmann kinetic theory [3, 44] and the linear irreversible thermodynamics [1,2]. The processes of dissipation and entropy production were investigated in detail [55], by considering the potential contributions to the heat flux for the high density case of the same hard disks. The contributions to the local entropy due to two-particle correlations in the configuration space were calculated and analyzed in Ref. [56].

These studies give an important insight into the nature of the heat-conduction steady state, but do not report any data for global thermodynamic quantities.

1.6. Difficulties

Among the methods applied to investigations of the thermodynamic quantities of a nonequilibrium steady state with heat flux, the EIT [16–18], the information theory [18, 22, 24, 28], and the kinetic theory [45] report explicit expressions for the scalar and tensorial pressures, the nonequilibrium temperature, and the entropy. Differences were observed [46] between the EIT and information-theoretical results and those

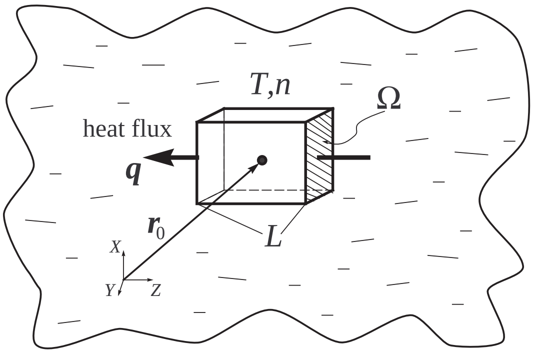

Fig. 1. Local nonequilibrium heat-conduction state

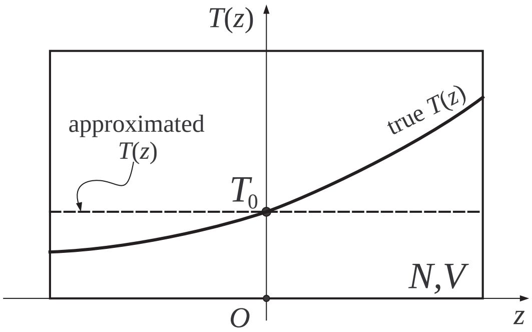

Fig. 2. Equilibrium system approximating the local nonequilibirum heat-conduction state; $N/V = n(\mathbf{r}_0)$

coming from the stationary Boltzmann kinetic equation. In addition, the kinetic-theoretical predictions for the pressure tensor and the entropy of low-density hard spheres and Maxwell molecules differ from each other too [46]. These facts revealed for the quantities of the thermodynamic nature in the low-density domain, where the mean interaction energy between molecules is negligible, look unusual and suspicious.

But the more serious difficulty of these approaches and results lies in that the conceptions of the local equilibrium [1, 2] and the normal solution [3, 5, 44] are used in the construction of thermodynamics and the calculations of the thermodynamic characteristics of the heat-conduction steady state. As a result, the final expressions (e.g., for the pressure) contain the local-equilibrium temperature and the particle density, which are space-dependent.

Our work shows for the simple case of the low-density gas that the steady-state thermodynamic quantities are achievable analytically within the continuum-media approach. The calculations are based on the gradient expansion of the local temperature and on the integration of local quantities. The results do not have the difficulties mentioned above.

The article is organized as follows. We discuss the method of local description of nonequilibrium states and some approximations in Section 2. For the low-density gas in the state with a temperature and its several successive gradients given, corrections to the pressure and the internal energy induced by the weak nonequilibrium stationarity are presented in Section 3. Expressions for the compressibilities and the heat capacities are derived. In Sections 4 and 5, the entropy and the free energy are calculated. The pressure and the entropy are compared to those calculated previously.

2. A Sequence of Approximations for the Local Nonequilibrium Heat-Conduction State

The notions and the conceptions of the theory of continuum media [1, 2] are among basic means for the description of nonequilibrium phenomena in gases and liquids. They are used in the linear irreversible thermodynamics, hydrodynamics, kinetic theory, and nonequilibrium statistical mechanics. As usual, a nonequilibrium state of a gas or liquid is described by means of densities of conserved quantities or corresponding intensive parameters [1, 2]. For the heat conduction phenomenon, the key role is attributed to a local temperature $T(\mathbf{r}, t)$, which depends on the space position $\mathbf{r}$ and the time t. The space nonuniformity of the temperature causes the appearance of a heat flux. Several approximations can be used to describe the local state of a nonequilibrium gas or liquid, Fig. 1.

2.1. Local-equilibrium approximation

In this approximation, local properties of the nonequilibrium system at an arbitrary point $\mathbf{r}_0$, Fig. 1, are described with the aid of the *suitable equilibrium system* with number density n_0 and temperature T_0, which are equal to the corresponding local values:

$$n_0 = n(\mathbf{r}_0), \quad T_0 = T(\mathbf{r}_0). \tag{1}$$

Such a substitution, Fig. 2, can meet success for quantities, which are well defined in equilibrium – internal energy, pressure, or entropy. A shortcoming of the approximation consists in that we cannot describe the very conduction of heat, as the heat flux is absent in equilibrium.

2.2. Local steady-state approximation

If the local gradient of the temperature field

$$\mathbf{G}_1 \equiv \nabla T(\mathbf{r})\big|_{\mathbf{r}=\mathbf{r}_0} \tag{2}$$

is added to set (1), we are able to characterize the local nonequilibrium state at $\mathbf{r}_0$ more completely. In fact, it is substituted by the *suitable system in the steady state* with parameters $\{n_0, T_0, \mathbf{G}_1\}$. Let the coordinate axis OZ with the origin at $\mathbf{r}_0$ be chosen along $\mathbf{G}_1$. Then the steady system is nonuniform along OZ only, and we choose the simplest case for it – a parallelepiped form, as shown in Fig. 1. The parameters $\{n_0, T_0, \mathbf{G}_1\}$ refer to its middle, that is, plane XOY divides the system of the steady approximation onto two parts with equal volumes, Fig. 3.

The total number of particles N is to be related to the linear size L along OZ and the cross area Ω in such a way that the local particle density $n(z)$ of the approximating system takes a correct value at the "middle point":

$$n(z)\big|_{z=0} = n(\mathbf{r}_0).$$

L is also restricted by the condition that the local temperature field

$$T(z) = T_0 + G_1 z, \tag{3}$$

where $\mathbf{G}_1 = (0, 0, G_1)$, differs weakly from the true temperature field $T(\mathbf{r})$ near $\mathbf{r}_0$ in the nonequilibrium system. The temperature gradient (2) ensures a nonzero heat flux. Thus, this local steady-state approximation describes the local nonequilibrium state qualitatively better and more accurately than the local-equilibrium one.

2.3. Approximations of higher orders

If the second-order gradient, $\mathsf{G}_2 \equiv \nabla\nabla T(\mathbf{r})\big|_{\mathbf{r}=\mathbf{r}_0}$, is added to the set $\{n_0, T_0, \mathbf{G}_1\}$, we further improve the accuracy of the description. In this case, the temperature dependence is given by the expression $T(z) = T_0 + G_1 z + \frac{1}{2} G_2 z^2$. If one proceeds further, *the sequence of approximations* for the description of nonequilibrium states in macroscopic systems can be build up.

3. Equations of Steady State for a Low-Density Gas

The considerations given above are applied here to a low-density gas in the weakly nonequilibrium heat-conduction steady state. The low density is understood in the sense that the mean free path is much greater than the characteristic radius of the interparticle interaction all over the gas [3, 5, 44]. The state is characterized by the values of temperature, T_0, and its first r successive gradients:

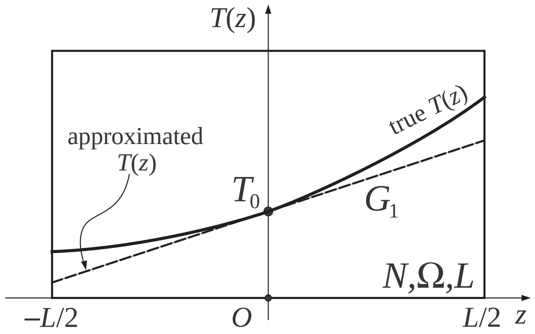

Fig. 3. Steady-state system approximating the local nonequilibrium heat-conduction state

$$\big\{N, \Omega, L;\ T_0, G_1, G_2, ..., G_r\big\}, \tag{4}$$

where $G_k \equiv \frac{\partial^k}{\partial z^k} T(z)\big|_{z=0}$. The local temperature dependence is expressed as

$$T(z) = T_0 + \sum_{k=1}^{r} \frac{1}{k!} G_k z^k. \tag{5}$$

The weakly nonequilibrium case means that the contribution of the next gradient is much less than that from the previous gradient for any z:

$$\tfrac{1}{k+1} \left|G_{k+1}\right| L/2 \ll \left|G_k\right|. \tag{6}$$

This condition is well-known in nonequilibrium theory, e.g. [3, 4, 44]. For such a weak deviation from equilibrium, an arbitrary quantity a can be represented as a development in the gradients $\{G\} \equiv \{G_1, G_2, ..., G_r\}$, where the order of each term is shown by a formal small parameter δ:

$$a = a_0 + \sum_{k=1}^{r} \delta^k a_k G_k. \tag{7}$$

3.1. Equations of state

Let us consider how the pressure P is expressed through the quantities of set (4). Note that there is no macroscopic movement in the steady state, and the gas rests in the mechanical equilibrium. This means that the pressure has a fixed value all over the system [57, 58]:

$$P = \text{const}. \tag{8}$$

At this place, we adopt a simple assumption that the low-density gas satisfies locally the ideal equation of state (e.g. [57–59]):

$$P = n(z)\, k_{\mathrm{B}} T(z), \tag{9}$$

where $n(z)$ is the local number density, and k_{B} is the Boltzmann constant. This approximation is well justified for the low-density domain by the Boltzmann kinetic theory [3, 5, 44]. Combining Eqs. (9) and (5) gives:

$$n(z) = n_0 \left[1 + \sum_{k=1}^{r} \delta^k g_k z^k \right]^{-1}; \tag{10}$$

here, $n_0 \equiv P/k_{\mathrm{B}}T$ and $g_k \equiv \frac{1}{T}\frac{1}{k!}\, \partial_z^k T(z)|_{z=0}$ (we suppress zero in the subscript of the temperature middle-point value).

The total number of particles N is accepted to be finite in the steady system, and we obtain the following normalization condition:

$$\int\limits_{\Omega\times L} \mathrm{d}\mathbf{r}\, n(z) = N,$$

where $\mathbf{r} \equiv (x, y, z)$. The integration over the transverse coordinates x and y transforms it to

$$\int\limits_{-L/2}^{L/2} \mathrm{d}z\, n(z) = N/\Omega. \tag{11}$$

Due to the inequalities of the weak deviation from equilibrium (6), expression (10) can be expanded in a series as:

$$[1 + x]^{-1} = 1 - x + x^2 - x^3 + x^4 \mp \dots . \tag{12}$$

If we restrict ourselves in set (4) to the fourth order, the expression $x = \delta\, g_1 z + \delta^2 g_2 z^2 + \delta^3 g_3 z^3 + \delta^4 g_4 z^4$ should be substituted into this series, in accordance to Eq. (7). The resulting expansion can be integrated explicitly:

$$\frac{N}{\Omega} = n_0 L \biggl[1 + \frac{1}{3}(g_1^2 - g_2)\, [L/2]^2 + \\ + \frac{1}{5}(g_1^4 - 3g_1^2 g_2 + g_2^2 + 2g_1 g_3 - g_4)\, [L/2]^4 + \dots \biggr],$$

where terms of the same order are gathered together with powers of δ omitted. It is sufficient to consider only the second-order correction. The fourth order is calculated to demonstrate the effectiveness of our method.

Next, we apply formula (12) to the expression for n_0 derived from the previous equation and obtain

$$P(N, \Omega, L; T, g_1, \dots, g_r) = \\ = \frac{N}{\Omega L}\, k_{\mathrm{B}} T \Bigl[1 + p_2 L^2 + p_4 L^4 + \dots \Bigr], \tag{13}$$

where coefficients read

$$p_2 \equiv \frac{1}{12}\bigl(g_2 - g_1^2\bigr),$$

$$p_4 \equiv \frac{1}{80}\left(g_4 - 2g_3 g_1 - \frac{4}{9} g_2^2 + \frac{17}{9} g_2 g_1^2 - \frac{4}{9} g_1^4 \right).$$

These can be expressed through $\{G\}$, by substituting $g_k = \frac{1}{T}\frac{1}{k!}\, G_k$. Equation (13) is of the form of expansion $P = P^{(0)} + P^{(2)} + P^{(4)} + \dots$, where $P^{(k)}$ contains terms of the k-th order in gradients.

An expression for the internal energy can be obtained. Accordingly to Eq. (9), we suppose $\varepsilon(z) = \frac{3}{2} n(z) k_{\mathrm{B}} T(z)$ for the local energy density. It follows from Eq. (9) that $E = \frac{3}{2} P \Omega L$ has the expansion

$$E = E^{(0)} + E^{(2)} + E^{(4)} + \dots = \\ = \frac{3}{2} N k_{\mathrm{B}} T \bigl[1 + e_2 L^2 + e_4 L^4 + \dots \bigr] \tag{14}$$

with coefficients $e_k = p_k$.

We have derived the baric (13) and caloric (14) equations of the weakly nonequilibrium heat-conduction steady state. The pressure and the internal energy are expressed through the macroscopic quantities N, Ω, and L and the temperature T with its derivatives $G_k \equiv \partial^k T/\partial z^k\bigr|_{z=0}$, which refer to the middle-point of the gas. It is important that the contributions from the gradients do not change at the inversion of the axis OZ: at the operation $z \to -z$, the transformation $g_k \to (-1)^k g_k$ holds. Note the signs of the contributions: the terms with a gradient in an even power (g_1^2, g_1^4, g_2^2) are negative, while the "pure" gradients of even orders (g_2, g_4) are positive.

Calculations of higher-order corrections to P and E are cumbersome, but feasible. This cannot be done within any approaches mentioned in Introduction.

3.2. Comparison with the extended irreversible thermodynamics

The result for a pressure can be compared to that of the extended irreversible thermodynamics [17, 18] (see [11, 14, 15]). In that approach, the entropy density expression following from the Grad formula [9] is chosen as a starting point. The nonequilibrium scalar pressure is introduced as a specific volume derivative of the entropy density: $\tilde{P}^{\rm EIT} = \tilde{P}^{\rm l.eq.} + \Delta\tilde{P}$, where $\tilde{P}^{\rm l.eq.} = \tilde{n}k_{\rm B}\tilde{T}$ is the local-equilibrium pressure, while $\tilde{n}$ and $\tilde{T}$ are the local number density and the local-equilibrium temperature. The tilde denotes here a dependence on the space position. The nonequilibrium correction [17, 18]

$$\Delta\tilde{P} \equiv -\frac{4}{5}\frac{m}{\tilde{n}k_{\rm B}^2\tilde{T}^2}\,\mathbf{q}\cdot\mathbf{q} \qquad (15)$$

appears due to the heat flux $\mathbf{q}$; m is particle's mass. The results of the information theory [17, 28] and kinetic theory [45] for a pressure were shown [46] to differ by a number coefficient in Eq. (15).

The quantity $\Delta\tilde{P}$ can be expressed through the temperature gradient. The linear relation $\mathbf{q} = -\lambda\nabla\tilde{T}$, where λ is the thermal conductivity, is known to be a quite good approximation [3, 4, 44]. Its substitution gives

$$\Delta\tilde{P} = -\frac{4}{5}\frac{m}{\tilde{n}k_{\rm B}^2}\,\lambda^2\,\frac{(\nabla\tilde{T})^2}{\tilde{T}^2}. \qquad (16)$$

We note that $\Delta\tilde{P}$ is inversely proportional to $\tilde{n}$ *contrary* to the direct proportionality in $\tilde{P}^{\rm l.eq.}$. Moreover, the dependence of $\Delta\tilde{P}$ on λ, a relaxation parameter of the gas, seems unusual, as there is *no relaxation process* in the steady state.

The well-established Chapman–Enskog analytic result for the thermal conductivity can be used [3, 4, 44]:

$$\lambda = \frac{25}{16}\,c_V\,\frac{k_{\rm B}\tilde{T}}{\Omega^{(2,2)}_{\rm hs}(\tilde{T})\,\Omega^{(2,2)*}(\tilde{T})}, \qquad (17)$$

where $c_V = \frac{3}{2}k_{\rm B}/m$ is the specific heat capacity of the equilibrium monatomic gas at a constant volume, $\Omega^{(2,2)}_{\rm hs}(\tilde{T}) = 2\sqrt{\pi}\,\sqrt{k_{\rm B}\tilde{T}/m}\,\sigma^2$ is the scattering integral of the hard-sphere model with diameter σ [4, 44], while $\Omega^{(2,2)*}(\tilde{T})$ is the reduced scattering integral describing the temperature dependence caused by peculiarities of the real interparticle potential. (This splitting of the conventional $\Omega^{(2,2)}$ onto $\Omega^{(2,2)}_{\rm hs}$ and $\Omega^{(2,2)*}$ is needed here to extract the characteristic $\sqrt{\tilde{T}}$ dependence [4, 44].) The substitution of expression (17) into Eq. (16) yields

$$\Delta\tilde{P} = -\frac{1125}{1024}\frac{1}{\pi}\,k_{\rm B}\frac{1}{\tilde{n}\sigma^4}\frac{(\nabla\tilde{T})^2}{\tilde{T}}\frac{1}{[\Omega^{(2,2)*}(\tilde{T})]^2}. \qquad (18)$$

$\Omega^{(2,2)*}(\tilde{T})$ makes the pressure corrections for different low-density gases (with the same $\tilde{n}$ and $\tilde{T}$) to differ from each other. Finally, Eq. (18) contains the local-equilibrium $\tilde{n}$ and $\tilde{T}$ rather than global quantities. We can compare this result to ours only formally.

Equation (13) shows that the correction

$$P^{(2)} = \frac{1}{12}\frac{N}{\Omega}L\,k_{\rm B}\Big(-\frac{G_1^2}{T} + \frac{1}{2}G_2\Big)$$

is expressed by the global variables and does not depend on the interaction. We also notice the strong difference in the coefficients at $(\nabla\tilde{T})^2$ and G_1^2. In addition, Eq. (18) contains no contribution from $\nabla\nabla\tilde{T}$.

3.3. Compressibilities

The results for P and E, Eqs. (13) and (14), can be used to calculate compressibilities and heat capacities.

The equilibrium isothermal compressibility [57–59]

$$\chi_T^{(0)} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P^{(0)}}\right)_T \qquad (19)$$

of the gas with the equation of state $P^{(0)} = (N/V) \times k_{\rm B}T$ reads $\chi_T^{(0)} = 1/P^{(0)}$. In the case we consider, the volume can be changed in two ways. When the plane surface confining the gas moves in the direction, which is a) parallel to the heat flux (L changes) and b) perpendicular to the heat flux (Ω changes). So, two compressibilities should be calculated: longitudinal ($\|$) and transverse ($\perp$) ones. Their definitions through a volume derivative like Eq. (19) can be reduced to the following:

$$\chi^{\|}_{T,\{G\}} \equiv -\frac{1}{L}\left(\frac{\partial L}{\partial P}\right)_{T,\{G\};\Omega}, \qquad (20)$$

$$\chi^{\perp}_{T,\{G\}} \equiv -\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial P}\right)_{T,\{G\};L}, \qquad (21)$$

where it is indicated that T, $\{G_1, ..., G_r\}$ and Ω (or L) are kept constant.

Starting from Eq. (13), it is convenient to use pressure derivatives. With the expression

$(\partial P/\partial\Omega)_{T,\{G\};L} = -P/\Omega$, the transverse compressibility obeys the same relation $\chi^{\perp}_{T,\{G\}} = 1/P$, as in equilibrium. The expansion into a series yields

$$\chi^{\perp}_{T,\{G\}} = \chi^{(0)}_T \left[1 - p_2L^2 + (-p_4 + p_2^2)L^4 + ...\right].$$

The pressure derivative for the longitudinal component $\chi^{\parallel}_{T,\{G\}}$ equals:

$$\left(\frac{\partial P}{\partial L}\right)_{T,\{G\};\Omega} = -\frac{P^{(0)}}{L}\left(1 - p_2L^2 - 3p_4L^4 - ...\right).$$

By substituting it into Eq. (20) for $\chi^{\parallel}_{T,\{G\}}$ and expanding into a series, we get

$$\chi^{\parallel}_{T,\{G\}} = \chi^{(0)}_T \left[1 + p_2L^2 + (3p_4 + p_2^2)L^4 + ...\right].$$

The second-order coefficients in $\chi^{\perp}_{T,\{G\}}$ and $\chi^{\parallel}_{T,\{G\}}$ differ by signs from each other, while the fourth-order terms differ quantitatively.

3.4. Heat capacities

The heat capacity $C_{V,\{G\}}$ at a constant volume and constant gradients can be obtained in the form:

$$C_{V,\{G\}} \equiv \left(\frac{\partial E}{\partial T}\right)_{V,\{G\}} = \frac{3}{2}Nk_{\rm B}\left[1 + c_2L^2 + c_4L^4 + ...\right], \tag{22}$$

where Eq. (14) for E is used; the coefficients read $c_2 \equiv \frac{1}{12}G_1^2/T$ and $c_4 \equiv \frac{1}{80}T^{-4}\times$ $\times\left(\frac{1}{3}T^2G_3G_1 + \frac{1}{9}T^2G_2^2 - \frac{17}{9}TG_2G_1^2 + \frac{4}{3}G_1^4\right)$. Expressions for c_2 and c_4 show that G_2 in the second order and G_4 in the fourth order do not contribute to $C_{V,\{G\}}$.

Another possibility to transfer heat to/from the system at a constant volume consists in transitions to such steady states, where the middle-point temperature T is kept fixed, while the value of gradient G_k is changed. The corresponding parameter

$$\tilde{C}_{V,T;(k)} \equiv \left(\frac{\partial E}{\partial G_k}\right)_{V,T;\{G_1,...,G_{k-1},G_{k+1},...,G_r\}}$$

describes such heat capacity and can be referred to as the *partial gradient heat capacity.* From Eq. (14), we derive

$$\tilde{C}_{V,T;(1)} = \frac{3}{2}Nk_{\rm B}\left[-\frac{1}{6}\frac{G_1}{T}L^2 + \right.$$

$$\left. + \frac{1}{240}\frac{1}{T^3}\left(-\frac{4}{3}G_1^3 + \frac{17}{3}TG_1G_2 - T^2G_3\right)L^4\right],$$

$$\tilde{C}_{V,T;(2)} = \frac{3}{2}Nk_{\rm B}\left[\frac{1}{24}L^2 + \frac{1}{720}\frac{1}{T^2}\left(\frac{17}{2}G_1^2 - 2TG_2\right)L^4\right],$$

$$\tilde{C}_{V,T;(3)} = -\frac{1}{160}Nk_{\rm B}\frac{G_1}{T}L^4,$$

$$\tilde{C}_{V,T;(4)} = \frac{1}{1280}Nk_{\rm B}L^4.$$

The expressions obtained for the compressibilities and the capacities are of a rather mathematical, than physical, meaning. For example, $\chi^{\parallel}_{T,\{G\}}$ does not involve variations of the gradients, when L changes. Similarly, $\tilde{C}_{V,T;(k)}$ describes the partial variation in E due to a change of G_k. If the system goes from one steady state to a close steady state at a constant volume, then the internal energy variation can be estimated by the linear combination

$$\Delta E = C_{V,\{G\}}\Delta T + \sum_{k=1}^{r}\tilde{C}_{V,T;(k)}\Delta G_k,$$

where ΔT and $\Delta G_k\big|_{k=1...r}$ are corresponding changes in the temperature and its gradients.

4. Entropy

Here, we calculate the steady-state entropy and show that it is less than the entropy of the equilibrium gas with the same internal energy.

The entropy of a weakly nonequilibrium heat-conduction steady state can be defined by means of the integration of its density $s(\mathbf{r})$:

$$S \equiv \int\limits_{\Omega\times L} d\mathbf{r}\, s(\mathbf{r}) = \Omega\int\limits_{-L/2}^{L/2} dz\, s(z). \tag{23}$$

The entropy $S_{\rm eq}$ of the equilibrium state of a gas of N particles confined in the volume ΩL reads [5]

$$S_{\rm eq} = Nk_{\rm B}\left[-\ln(N/\Omega L) + \tfrac{3}{2}\ln T_{\rm eq} + \xi_{5/2}\right], \tag{24}$$

where $T_{\rm eq}$ is the equilibrium temperature, $\xi_{5/2} \equiv \xi +$ $+\frac{5}{2}$, while the constant $\xi \equiv \frac{3}{2}\ln(2\pi k_{\rm B}m/h^2)$ is related to the quantum statistics of states in the phase space for particles with mass m, h is the Planck constant.

For $s(z)$, let us use the entropy density obtained from the density $S_{\rm eq}/\Omega L$ of the equilibrium entropy

(24), by making the thermodynamic quantities in it to be *local*:

$$s(z) = k_{\mathrm{B}} n(z)\left[\frac{5}{2}\ln T(z) - \ln\big(P/k_{\mathrm{B}}\big) + \xi_{5/2}\right], \tag{25}$$

where $\ln n(z)$ has been expressed through $\ln T(z)$ due to Eq. (9). In correspondence to the expression in the square brackets, the total entropy (23) consists of three terms:

$$S = S_T + S_P + S_\xi.$$

We look for each of them in the form of expansion (7) in the gradients.

4.1. Entropy contributions

The normalization condition (11) for $n(z)$ yields

$$S_P = -N k_{\mathrm{B}} \ln\big(P/k_{\mathrm{B}}\big), \quad S_\xi = N k_{\mathrm{B}} \xi_{5/2}.$$

The expansion of $\ln\left[1 + p_2 L^2 + p_4 L^4 + ...\right]$ in Eq. (13) transforms S_P to the following form:

$$S_P = N k_{\mathrm{B}}\left[\ln\frac{\Omega L}{N} - \ln T - p_2 L^2 - (p_4 - \frac{1}{2}p_2^2)L^4 - ...\right]; \tag{26}$$

the coefficients at L^2 and L^4 read

$$s_{P,2} \equiv -\frac{1}{12}g_2 + \frac{1}{12}g_1^2,$$
$$s_{P,4} \equiv \frac{1}{80}\left[-g_4 + 2g_3 g_1 + \frac{13}{18}g_2^2 - \frac{22}{9}g_2 g_1^2 + \frac{13}{18}g_1^4\right].$$

Let us calculate S_T. For the functions in the integral

$$S_T = \Omega\, k_{\mathrm{B}} \frac{5}{2}\int\limits_{-L/2}^{L/2} \mathrm{d}z\, n(z) \ln T(z), \tag{27}$$

we use the expansions into series

$$n(z) = n_0\left[\nu_0 + \nu_1 z + \nu_2 z^2 + ...\right]$$

with the coefficients $\{\nu\}$ found from Eq. (10):

$$\nu_0 = 1,$$
$$\nu_1 = -g_1,$$
$$\nu_2 = -g_2 + g_1^2,$$
$$\nu_3 = -g_3 + 2g_2 g_1 - g_1^3,$$
$$\nu_4 = -g_4 + 2g_3 g_1 + g_2^2 - 3g_2 g_1^2 + g_1^4;$$

and, by the same way,

$$\ln T(z) = \tau_0 + \tau_1 z + \tau_2 z^2 + ...$$

with $\{\tau\}$ found from Eq. (5),

$$\tau_0 = \ln T,$$
$$\tau_1 = g_1,$$
$$\tau_2 = g_2 - \frac{1}{2}g_1^2,$$
$$\tau_3 = g_3 - g_2 g_1 + \frac{1}{3}g_1^3,$$
$$\tau_4 = g_4 - g_3 g_1 - \frac{1}{2}g_2^2 + g_2 g_1^2 - \frac{1}{4}g_1^4.$$

Integrating the series $n_0\sum_{i=0}^{r} w_i z^i$ for the product $w(z) \equiv n(z)\ln T(z)$ according to Eq. (27) yields

$$S_T = \Omega\, k_{\mathrm{B}} \frac{5}{2} n_0 L\left[w_0 + \frac{1}{3}w_2(L/2)^2 + \frac{1}{5}w_4(L/2)^4 + ...\right]. \tag{28}$$

The coefficients are convolutions over a discrete index, $w_i = \sum_{k=0}^{i}\nu_k \tau_{i-k}$. The substitution of the expressions for $\{\nu\}$ and $\{\tau\}$ yields

$$w_0 = \ln T,$$
$$w_2 = -g_2\Lambda_1 + g_1^2\Lambda_{3/2},$$
$$w_4 = -g_4\Lambda_1 + 2g_3 g_1\Lambda_{3/2} + g_2^2\Lambda_{3/2} - 3g_2 g_1^2\Lambda_{11/6} + $$
$$+ g_1^4\Lambda_{25/12},$$

where the notation $\Lambda_f \equiv \ln T - f$ has been used.

The amplitude in Eq. (28) reduces to $\Omega\,\frac{5}{2}(P/T)L$. Inserting expansion (13) for P here and performing some algebra in S_T, we obtain

$$S_T = N k_{\mathrm{B}}\left[s_{T,0} + s_{T,2}L^2 + s_{T,4}L^4 + ...\right], \tag{29}$$

where the coefficients are convolutions: $s_{T,0} \equiv \frac{5}{2}p_0 w_0$, $s_{T,2} \equiv \frac{5}{2}[\frac{1}{12}p_0 w_2 + p_2 w_0]$, $s_{T,4} \equiv \frac{5}{2}[\frac{1}{80}p_0 w_4 + \frac{1}{12}p_2 w_2 + {} + p_4 w_0]$ with $p_0 = 1$. We express these in terms of $\{g\}$ as follows:

$$s_{T,0} = \frac{5}{2}\ln T,$$
$$s_{T,2} = \frac{5}{2^3\, 3}\left[g_2 - \frac{3}{2}g_1^2\right],$$
$$s_{T,4} = \frac{1}{2^7\, 3^2}\left[36g_4 - 108g_3 g_1 - 34g_2^2 + 148g_2 g_1^2 - 45g_1^4\right].$$

Gathering together S_T and S_P given by Eqs. (29) and (26) and S_ξ results in the final formula for the entropy of the weakly nonequilibrium heat-conduction steady state:

$$S = S^{(0)} + S^{(2)} + S^{(4)} + ... =$$
$$= N k_{\mathrm{B}}\left[s_0 + s_2 L^2 + s_4 L^4 + ...\right] \tag{30}$$

with the coefficients $s_i \equiv s_{T,i} + s_{P,i} + s_{\xi,i}$:

$$\begin{aligned}
&s_0 = \ln(\Omega L/N) + \frac{3}{2}\ln T + \xi_{5/2},\\
&s_2 = \frac{1}{8}g_2 - \frac{11}{48}g_1^2,\\
&s_4 = \frac{1}{2^7\, 3^2\, 5}\big[108 g_4 - 396 g_3 g_1 - 118 g_2^2 + \\
&+ 564 g_2 g_1^2 - 173 g_1^4\big].
\end{aligned}$$

4.2. Compatibility with the second law

Next, we show explicitly that entropy (30) is *less* than the entropy of the corresponding equilibrium state. To this end, let us imagine that, at some instant, we isolate the system at the boundaries $z = -L/2$ and $z = L/2$. We let the gas to relax to the equilibrium during a macroscopic interval of time.

The internal energy does not change at the relaxation: $E = \text{const}$. The final equilibrium temperature T_{fin} can be found from the well-known relation $E = \frac{3}{2}Nk_{\text{B}}T_{\text{fin}}$. According to Eq. (14), we find out

$$T_{\text{fin}} = T\big[1 + e_2 L^2 + e_4 L^4 + ...\big].$$

Then expression (24) for the equilibrium entropy yields

$$\begin{aligned}
&S_{\text{fin}} = Nk_{\text{B}}\Bigg[\ln(\Omega L/N) + \frac{3}{2}\ln T + \xi_{5/2} + \\
&+ \frac{3}{2}\left(p_2 L^2 + \left[p_4 - \frac{1}{2}p_2^2\right]L^4 + ...\right)\Bigg],
\end{aligned}$$

where we take in mind that $e_k = p_k$, while $\ln[1 + ...]$ has been expanded.

Finally, the difference $\Delta S \equiv S - S_{\text{fin}}$ reads

$$\begin{aligned}
&\Delta S = Nk_{\text{B}}\Bigg[-\frac{5}{48}\,g_1^2 L^2 + \\
&+ \frac{1}{2^7\, 3^2}\big(-36 g_3 g_1 - 8 g_2^2 + 60 g_2 g_1^2 - 19 g_1^4\big)L^4\Bigg].
\end{aligned}$$

The sign of $\Delta S^{(4)} \sim L^4$ cannot be determined, as it depends on the values of gradients. Nevertheless, due to assumption (6), the inequality $|\Delta S^{(4)}| \ll |\Delta S^{(2)}|$ holds, and $\Delta S^{(4)}$ can be neglected in our analysis. The inequality $\Delta S^{(2)} < 0$ shows that the entropy S of the weakly nonequilibrium steady state is *less* than its equilibrium counterpart S_{fin}. Thus, our results are in accordance with the second law of thermodynamics for nonequilibrium processes [57].

4.3. Comparison with other theories

Kim and Hayakawa compare [46] the results of the information theory (IT) [17, 28] and the kinetic theory (KT) [45] for the nonequilibrium entropy density of the weakly nonequilibrium heat-conduction steady state, which can be written as

$$\tilde{s} = \tilde{s}^{\text{l.eq.}} + \Delta\tilde{s},$$

where

$$\tilde{s}^{\text{l.eq.}} \equiv -\tilde{n}k_{\text{B}}\ln\left[\tilde{n}\left(\frac{m}{2\pi k_{\text{B}}\tilde{T}}\right)^{3/2}\right] + \frac{3}{2}\,\tilde{n}k_{\text{B}} \tag{31}$$

is the local-equilibrium entropy density of a low-density gas of particles with classical statistics and

$$\Delta\tilde{s} \equiv \lambda_S\frac{m}{\tilde{n}k_{\text{B}}^2\tilde{T}^3}q^2$$

is the lowest nonequilibrium heat-flux correction. The number coefficient λ_S takes values $\lambda_S^{\text{IT}} = -\frac{1}{5}$, $\lambda_S^{\text{KT,Mm}} = -\frac{1}{5}$ for Maxwell molecules and $\lambda_S^{\text{KT,hs}} = -0.2035$ for hard spheres. As the local functions $\tilde{n}$ and $\tilde{T}$ depend on the position coordinate, the density $\tilde{s}$ cannot be integrated explicitly to give the total entropy, as it is mistakenly stated in Ref. [17].

Similarly to Section 3, the substitution of the Fourier law into $\Delta\tilde{s}$ leads to the expression:

$$\Delta\tilde{s} = \lambda_S\frac{75^5}{64^2\pi}k_{\text{B}}\frac{1}{\tilde{n}\sigma^4}\frac{(\nabla\tilde{T})^2}{\tilde{T}^2}\frac{1}{[\Omega^{(2,2)*}(\tilde{T})]^2}.$$

Though it cannot be integrated explicitly, one can conclude that it differs substantially from our result:

$$S^{(2)} = Nk_{\text{B}}\left[\frac{1}{16}\frac{G_2}{T} - \frac{11}{48}\frac{G_1^2}{T^2}\right].$$

In addition, $\Delta\tilde{s}$ depends on the interaction potential through $\Omega^{(2,2)*}(\tilde{T})$, and it does not contain any contribution from the local second gradient $\nabla\nabla\tilde{T}$.

It is obvious that $\tilde{s} \leq \tilde{s}^{\text{l.eq.}}$ due to the negative definiteness of $\Delta\tilde{s}$. But this inequality means something different from the consistence with the second law of thermodynamics. If $\mathbf{q}$ tends to zero, $\tilde{s}$ tends to some *equilibrium* entropy density s^{eq} given by formula (31) with corresponding equilibrium values n^{eq} and T^{eq} substituted, rather than to the local-equilibrium density $\tilde{s}^{\text{l.eq.}}$. In order to verify whether $\tilde{s}$ satisfies the second law of thermodynamics for nonequilibrium processes, one should first calculate n^{eq} and T^{eq} and insert them into Eq. (31) to find the final equilibrium counterpart s^{eq} and compare it with $\tilde{s}$.

5. Free Energy

As was discussed in Introduction, some authors attempted by a variety of methods [7, 32, 41, 42] to solve the problem of the free energy definition and calculation for nonequilibrium or steady states. Their purposes were to obtain the complete thermodynamic description in the analogy with the equilibrium case. Our results of calculations of the pressure, internal energy, and entropy evoke the expectation that the way presented above can provide the free energy of the weakly nonequilibrium heat-conduction steady state explicitly. From the viewpoint of thermodynamics, it would give the complete description of the low-density gas in this state.

Similarly to the entropy case, Eq. (23), the free energy F is defined by the integration [60]:

$$F \equiv \Omega \int\limits_{-L/2}^{L/2} \mathrm{d}z\, f(z). \tag{32}$$

Its local density $f(z)$ is derived from the equilibrium free energy F_{eq} of the low-density gas (e.g. [5])

$$F_{\mathrm{eq}} = -Nk_{\mathrm{B}}T_{\mathrm{eq}}\left[\ln(\Omega L/N) + \frac{3}{2}\ln T_{\mathrm{eq}} + \xi_1\right], \tag{33}$$

where $\xi_1 \equiv \frac{3}{2}\ln(2\pi k_{\mathrm{B}} m/h^2) + 1$. All the thermodynamic quantities in the corresponding density $F_{\mathrm{eq}}/\Omega L$ are replaced by the *local* counterparts:

$$f(z) = -P\left[\frac{5}{2}\ln T(z) - \ln\big(P/k_{\mathrm{B}}\big) + \xi_1\right]. \tag{34}$$

Here, condition (9) has been used to express $\ln n(z)$ through $\ln T(z)$.

After the integration, this free energy density produces three contributions

$$F = F_T + F_P + F_\xi$$

of the following form:

$$F_T = -P\Omega L\,\frac{5}{2}\left[\tau_0 + \frac{1}{12}\tau_2 L^2 + \frac{1}{80}\tau_4 L^4 + \ldots\right],$$
$$F_P = P\Omega L \ln\big(P/k_{\mathrm{B}}\big),$$
$$F_\xi = -P\Omega L\,\xi_1.$$

The sum of these terms, after the substitution of Eq. (13) for P, yields the free energy expansion [60]:

$$F(N,\Omega,L;T,g_1,\ldots,g_4) = -Nk_{\mathrm{B}}T\Big[f_0 + f_2L^2 + f_4L^4 + \ldots\Big]. \tag{35}$$

The coefficients f_i are expressed in terms of $\Phi_p \equiv \ln(\Omega L/N) + \frac{3}{2}\ln T + \xi + p$:

$$f_0 \equiv \Phi_1,$$
$$f_2 \equiv \frac{1}{12}\big[g_2\Phi_{5/2} - g_1^2\Phi_{5/4}\big],$$
$$f_4 \equiv \frac{1}{80}\Big[g_4\Phi_{5/2} - 2g_3g_1\Phi_{5/4} - \frac{4}{9}g_2^2\Phi_{5/16} + \frac{17}{9}g_2g_1^2\Phi_{35/68} - \frac{4}{9}g_1^4\Phi_{25/32}\Big].$$

Next, we analyze this result from the viewpoint of the Gibbs method of thermodynamic potentials of equilibrium thermodynamics. As is well-known [5,57–59], the free energy in the equilibrium state is a thermodynamic potential, if expressed through the variables of temperature T_{eq}, volume V, and number of particles N. Its exact differential reads

$$\mathrm{d}F_{\mathrm{eq}} = -S_{\mathrm{eq}}\mathrm{d}T_{\mathrm{eq}} - P_{\mathrm{eq}}\mathrm{d}V + \mu_{\mathrm{eq}}\mathrm{d}N,$$

where μ_{eq} is the equilibrium chemical potential. It is necessary to consider whether the nonequilibrium free energy given by Eq. (35) has thermodynamic potential properties for the set of variables (4). If we suppose this is the case, then its exact differential can be represented by

$$\mathrm{d}F = -S_F\mathrm{d}T - \Pi_\perp\mathrm{d}\Omega - \Pi_\parallel\mathrm{d}L + \mu\mathrm{d}N + \sum_{i=1}^{r}\alpha_i\mathrm{d}\Gamma_i,$$

where S_F is the entropy obtained as the temperature derivative of F; we bear in mind that $\mathrm{d}V = L\mathrm{d}\Omega + \Omega\mathrm{d}L$, and the differentials $\mathrm{d}\Omega$ and $\mathrm{d}L$ are considered as independent; and μ is the nonequilibrium chemical potential. The variables $\{\Gamma\}$ denote gradients $\{G\}$ or $\{g\}$, while $\{\alpha\}$ is the set of corresponding thermodynamic conjugates. We note that, due to the isotropy of the pressure, the following conditions must be satisfied: $\Pi_\perp/L = \Pi_\parallel/\Omega = P$.

There are various possibilities to choose $\{\Gamma\}$. In the case $\{\Gamma\} = \{G\}$, the derivatives of the free energy read

$$\Pi_\perp \equiv -\left(\frac{\partial F}{\partial \Omega}\right)_{N,L,T,\{G\}} = LP,$$
$$\Pi_\parallel \equiv -\left(\frac{\partial F}{\partial L}\right)_{N,\Omega,T,\{G\}} = \Omega(P + \Delta P_\parallel),$$
$$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\Omega,L,T,\{G\}} = k_{\mathrm{B}}T\big[m_0 + m_2L^2 + m_4L^4 + \ldots\big],$$

$$S_F \equiv -\left(\frac{\partial F}{\partial T}\right)_{N,\Omega,L,\{G\}} = Nk_\mathrm{B}\left[s_{F,0} + s_{F,2}L^2 + \right.$$
$$\left. + s_{F,4}L^4 + ...\right],$$

where $\Delta P_\| \equiv (N/\Omega)k_\mathrm{B}T[2f_2L + 4f_4L^3 + ...]$, the coefficients in the expansion of μ equal $m_k = f_k - p_k$, while $s_{F,k}$ are given elsewhere [60].

We have obtained $\Pi_\|/\Omega \neq P$ due to the term $\Delta P_\|$, coming from the differentiation of powers of L in the expansion of F. The reason is that if L changes, the values of gradients $\{G\}$ can also change. When we introduce new variables $\Theta_k \equiv \frac{1}{k!}G_kL^k$ instead of $\{G\}$, the derivative of the free energy expressed through the new set yields a correct expression for $\Pi_\| \equiv -\left(\frac{\partial F}{\partial L}\right)_{N,\Omega,T,\{\Theta\}} = \Omega P$. In addition, the new isothermal compressibilities $\chi^\perp_{T,\{\Theta\}}$ and $\chi^\|_{T,\{\Theta\}}$ become equal to each other, and their equality to $1/P$ is fully recovered.

The derivative with respect to N might be interpreted as the nonequilibrium chemical potential of the gas being in contact with the particle reservoir characterized by the same values of $P, T, \{G\}$ (or $\{\Theta\}$). But, until the thermodynamic status of F is elucidated, the meaning of its derivative μ stays unknown.

We have verified [60] that S_F and S differ from each other in the second order. Which of the sets $\{G\}$, $\{g\}$, or $\{\Theta\}$ we use, the equality $S_F = S$ cannot be attained. Multiplying these sets by an adjusting function of the temperature does not improve the situation.

In other words, the quantity F calculated by the integration of the local-equilibrium free energy density does not possess the properties of a thermodynamic potential. As a result, it does not ensure the complete thermodynamic description. Possible solutions are to find out a suitable set of variables or to search for another function for the role of thermodynamic potential.

6. Conclusions

The phenomenological approach of continuous media has been applied to the thermodynamic description of a low-density gas in the weakly nonequilibrium heat-conduction steady state. Expressions for thermodynamic quantities such as the pressure, internal energy, and entropy are obtained in the forms of expansions in small temperature gradients up to the fourth order. The derived entropy is in agreement with the second law of thermodynamics for nonequilibrium processes. It is revealed that the calculated nonequilibrium free energy does not manifest the properties of a thermodynamic potential.

The distinctive feature of the results concerning the pressure, internal energy, and entropy consists in that they do not contain neither dissipative properties of the heat conduction process (as in the EIT), nor phase-space integrations (as in the fluctuation theorem approach for the free energy difference). These quantities are expressed only through macroscopic parameters. Such a form corresponds fully to the idea of thermodynamic relations.

We expect that these results may be regarded as the lowest approximation in the construction of the thermodynamic theory of heat-conduction steady states of gases and liquids within microscopic approaches.

The author is grateful to V.M. Kuporov for the aid on working out publications on the subject and to Dr. T.Ye. Krokhmalskii for pointing out the works by M.A. Leontovich. The author is indebted to Dr. B.M. Lisnyi and Dr. T.M. Verkholyak for fruitful discussions on many aspects of the work.

This research has made use of NASA's Astrophysics Data System.

1. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
2. I. Gyarmati, *Non-Equilibrium Thermodynamics. Field Theory and Variational Principles* (Springer, Berlin, 1970).
3. S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge Univ. Press, Cambridge, 1970).
4. V.P. Silin, *Introduction to the Kinetic Theory of Gases* (Nauka, Moscow, 1971) (in Russian).
5. R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley-Interscience, New York, 1975).
6. D.N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).
7. M.A. Leontovich, Zhurn. Exp. Teor. Fiz. **8**, 844 (1938).
8. M.A. Leontovich, *Introduction to Thermodynamics. Statistical Physics* (Nauka, Moscow, 1983) (in Russian).
9. H. Grad, Comm. Pure Appl. Math. **2**, 311 (1949).
10. H. Grad, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1958).
11. D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105 (1988).
12. *Extended Thermodynamic Systems*, edited by S. Sieniutycz and P. Salamon (Taylor and Francis, New York, 1992).
13. I. Müller and T. Ruggeri, *Rational Extended Thermodynamics* (Springer, New York, 1999).

14. D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **62**, 1035 (1999).
15. D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics* (Springer, Berlin, 2001).
16. J. Casas-Vázquez and D. Jou, Phys. Rev. E **49**, 1040 (1994).
17. R. Domínguez and D. Jou, Phys. Rev. E **51**, 158 (1995).
18. J. Camacho and D. Jou, Phys. Rev. E **52**, 3490 (1995).
19. J. Casas-Vázquez and D. Jou, Rep. Prog. Phys. **66**, 1937 (2003).
20. D. Jou and A. Salhoumi, Phys. Lett. A **283**, 163 (2001).
21. L.S. García-Colín and Fuentes y Martínez G.J., J. Stat. Phys. **29**, 387 (1982).
22. R.E. Nettleton, J. Phys. A: Math. Gen. **21**, 3939 (1988).
23. R.E. Nettleton, J. Phys. A: Math. Gen. **22**, 5281 (1989).
24. R.E. Nettleton, Phys. Rev. A **42**, 4622 (1990).
25. A.R. Vasconcellos, R. Luzzi, and L. S. García-Colín, Phys. Rev. A **43**, 6622 (1991).
26. L.S. García-Colín, A.R. Vasconcellos, and R. Luzzi, J. Non-Equilib. Thermodyn. **19**, 24 (1994).
27. R.E. Nettleton, J. Chem. Phys. **106**, 10311 (1997).
28. R.E. Nettleton, J. Chem. Phys. **93**, 8247 (1990).
29. B.N. Miller and P.M. Larson, Phys. Rev. A **20**, 1717 (1979).
30. B.C. Eu, J. Chem. Phys. **108**, 5834 (1998).
31. Y. Oono and M. Paniconi, Prog. Theor. Phys. Suppl. **130**, 29 (1998).
32. S.-i. Sasa and H. Tasaki, J. Stat. Phys. **125**, 126 (2006).
33. C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
34. G.E. Crooks, Phys. Rev. E **60**, 2721 (1999).
35. G.E. Crooks, Phys. Rev. E **61**, 2361 (2000).
36. T.S. Komatsu, N. Nakagawa, S.-i. Sasa, and H. Tasaki, Phys. Rev. Lett. **100**, 230602 (2008), arXiv:0711.0246v4.
37. T.S. Komatsu, N. Nakagawa, S.-i. Sasa, and H. Tasaki, J. Stat. Phys. **142**, 127 (2011), arXiv:1009.0970v2.
38. S.-i. Sasa, J. Stat. Mech.: Theory Exper. 01004 (2014).
39. T.S. Komatsu, N. Nakagawa, S.-i. Sasa, and H. Tasaki, J. Stat. Phys. **134**, 401 (2009), arXiv:0805.3023v1.
40. T.S. Komatsu and N. Nakagawa, Phys. Rev. Lett. **100**, 030601 (2008), arXiv:0708.3158v1.
41. N. Nakagawa, Phys. Rev. E **85**, 051115 (2012), arXiv:1109.1374v4.
42. N. Nakagawa and S.-i. Sasa, Phys. Rev. E **87**, 022109 (2013), arXiv:1211.6203v2.
43. T. Sagawa and H. Hayakawa, Phys. Rev. E **84**, 051110 (2011), arXiv:1109.0796v4.
44. J.H. Ferziger and H.G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
45. H.-D. Kim and H. Hayakawa, J. Phys. Soc. Jpn. **72**, 1904 (2003), arXiv:0202003v5.
46. H.-D. Kim and H. Hayakawa, J. Phys. Soc. Jpn. **72**, 2473 (2003), arXiv:cond-mat/0203036v5.
47. H.-D. Kim, Phys. Rev. E **71**, 041203 (2005), arXiv:cond-mat/0501142v2.
48. T.H. Nishino and H. Hayakawa, J. Phys. Soc. Jpn. **74**, 2655 (2005), arXiv:cond-mat/0506491v2.
49. H. Hayakawa, T.H. Nishino, and H.-D. Kim, e-print arXiv:cond-mat/0412011v1 (2004).
50. S. Taniguchi, M. Nakamura, M. Sugiyama, M. Isobe, and N. Zhao, J. Phys. Soc. Jpn. **77**, 014004 (2008).
51. C.S. Kim and G.P. Morriss, Phys. Rev. E **80**, 061137 (2009).
52. T. Taniguchi and G.P. Morriss, Phys. Rev. E **68**, 026218 (2003).
53. G.P. Morriss, T. Chung, and C. Angstmann, Entropy **10**, 786 (2008).
54. G.P. Morriss and D. Truant, Entropy **14**, 1011 (2012).
55. G.P. Morriss and D.P. Truant, Phys. Rev. E **87**, 062144 (2013), arXiv:1305.2911v1.
56. G.P. Morriss, e-print arXiv:1409.3259v1 (2014).
57. I.P. Bazarov, *Thermodynamics* (Vysshaya Shkola, Moscow, 1983) (in Russian).
58. R. Kubo, *Thermodynamics* (North-Holland–Wiley, Amsterdam–New York, 1968).
59. V.B. Kobylyanskyi, *Statistical Physics* (Vyshcha Shkola, Kyiv, 1972) (in Ukrainian).
60. Y.A. Humenyuk, Preprint of ICMP NASU, ICMP–15–06U, Lviv, 2015 (in Ukrainian).

Received 19.08.15

Й.А. Гуменюк

ТЕРМОДИНАМІЧНІ ВЕЛИЧИНИ ГАЗУ НИЗЬКОЇ ГУСТИНИ У СЛАБОНЕРІВНОВАЖНОМУ ТЕПЛОПРОВІДНОМУ СТАЦІОНАРНОМУ СТАНІ

Резюме

Розглядається газ низької густини у теплопровідному стаціонарному стані. Засобами теорії суцільного середовища отримано поправки до тиску та внутрішньої енергії, зумовлені ґрадієнтами локальної температури різних порядків. Одержано відповідні вирази для стисливостей вздовж і впоперек теплового потоку, а також для теплоємностей. Показано, що вираз для нерівноважної ентропії задовольняє другий закон термодинаміки. Виявлено, що розрахована вільна енергія не володіє властивостями термодинамічного потенціалу.