THERMODYNAMIC QUANTITIES OF THE LOW-DENSITY GAS IN THE WEAKLY NONEQUILIBRIUM HEAT-CONDUCTION STEADY STATE IN THE LINEAR TEMPERATURE PROFILE APPROXIMATION

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(Received by September 27, 2016; in final form — April 11, 2017)

The weakly nonequilibrium low-density gas with a steady heat flow is considered within the approximation of a linear temperature profile. Simple analytical estimates for pressure, internal energy, and entropy are obtained. Compressibilities and heat capacities are analyzed. The result for the entropy is shown to be compatible with the second law of thermodynamics. The approximation of the displaced linear temperature profile is introduced, which is aimed to take into account the higher temperature gradients.

Key words: heat flow, equation of state, entropy, thermodynamics.

PACS number(s): 05.70.Ln, 51.30.+i, 44.10.+i

I. INTRODUCTION

Heat-conduction properties of macroscopic systems in the weakly nonequilibrium states with a heat flow are well-described by the Fourier law, which expresses a linear relation between the heat flux through the system and the temperature gradient. Being one of the cornerstones of linear irreversible thermodynamics [1, 2], this law has experimental and phenomenological origin. It is also applicable to the steady states of heat-conductive systems.

As to thermodynamic description of these states, at the present time there is no generally accepted method of calculation of such quantities as pressure, internal energy, or entropy even for gases. A closer inspection reveals that the general thermodynamic formalism for the heat-conduction steady states (analogous to the Gibbs method of characteristic functions, e.g. [3, 4]) does not exist, and appropriate statistical ensembles and their distributions are not constructed as well.

A number of approaches have been applied in order to obtain thermodynamic quantities of the systems in the heat-conduction steady state. The Boltzmann kinetic equation [5–7] and the information theory [8–10] for low-density gases and the Enskog kinetic equation [11–13] for hard spheres use the weakly nonequilibrium results for the one-particle distribution function. The nonequilibrium pressure and entropy corrections calculated are quadratic in the heat flux variable. Even in the simple case of the low-density gas, the kinetic-theoretical and information-theoretical results have been shown [6] to differ from each other.

Applications of the fluctuation theorem approach give rather formal results for thermodynamic quantities in the form of averages over the trajectories in the phase space [14–19]. To our knowledge, however, those expressions have not been explicitly calculated for any simple model.

In recent works [20–22] the problem of nonequilibrium pressure in liquids in the heat-conduction steady states is considered by the theory of hydrodynamic fluctuations. The authors calculate the nonequilibrium pressure contribution from long-range correlations originated from the temperature nonuniformity, which is interpreted as the nonequilibrium Casimir-like effect.

Formulations of general grounds for the steady state thermodynamics encountered in the literature can be considered as the first attempts. In particular, the extended irreversible thermodynamics [23–28] exploits the idea of the extension of the local-equilibrium thermodynamics. Namely, the Gibbs equation (the basic thermodynamic equality) written for the local entropy density as a function of the local energy density and specific volume is supplemented by the differential contribution from the heat flux. The latter is treated as a new thermodynamic degree of freedom. Unfortunately, the connection between the extended Gibbs equality and the local form of the first law of thermodynamics has not been established.

An appreciable influence of the concepts and notions of equilibrium and local-equilibrium thermodynamics is felt in the phenomenological constructions of the steady state thermodynamics proposed in Refs. [29,30]. Despite some methodological progress, it is quite evident that these ideas need further development and improvement.

Computer simulations can serve as verifying tool for theoretical models or as the origin of new information and qualitative objective laws. In [31,32] simulation data for the two-dimensional hard disks in heat-conduction steady states are analyzed from the viewpoint of the local-equilibrium equation of state and the Fourier law. Specific scaling relations revealed for the temperature and density profiles are shown to be applicable even for strong deviations from equilibrium.

Nevertheless, only theoretical approaches can provide explicit expressions for the thermodynamic quantities. Specifically, it would be desirable to have at hand an example of simple description, which could in the

lowest approximation catch the physics of the heat-conduction steady state and could give reliable estimates for the macroscopic characteristics. In Ref. [33] the continuous media approach is used for the description of the low-density gas in the weakly nonequilibrium heat-conduction stationary conditions. The results for the pressure, internal energy, and entropy are obtained as series in temperature gradients up to the forth order. We consider here the particular case when the temperature profile can be modelled by a linear space dependence. Such a "minimal" approximation, being in consistence with the linear Fourier law, results in simple but analytic estimates for the thermodynamic quantities.

In Sec. II some analysis of the weakly nonequilibrium heat-conduction steady state is given. Pressure, internal energy, and entropy as well as compressibilities and heat capacities are calculated for the linear temperature profile within the assumption of stationarity (Sec. III). The approximation of the displaced linear profile is formulated in Sec. IV in order to make use of these results. The conclusions are given in Sec. V.

II. WEAKLY NONEQUILIBRIUM HEAT-CONDUCTION STATE

We consider a system of particles contained in the vessel of the parallelepiped form. One pair of opposite sides are maintained in contact with thermal baths of different temperatures T_1 and T_2. The separation of the baths is denoted by L and the cross-section area is Ω (Fig. 1). The invariable conditions ensure the stationarity of the state with a constant value of the heat flux. In the transverse directions the system is spatially uniform and isotropic. For the weakly nonequilibrium case, the values T_1 and T_2 differ little from each other:
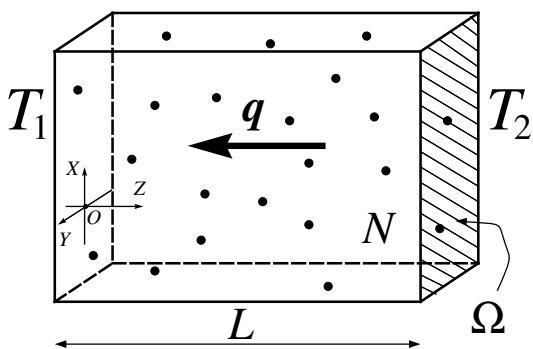
$$|T_1 - T_2| \ll T_1,\, T_2. \qquad (1)$$

Fig. 1. A system of particles in the weakly nonequilibrium heat-conduction steady state.

Let us try to deduce any useful thermodynamic information about this state for the domian of low density. That the state deviates weakly from equilibrium induces the idea that the equilibrium-like relations [3, 4] for the

nonequilibrium pressure P and internal energy E would be a quite good approximation:

$$P = \frac{N}{V}k_{\mathrm{B}}T_{\mathrm{eff}}, \qquad E = \frac{D}{2}Nk_{\mathrm{B}}T_{\mathrm{eff}}, \qquad (2)$$

where D is a dimentionality of space; T_{eff} is an effective parameter of the approximation by which we interpret the weakly nonequilibrium pressure and energy in terms of the equilibrium equations of state.

One has to make a choice for T_{eff} in the situation when the gas is in contact with two thermal baths with the temperatures T_1 and T_2. The simplest variant is to take T_{eff} as a half-sum $\frac{1}{2}(T_1 + T_2)$ owing to the *weak nonequilibrium*. This gives the following approximate expressions:

$$P \approx \frac{N}{V}k_{\mathrm{B}}\frac{T_1 + T_2}{2}, \qquad E \approx \frac{D}{2}Nk_{\mathrm{B}}\frac{T_1 + T_2}{2}. \qquad (3)$$

However, they do not contain any dependence on the temperature difference $T_2 - T_1$. In other words, the two states A and B with the bath temperatures

$$T_1^A = T - t,\; T_2^A = T + t \;\; \text{and} \;\; T_1^B = T - 2t,\; T_2^B = T + 2t,$$

where $|t| \ll T$, are characterized by the same values of P and E. The half-sum approximation does not also take into account the nonuniform thermal expansion phenomenon, which causes at $T_1 \neq T_2$ that the left and right halves of the vessel contain substantially different numbers of particles. These arguments indicate that equations (3) are *incorrect qualitatively*.

We show below that the pressure and internal energy of the gas in the heat-conduction steady state can be calculated in the particular case, when the spatial change of the temperature is approximately modelled by a *linear dependence*. The corresponding results do not have the defects mentioned above. This approximation is discussed in Sec. IV.

III. THERMODYNAMIC QUANTITIES

We choose coordinate axis OZ to be parallel to the heat flux vector, while its origin is placed on one of the two thermal-bath plates (Fig. 1). Then, the local temperature dependence on position z reads:

$$T(z) = T_1 + \frac{T_{21}}{L}z, \qquad (4)$$

where $T_{21} \equiv T_2 - T_1$ is the temperature difference. Let us find equations of state for the pressure and internal energy as well as the entropy expression for the steady state with the linear profile, Eq. (4).

As before [33, 34], it is assumed that the fact of mechanical equilibrium of the gas means that the pressure takes the same value everywhere in the vessel:

$$P = \mathrm{const}. \qquad (5)$$

For the low-density domain, the ideal-gas equation of state, e.g. [3, 35], is adopted to be valid locally:

$$P = n(z)\,k_{\mathrm{B}}T(z), \qquad (6)$$

where $n(z)$ is the number density, k_B is Boltzmann's constant. This equation relates the spatial dependences $n(z)$ and $T(z)$.

The following expressions for the local densities of internal energy $\varepsilon(z)$ and entropy $s(z)$ correspond to the local assumption (6), see e.g. [3, 36]:

$$\varepsilon(z) \equiv \tfrac{1}{2} D\, n(z) k_B T(z), \qquad (7)$$

$$s(z) \equiv k_B n(z) \left[-\ln n(z) + \tfrac{1}{2} D \ln T(z) + \xi_S^{(D)} \right], \qquad (8)$$

where the constant in $s(z)$ is defined by $\xi_S^{(D)} \equiv \frac{D}{2} \ln(2\pi k_B m / h^2) + 1 + \frac{1}{2} D$, m is particle's mass and h is Planck's constant. These expressions are derived from the equilibrium counterparts, when the equilibrium temperature and number density are substituted by the local ones [33, 34].

The possibility of introduction of the local quantities implies that the gas is considered as continuous media. This is admissible if the characteristic spatial scales are much larger than the intermolecular distances [36–39]:

$$L \gg l_{\text{free}}, \qquad \Omega \gg l_{\text{free}}^2,$$

where l_{free} is the mean free path of a particle in the gas.

A total additive quantity A is determined by the integration of its local density $a(z)$ over the volume $\Omega \times L$ of the vessel. In regard of spatial uniformity in the directions transverse with respect to the heat flux, it is defined as

$$A \equiv \Omega \int_0^L \mathrm{d}z\, a(z). \qquad (9)$$

We set $\Omega = 1$ for the one-dimentional case, while for the $D = 2$ case Ω is the transverse linear size.

A. Equations of the steady state

a. Pressure and internal energy.   The pressure can be found from the normalization condition

$$\Omega \int_0^L \mathrm{d}z\, n(z) = N, \qquad (10)$$

where N is the total number of particles. Inserting here the expression

$$n(z) = \frac{PL}{k_B T_{21}} \frac{1}{z + T_1 L / T_{21}},$$

derived from Eqs. (5) and (4), we can integrate with the explicit result

$$P = \frac{N}{\Omega L} k_B \frac{T_2 - T_1}{\ln(T_2/T_1)}, \qquad (11)$$

which is the baric equation of the weakly nonequilibrium steady state. The pressure takes the same value for different pairs Ω_1, L_1 and Ω_2, L_2 with identical volumes $\Omega_1 L_1 = \Omega_2 L_2$.

The energy density does not depend on z, as $\varepsilon(z) = \frac{1}{2} DP$. As a consequence, Eqs. (9) and (11) result in the following caloric equation of state:

$$E = \frac{D}{2} N k_B \frac{T_{21}}{\ln T_{2/1}}, \qquad (12)$$

where we denote $T_{2/1} \equiv T_2 / T_1$. As for equilibrium, the total energy does not depend on the volume due to large separations between particles.

The expressions for P and E are of the inherently *thermodynamic form*, as they contain only global parameters of the gas: the number of particles, the sizes of the vessel, and the bath temperatures. Besides that, T_1 and T_2 appear on equal rights so that P and E remain unchanged under the permutation of the indices, $1 \rightleftarrows 2$. The principal value of these approximate results consists, to our mind, in that P and E are represented as unambiguous functions rather than in the form of series [33], which enables one to make immediate estimations.

The equations of steady state obtained are compatible with the equilibrium conterparts. Let the system be changed over to the equilibrium state by shifting the temperature, say, of the second bath from T_2 to T_1. The corresponding limit of the fraction in Eqs. (11) and (12) calculated e.g. by de L'Hôpital's rule reads:

$$\lim_{T_2 \to T_1} \frac{T_{21}}{\ln(T_2/T_1)} = \lim_{T_2 \to T_1} \frac{1}{1/T_2} = T_1.$$

This confirms the proper limit behaviours of P and E.

Comparing Eqs. (11) and (12) to the anticipated ones (2), we can identify the effective temperature:

$$T_{\text{eff}} = \frac{T_{21}}{\ln T_{2/1}}. \qquad (13)$$

Its expansion near the arithmetic mean $T_{\text{am}} \equiv \frac{1}{2}(T_1 + T_2)$ gives more information. We can find from the relations

$$T_1 = T_{\text{am}} - \tfrac{1}{2} T_{21}, \qquad T_2 = T_{\text{am}} + \tfrac{1}{2} T_{21} \qquad (14)$$

that $\ln T_{2/1} = 2 \operatorname{arth} \delta$, where $\delta \equiv \frac{1}{2} T_{21}/T_{\text{am}}$ and the identity $\frac{1}{2} \ln \frac{1+\delta}{1-\delta} = \operatorname{arth} \delta$ has been used, see [40]. Substituting the series

$$\operatorname{arth} \delta = \delta + \tfrac{1}{3} \delta^3 + \tfrac{1}{5} \delta^5 + \tfrac{1}{7} \delta^7 + \dots, \qquad \delta^2 < 1$$

and recovering its inverse lead to the expansion:

$$T_{\text{eff}} = \frac{T_1 + T_2}{2} \left[1 - \tfrac{1}{3} \delta^2 - \tfrac{4}{45} \delta^4 - \tfrac{44}{945} \delta^6 - \dots \right]. \qquad (15)$$

That the effective temperature is less than the half-sum of T_1 and T_2 is a consequence of the nonuniformity of the particle density $n(z)$. This series yeilds expansions for P and E near T_{am}.

b. Comparison with the equilibrium state. Let us elucidate to what extent the steady-state pressure differs from the equilibrium one. Initially, the gas rests in the vessel $\Omega \times L$ at the equilibrium temperature $T_{\rm eq}$ under pressure $P_{\rm eq} = (N/\Omega L)k_{\rm B}T_{\rm eq}$. Next, we switch to the heat-conduction steady state (Fig. 1) with temperatures $T_{\rm eq}-t$ and $T_{\rm eq}+t$, where $|t| \ll T$. The pressure difference can be easily calculated

$$P(t) - P_{\rm eq} = P_{\rm eq}\left[\frac{T_{\rm eff}(t)}{T_{\rm eq}} - 1\right],$$

with $T_{\rm eff}(t) \equiv 2t/\ln\left([T_{\rm eq}+t]/[T_{\rm eq}-t]\right)$ deduced from Eq. (13). The behaviour of the reduced pressure $P(\delta)/P_{\rm eq}$ with $\delta = t/T_{\rm eq}$ displays decreasing in comparison to the initial value (Fig. 2). The approximation of the second order in δ according to Eq. (15) yields quite good estimation even for $|\delta| \leq 0.5$.
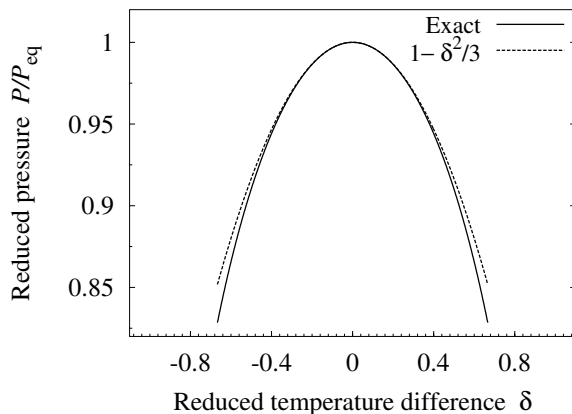

Fig. 2. Ratio of the weakly nonequilibrium steady-state pressure to the equilibrium one: Result (11) and the second-order approximation followed from Eq. (15). If quantities $2|t|$ and $T_{\rm eq}$ differ by one order, then the corresponding domain of the weak nonequilibrium is $-0.05 \leq \delta \leq 0.05$.

The difference $P(t) - P_{\rm eq}$ for a similar situation when the initial temperature is $T_{\rm eq} = 300\,{\rm K}$ and $P_{\rm eq}$ equals the atmospheric value is presented in Table 1.

t, K	1	3	5	10	15	20
$P(t) - P_{\rm eq}$, Pa	−0.375	−3.37	−9.38	−37.54	−84.49	−150.28

Table 1. Deviation of the nonequilibrium pressure from $P_{\rm eq} = 101325$ Pa for the gas in steady states at various t and $T_{\rm eq} = 300$ K.

c. Fluctuation-induced pressure. Works [20–22] consider the problem of nonequilibrium pressure in liquids, which are maintained in the heat-conduction stationary conditions. Using the approach of hydrodynamic fluctuations those authors calculate the nonequilibrium fluctuation-induced contribution to the pressure interpreted as the nonequilibrium Casimir-like effect. The scheme of perturbations about the *local-equilibrium state* leads to corrections of the second order in fluctuations. The corrections are found to be space-dependent on the

position along the heat flux and proportional to the temperature gradient squared. They also depend on the thermal bath separation L and are claimed to be inversely proportional to L for the fixed temperature difference. The (nonlinear) Burnett coefficient of this proportionality contains the specific heat capacity and the coefficients of thermal expansion, thermal conductivity, and shear viscosity.

The authors report that the fluctuation-induced pressure contribution averaged along the heat flux is equal to $+10$ Pa for liquid water when the temperature difference is of 25 K and the bath separation equals to 10^{-7} m. Other thermo-physical quantities are taken for the "average" temperature of 298 K (and most likely for the atmospheric pressure value). The fluctuation effect is to be distinguished from the regular local-equilibrium pressure for which no relation is supplied in the cited works. The problem lies in that it is not clear exactly from which value one has to measure the fluctuation-induced contribution.

Though our results refer to the gas phase, but they explicitly show that independently of the intensity of fluctuations the *very nonequilibrium stationary conditions* cause the decrease of the pressure value with respect to which one has to measure the nonequilibrium fluctuation-induced contribution. Our result does not depend on the bath separation and for the same values of the "average" temperuture of 298 K (which is accepted here as the arithmetic mean), the temperature difference of 25 K, and the atmospheric pressure value of the gas we find -59.5 Pa. The order of magnitude turns out to be the same as that predicted by the fluctuation approach for liquids. So, to our mind, at first it is necessary to determine exactly the pressure drop in liquids caused by the nonequilibrium stationary conditions (which does not depend on fluctuations) and afterwards the subtle fluctuation effect mentioned in [20–22] can be registered.

B. Derivative thermodynamic quantities

a. Isothermal compressibilities. In view of the direction related to the heat flux, it is appropriate to distinguish between the compressibility along the heat flux, $\chi_{T_1,T_2}^{\parallel}$, and the compressibility in transverse directions, $\chi_{T_1,T_2}^{\perp}$. The corresponding definitions can be derived from the conventional one [3, 4, 35] generalized to

$$\chi_{T_1,T_2} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T_1,T_2}.$$

The desirable expressions read:

$$\chi_{T_1,T_2}^{\parallel} \equiv -\frac{1}{L}\left(\frac{\partial L}{\partial P}\right)_{T_1,T_2,\Omega}, \quad \chi_{T_1,T_2}^{\perp} \equiv -\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial P}\right)_{T_1,T_2,L}.$$
(16)

The inverse derivatives can be easily calculated from Eq. (11) as

$$\left(\frac{\partial P}{\partial L}\right)_{T_1,T_2,\Omega} = -\frac{P}{L}, \qquad \left(\frac{\partial P}{\partial \Omega}\right)_{T_1,T_2,L} = -\frac{P}{\Omega},$$

yielding:

$$\chi^{\parallel}_{T_1,T_2} = \frac{1}{P}, \qquad \chi^{\perp}_{T_1,T_2} = \frac{1}{P}. \tag{17}$$

So, the compressibilities along and across the flux are found to be equal to each other and related to the non-equilibrium pressure in the same way as in equilibrium.

b. Heat capacities. The equilibrium heat capacity is known [3, 4] to depend on the conditions of heat exchange: $C_{\mathrm{cond}} \equiv (\delta Q/\mathrm{d}T_{\mathrm{eq}})_{\mathrm{cond}}$, where δQ is the heat transferred to or from the system and $\mathrm{d}T_{\mathrm{eq}}$ is the related small change in the equilibrium temperature. It is naturally for the heat-conduction steady state to define two heat capacities with respect to each thermal bath:

$$C^{(1)}_{\mathrm{cond};T_2} \equiv \left(\frac{\delta Q}{\mathrm{d}T_1} \right)_{\mathrm{cond},T_2}, \qquad C^{(2)}_{\mathrm{cond};T_1} \equiv \left(\frac{\delta Q}{\mathrm{d}T_2} \right)_{\mathrm{cond},T_1}, \tag{18}$$

where the upper indices in the brackets indicate which bath temperature changes. Similarly to the equilibrium case, the transfered heat δQ is coupled to the internal energy change $\mathrm{d}E$ and the work δA done by the system by the first law of thermodynamics [3, 4]:

$$\delta Q = \mathrm{d}E + \delta A, \tag{19}$$

which expresses the total energy balance for the thermodynamic transitions between two close steady states. Next, we consider physically interesting regimes of constant volume[1] $V = \mathrm{const}$ and pressure $P = \mathrm{const}$.

b.1. Isochoric heat capacities. In the case of constant volume, the work is not done and according to the first law (19) the capacities can be introduced through the internal energy:

$$C^{(1)}_{V,T_2} = \left(\frac{\partial E}{\partial T_1} \right)_{V,T_2}, \qquad C^{(2)}_{V,T_1} = \left(\frac{\partial E}{\partial T_2} \right)_{V,T_1}. \tag{20}$$

For example, $C^{(1)}_{V,T_2}$ describes the internal energy change due to a small isochoric change in the temperature of the first thermal bath when the temperature of the second one is unchanged.

For the low-density gas $E = \frac{D}{2} N k_{\mathrm{B}} T_{\mathrm{eff}}(T_1, T_2)$, which yields

$$C^{(1)}_{V,T_2} = \frac{D}{2} N k_{\mathrm{B}} \left(\frac{\partial T_{\mathrm{eff}}}{\partial T_1} \right)_{T_2}. \tag{21}$$

Differentiating expression (13) results in

$$C^{(1)}_{V,T_2} = \frac{D}{2} N k_{\mathrm{B}} \left[-\frac{1}{\ln T_{2/1}} + \frac{T_{21}}{T_1(\ln T_{2/1})^2} \right]. \tag{22}$$

The interchange of the indices gives the second capacity:

$$C^{(2)}_{V,T_1} = \frac{D}{2} N k_{\mathrm{B}} \left[\frac{1}{\ln T_{2/1}} - \frac{T_{21}}{T_2(\ln T_{2/1})^2} \right]. \tag{23}$$

b.2. Isobaric heat capacities. At constant pressure, the heat transfered to the gas is spent partially on the work. It follows from Eq. (19) that

$$C^{(1)}_{P,T_2} \equiv \left(\frac{\delta Q}{\mathrm{d}T_1} \right)_{P,T_2} = \left(\frac{\mathrm{d}E}{\mathrm{d}T_1} \right)_{P,T_2} + \left(\frac{\delta A}{\mathrm{d}T_1} \right)_{P,T_2}. \tag{24}$$

The differetial of E as a function of T_1, T_2 and V equals:

$$\mathrm{d}E = \left(\frac{\partial E}{\partial T_1} \right)_{V,T_2} \mathrm{d}T_1 + \left(\frac{\partial E}{\partial T_2} \right)_{V,T_1} \mathrm{d}T_2 + \left(\frac{\partial E}{\partial V} \right)_{T_1,T_2} \mathrm{d}V.$$

Derivative of the energy in Eq. (24) for $P = \mathrm{const}$ can be written as

$$\left(\frac{\mathrm{d}E}{\mathrm{d}T_1} \right)_{P,T_2} = \left(\frac{\partial E}{\partial T_1} \right)_{V,T_2} + \left(\frac{\partial E}{\partial V} \right)_{T_1,T_2} \left(\frac{\partial V}{\partial T_1} \right)_{P,T_2}.$$

The work term can be identified from $\delta A = P\mathrm{d}V$ in the form:

$$\left(\frac{\delta A}{\mathrm{d}T_1} \right)_{P,T_2} = P \left(\frac{\partial V}{\partial T_1} \right)_{P,T_2}.$$

These expressions substituted into Eq. (24) result in the generalization of the relation between the isobaric and isochoric heat capacities for the heat-conduction steady-state case:

$$C^{(1)}_{P,T_2} = C^{(1)}_{V,T_2} + \left[\left(\frac{\partial E}{\partial V} \right)_{T_1,T_2} + P \right] \left(\frac{\partial V}{\partial T_1} \right)_{P,T_2}. \tag{25}$$

For low densities, the first term in the square brackets vanishes. Using equation $V = (N/P) k_{\mathrm{B}} T_{\mathrm{eff}}$, see Eq. (11), we obtain:

$$C^{(1)}_{P,T_2} = \left(\tfrac{D}{2} + 1 \right) N k_{\mathrm{B}} \left(\frac{\partial T_{\mathrm{eff}}}{\partial T_1} \right)_{T_2}. \tag{26}$$

It follows from Eqs. (21) and (26) that for low densities the ratio $\gamma \equiv C^{(1)}_{P,T_2}/C^{(1)}_{V,T_2}$ is the same as in equilibrium: $\gamma = 1 + 2/D$. In regard to this numerical factor, we consider further only the isochoric heat capacities.

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[1] The variables Ω and L are not analyzed apart from each other as the baric equation of state, Eq. (11), includes only their product $V \equiv \Omega L$.

b.3. Symmetric and antisymmetric heat capacities. Another possibility exists to thransfer heat to or from the system at constant volume (or pressure) when one of the two following quantities — the half-sum of the bath temperatures $T_{\mathrm{am}} \equiv \frac{1}{2}(T_1 + T_2)$ and their difference T_{21} — changes and the other is fixed. In the first case we change the bath temperatures by the same value, while in the second case one bath temperature is increased and the other is decreased by the same value. These changes are described by another pair of heat capacities:

$$C_{V,T_{21}}^{(\mathrm{am})} \equiv \left(\frac{\partial E}{\partial T_{\mathrm{am}}}\right)_{V,T_{21}}, \quad C_{V,T_{\mathrm{am}}}^{(21)} \equiv \left(\frac{\partial E}{\partial T_{21}}\right)_{V,T_{\mathrm{am}}}. \quad (27)$$

The final expressions for these can be deduced directly from Eq. (12) written in terms of T_{am} and T_{21} and using differetiations. However, the pairs $\{T_1, T_2\}$ and $\{T_{\mathrm{am}}, T_{21}\}$ are interrelated linearly by Eqs. (14), and as a consequence the following relations hold: $\frac{\partial}{\partial T_{\mathrm{am}}} = \frac{\partial}{\partial T_1} + \frac{\partial}{\partial T_2}$ and $\frac{\partial}{\partial T_{21}} = -\frac{1}{2}\frac{\partial}{\partial T_1} + \frac{1}{2}\frac{\partial}{\partial T_2}$. These equalities show that the pairs of capacities (20) and (27) are expressed by each other:

$$C_{V,T_{21}}^{(\mathrm{am})} = C_{V,T_2}^{(1)} + C_{V,T_1}^{(2)}, \qquad C_{V,T_{\mathrm{am}}}^{(21)} = -\frac{1}{2}C_{V,T_2}^{(1)} + \frac{1}{2}C_{V,T_1}^{(2)}. \quad (28)$$

Calculations yield:

$$C_{V,T_{21}}^{(\mathrm{am})} = \frac{D}{2}Nk_{\mathrm{B}}\frac{1}{T_1 T_2}\left(\frac{T_{21}}{\ln T_{2/1}}\right)^2 \qquad (29)$$

and

$$C_{V,T_{\mathrm{am}}}^{(21)} = \frac{D}{2}Nk_{\mathrm{B}}\left[\frac{1}{\ln T_{2/1}} - \frac{1}{2}\frac{1}{T_1 T_2}\frac{T_2^2 - T_1^2}{\ln^2 T_{2/1}}\right]. \quad (30)$$

$C_{V,T_{21}}^{(\mathrm{am})}$ is symmetric and $C_{V,T_{\mathrm{am}}}^{(21)}$ is antisymmetric in the bath indices because they describe symmetric and antisymmetric changes of external conditions.

Heat capacities (22), (23) and (29), (30) can be expanded into series [41] in the small reduced temperature difference δ at the point T_{am}. Their exact dependences on δ are given in Fig. 3. That of the two capacities $C_{V,T_2}^{(1)}$ and $C_{V,T_1}^{(2)}$ is larger which corresponds to the temperature change of the colder bath. This is the consequence of the thermal expansion phenomenon in a nonuniformly heated stationary gas. The number of particles in the colder half of the vessel is larger than that in the hotter half, and the first one needs more heat when the gas is switched to a close steady state by raising the lower temperature by 1 K, rather than the higher bath temperature is raised by 1 K with the smaller number of particles in the hotter half on the vessel.
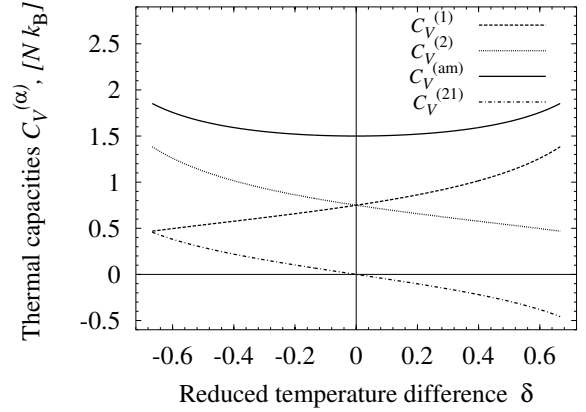
Fig. 3. Heat capacities as functions of the reduced temperature difference δ. The corresponding weak nonequilibirum domain is $-0.05 \leq \delta \leq 0.05$.

An interesting behaviour is demonstrated by the antisymmetric heat capacity $C_{V,T_{\mathrm{am}}}^{(21)}$. When the temperature difference increases at fixed T_{am} in the domain of its negative values ($T_{21} < 0$, $\delta < 0$), the internal energy increases so that $C_{V,T_{\mathrm{am}}}^{(21)} > 0$, while in the domain of positive values ($T_{21} > 0$, $\delta > 0$) the internal energy decreases and $C_{V,T_{\mathrm{am}}}^{(21)} < 0$. This is also the consequence of the nonuniform thermal expansion. Series (15) confirms such a behaviour of $C_{V,T_{\mathrm{am}}}^{(21)}$: when the $|\delta|$ decreases at fixed T_{am}, the internal energy increases and in the equilibrium ($\delta = 0$) the energy takes a maximal value.

C. Entropy

In order to find the entropy of the gas, we represent its density (8) in the form

$$s(z) = k_{\mathrm{B}}n(z)\left[d_1 \ln T(z) - \ln\left(P/k_{\mathrm{B}}\right) + \xi_S^{(D)}\right], \quad (31)$$

where $d_1 \equiv \frac{1}{2}D + 1$ and the local equation of state (6) has been used. Integration of this expression according to Eq. (9) produces three contributions

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

which correspond to the terms in the square brackets of Eq. (31).

The first one reads:

$$S_T \equiv \Omega\, k_{\mathrm{B}}d_1\int_0^L \mathrm{d}z\, n(z)\ln T(z) = \Omega\, d_1 P\int_0^L \mathrm{d}z\frac{\ln T(z)}{T(z)}, \quad (32)$$

where Eq. (6) has been substituted, while $T(z)$ is given by the linear dependence, Eq. (4). Integrating with respect to the new variable $T \equiv T_1 + T_{21}z/L$, we obtain the following result:

$$S_T = \Omega\, d_1 P\frac{L}{T_{21}} \times \frac{1}{2}\left[(\ln T_2)^2 - (\ln T_1)^2\right]. \quad (33)$$

S_P and S_ξ are easily calculated by the aid of the normalization condition, Eq. (10). The total entropy reads:

$$S = Nk_{\rm B} \left[\ln \frac{\Omega L}{N} + \tfrac{1}{2}(\tfrac{1}{2}D+1) \ln (T_1 T_2) - \ln \frac{T_{21}}{\ln T_{2/1}} + \xi_S^{(D)} \right].$$ (34)

Like pressure (11) and internal energy (12), it is symmetric in the temperature variables T_1 and T_2. The expansion near $T_{\rm am}$ in the reduced temperature difference $\delta \equiv \tfrac{1}{2} T_{21}/T_{\rm am}$ can be deduced [41] from this formula.

Let us show that expression (34) is consistent with the second law of thermodynamics. If we remove the baths and isolate the system, it will relax to an equilibrium state. The internal energy keeps constant during relaxation: $E = $ const. The well-known equality holds for the equilibrium, $E = \frac{D}{2} N k_{\rm B} T_{\rm fin}$, where $T_{\rm fin}$ is the temperature ascribed to the final state. Inserting it into the equilibrium entropy formula for the low-density gas [36] yields:

$$S_{\rm fin} = Nk_{\rm B} \left[\ln(\Omega L/N) + \tfrac{D}{2} \ln T_{\rm fin} + \xi_S^{(D)} \right],$$ (35)

with $T_{\rm fin} = T_{\rm eff}$, Eq. (13). The result for the difference $\Delta S \equiv S - S_{\rm fin}$ is reduced to

$$\Delta S = Nk_{\rm B} \left(\tfrac{D}{2} + 1 \right) \ln \frac{\sqrt{T_1 T_2} \ln T_2/T_1}{T_{21}}.$$ (36)

The fraction in the logarithm can be expressed as $\sigma(\phi) \equiv \sqrt{\phi} \ln \phi / [\phi - 1]$, where $\phi \equiv T_2/T_1 > 0$. This fraction remains the same under the interchange $\phi \to 1/\phi$. Its behaviour shows (Fig. 4) that $\sigma(\phi) \leq 1$, while an equality is attained at $\phi = 1$, that is when $T_1 = T_2$. The same can be concluded from the expansion of $\sigma(\phi)$ for the values of $\phi = 1 + x$ close to 1:

$$\sigma(1 + x) = 1 - \tfrac{1}{24}x^2 + \tfrac{1}{24}x^3 - \tfrac{71}{3 \cdot 5 \cdot 2^7}x^4 + \dots$$

It follows from Eq. (36) that $\Delta S \leq 0$, which indicates that entropy (34) satisfies the second law of thermodynamics for nonequilibrium processes [3, 4].
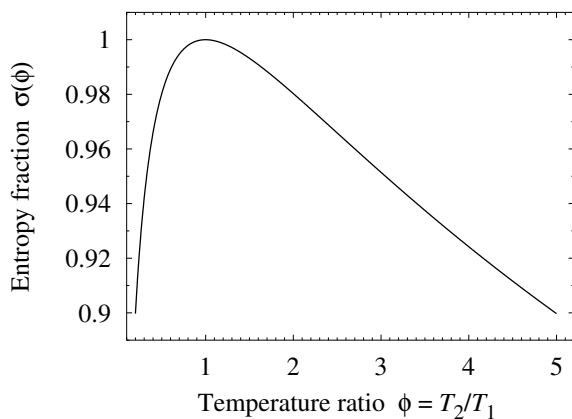

Fig. 4. Dependence of function $\sigma(\phi) \equiv \sqrt{\phi} \ln \phi / [\phi - 1]$ on the temperature ratio $\phi \equiv T_2/T_1$.

We have introduced above the effective temperature (13) related to the baric and caloric equations of the steady state. It is easy to note that the nonequilibrium entropy (34) can be written in the equilibrium-like form similar to Eq. (35). Comparison of Eqs. (34) and (35) shows that the entropic effective temperature

$$T_{\rm eff}^S \equiv \left[(T_1 T_2)^{\frac{1}{4}(D+2)} \frac{\ln T_{2/1}}{T_{21}} \right]^{2/D}$$

differs essentially from $T_{\rm eff}$, defined above. The difference means that the very conception of the effective temperature for the heat-conduction steady state is not self-consistent even for the weakly nonequilibtium case and cannot describe all its peculiarities. Maybe, this is the reason why various attempts of defining the effective temperature in nonequilibrium conditions [42] cannot be reconciled with each other. Most likely, they are dictated to a greater extent by immediate circumstances of the investigated processes and systems in specific nonequilibrium conditions [42], rather than by the ability of the concept of the effective temperature to describe a nonequilibrium state in a proper way.

IV. APPROXIMATION OF THE DISPLACED LINEAR PROFILE

a. Interpretations of the Fourier law. For the weakly nonequilibrium heat-conduction state, the Fourier law for the heat flux is recognized to be well-established [1–3]:

$$\mathbf{q} = -\lambda \nabla T,$$ (37)

where λ is the linear thermal conductivity. Though the origin of the law is experimental and phenomenological, it was confirmed by kinetic theory [37, 38, 43] and nonequilibrium statistical mechanics [36, 39]. The law is an approximation for it neglects the contributions to $\mathbf{q}$ from higher gradients $(\partial^i T/\partial \mathbf{r}^i)\big|_{i \geq 2}$ and their products.

There are two different interpretations. In the continuous media approach [1, 2] any state of the system is described locally by hydrodynamic fields. For this case, the thermal conductivity coefficient in Eq. (37) depends on space positions through the temperature and particle density fields:

$$\mathbf{q}(\mathbf{r}) = -\lambda \left(T(\mathbf{r}), n(\mathbf{r}) \right) \nabla T(\mathbf{r}).$$

Such *local nature* of the Fourier law is more close to the ideas of linear irreversible thermodynamics [1, 2], kinetic theory [37, 38, 43], and nonequilibrium statistical mechanics [36, 39].

Another interpretation assumes that if a small temperature difference exists between positions A and B separated by distance L, then the gradient in Eq. (37) is meant as a quantity

$$\nabla T_{BA} = \frac{T_B - T_A}{L} \mathbf{k},$$

where $\mathbf{k}$ is the unit vector directed from point A to point B. In regard of weak deviation from equilibrium, usually it is not payed much attention to the spatial dependence

of the temperature field between A and B, while the coefficient λ is taken to be constant and depends on some "average" temperature and particle density. ∇T_{BA} is considered as some *averaged* temperature gradient.

Sometimes the heat-conduction steady state is thought as a state with the temperature gradient being *uniform* along the heat flux, e.g. [36], which differs from reality. Nevertheless, the approximation of the first gradient (and consequently, of a linear space dependence of the temperature) is used in description of the heat-conduction steady state, e.g., concerning the influence of thermal nonequilibrium on light scattering [44–49].

b. Approximation. Numerical simulations [31, 32, 50, 51] show the concavity of the temperature profile in the heat-conduction steady state. The linear profile assumption made in Sec. III for the calculations of thermodynamic quantities means that we have *substituted* the gas with the true profile by the one with the linear profile. The latter was treated as if the gas were stationary. Now it is necessary to relate the temperature parameters of the linear profile with the real bath temperatures T_1 and T_2.
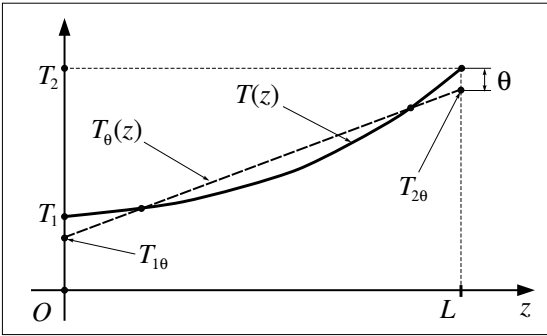

Fig. 5. True temperature profile $T(z)$ and its linear approximation $T_\theta(z)$.

The approximation proposed here consists in placing the linear profile as though it crosses the true profile in two points (Fig. 5), while its slope corresponds to the "averaged" gradient $(T_2 - T_1)/L$. This choice is in consistence with the "averaged" Fourier law. The value of displacement θ of the approximate linear profile about the line traversing points $(0; T_1)$ and $(L; T_2)$ is a free parameter. It depends on both T_1 and T_2 and probably on L. The temperatures of the "displaced" thermal baths are denoted by

$$T_{1\theta} \equiv T_1 - \theta, \qquad T_{2\theta} \equiv T_2 - \theta. \qquad (38)$$

Then, the displaced temperature profile is given by:

$$T_\theta(z) \equiv T_{1\theta} - \frac{T_{21}}{L} z.$$

The displacement introduced is an attempt to compensate the nonlinearity of the true profile being neglected, that is, higher temperature gradients. Thermodynamic quantities will experience distortions from this approximation.

c. Estimation for θ. In order to establish the simplest estimation for θ, let us find restrictions for the value taken by the true profile in the middle-point $T_0 \equiv T(\frac{1}{2}L)$. Due to the concavity, T_0 has the lower bound which is equal to the colder bath temperature T_1 (for the case $T_{21} > 0$) and the upper bound being equal to the arithmetic mean $T_{\mathrm{am}} \equiv \frac{1}{2}(T_1 + T_2)$: that is $T_1 < T_0 < T_{\mathrm{am}}$. Thus, it follows strictly that $\theta < \frac{1}{2}|T_{21}|$.

Now, we make an *assumption* concerning $T(z)$ that the value of T_0 is not less than the arithmetic mean of T_1 and T_{am}. In other words, the temperature increase for the interval $(0; \frac{1}{2}L)$ is larger than or equal to $\frac{1}{4}T_{21}$, while for the interval $(\frac{1}{2}L; L)$ it is not larger than $\frac{3}{4}T_{21}$. This strengthens the estimation to $\theta \leq \frac{1}{4}|T_{21}|$. Choosing the position of the displaced profile $T_\theta(z)$ in the middle of T_0 and T_{am}, we obtain [41]:

$$\theta \approx \tfrac{1}{8}|T_{21}|.$$

We can accept from this primitive estimation that the displacement θ is *nearly one order less* than the bath temperature difference $|T_{21}|$.

d. Application of the approximation. Let us use the approximation of the displaced temperature profile in the expressions for the pressure, Eq. (11), and the internal energy, Eq. (12), by substituting Eqs. (38) for $T_{1\theta}$ and $T_{2\theta}$ instead of T_1 and T_2. The pressure P_θ in this approximation reads:

$$P_\theta = \overline{n}k_{\mathrm{B}} \frac{T_{21}}{\ln(T_2 - \theta) - \ln(T_1 - \theta)}. \qquad (39)$$

where $\overline{n} \equiv N/(\Omega L)$. Expanding the fraction into a series in small values $\frac{\theta}{T_i}$, we obtain the first two corrections as follows:

$$P_\theta = \overline{n}\, k_{\mathrm{B}} T_{\mathrm{eff}} \Big[1 - \frac{T_{21}}{\ln T_{2/1}} \frac{\theta}{T_1 T_2}$$
$$- \left(\frac{1}{2} \frac{T_2^2 - T_1^2}{\ln T_{2/1}} - \frac{T_{21}^2}{\ln^2 T_{2/1}} \right) \frac{\theta^2}{T_1^2 T_2^2} + \dots \Big]. \qquad (40)$$

Analogous formula holds for the internal energy:

$$E_\theta = \tfrac{1}{2} D N k_{\mathrm{B}} T_{\mathrm{eff}} \Big[1 - T_{\mathrm{eff}} \frac{\theta}{T_1 T_2}$$
$$- T_{\mathrm{eff}}(T_{\mathrm{am}} - T_{\mathrm{eff}}) \frac{\theta^2}{T_1^2 T_2^2} + \dots \Big], \qquad (41)$$

where the coefficients at θ and θ^2 have been expressed through T_{am} and T_{eff}, Eq. (13).

The negative signs of the corrections indicate that the displacement lowers the values of the pressure and internal energy. The first-order corrections can be approximated by $-\frac{1}{2}\frac{T_1 + T_2}{T_1 T_2}\theta$. The second-order ones turn out to be very small and have an upper bound as $\sim \frac{1}{48}T_{21}^4$, see Ref. [41].
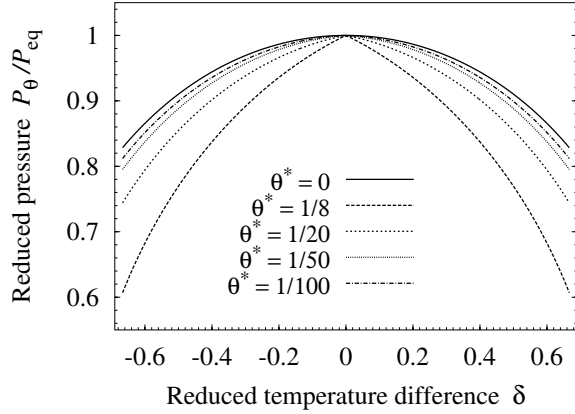
Fig. 6. Dependence of reduced pressure (39) on the reduced temperature difference δ for variuos values of the linear profile displacement $\theta = \theta^*|T_{21}|$.

Fig. 6 shows the impact of the displacement on pressure. The assumption of proportionality $\theta \sim |T_{21}|$ used in Eq. (39) breaks analytical properties of the pressure so that the function $P_\theta(\delta)$ has a cusp in the equilibrium point $\delta = 0$. The cusp weakens when the proportionality coefficient θ^* in the relation $\theta = \theta^*|T_{21}|$ decreases. The nonanalyticity indicates on a rather rough nature of the approximation. This can be easily understood, since at first we obtained Eq. (11) for the pressure and afterwards the displacement was artificially inserted to give Eq. (39).

Considering the entropy, $T_{1\theta}$ and $T_{2\theta}$ are inserted into Eq. (34) instead of T_1 and T_2 with subsequent expanding of the logarithms in powers of θ up to the second order:

$$S_\theta = Nk_{\rm B}\left[\ln\frac{\Omega L}{N} + \tfrac{1}{2}\left(\tfrac{D}{2}+1\right)\ln\left(T_1 T_2\right) - \ln\frac{T_{21}}{\ln T_{2/1}}\right.$$

$$+\xi_S^{(D)} - \left(\left[\tfrac{D}{2}+1\right]T_{\rm am} - T_{\rm eff}\right)\frac{\theta}{T_1 T_2} - \tfrac{1}{2}\left(\left[\tfrac{D}{2}+1\right]\frac{T_1^2+T_2^2}{2}\right.$$

$$\left.\left.-T_{\rm eff}[2T_{\rm am} - T_{\rm eff}]\right)\frac{\theta^2}{T_1^2 T_2^2} - \ldots\right], \tag{42}$$

where the corrections from θ take partially into account the nonlinearity of the true temperature profile.

V. CONCLUSIONS

For the low-density gas in the weakly nonequilibrium heat-conduction steady state, one of the simplest approximations is considered when the local temperature depends linearly on the space position along the heat flux. Analytical expressions for the pressure, internal energy, and entropy as well as for compressibilities and heat capacities derived in the continuous media approach describe qualitatively the deviation of the state from equilibrium. They establish common behaviour of these quantities and are examples of typical nonequilibrium steady-state thermodynamic relations. The results are expressed in terms of global macroscopic parameters and do not contain any dissipative characteristics (such as thermal conductivity, relaxation time, etc.) Another positive feature is the compatibility of the entropy found with the second law of thermodynamics for nonequilibrium processes.

The pressure is compared to that for liquids obtained by the approach of hydrodynamic fluctuations. It is suggested that the pressure drop originated from the nonequilibrium conditions is comparable to the fluctuation-induced contribution even when the thermal bath separation decreases to 10^{-7} m.

The nonlinearity of the true temperature profile is taken into account by means of displacement of the model linear profile. This approximation is rather artificial and has been introduced on qualitative grounds. For this reason, the corresponding results are of estimative nature. Nevertheless, we expect that they can play the role of a test instrument for the forthcoming more realistic and detailed approximations and approaches.

ACKNOWLEDGEMENT

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ТЕРМОДИНАМІЧНІ ВЕЛИЧИНИ ГАЗУ НИЗЬКОЇ ГУСТИНИ У СЛАБОНЕРІВНОВАЖНОМУ ТЕПЛОПРОВІДНОМУ СТАЦІОНАРНОМУ СТАНІ В НАБЛИЖЕННІ ЛІНІЙНОГО ХОДУ ТЕМПЕРАТУРИ

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Слабонерівноважний газ низької густини зі стаціонарним потоком тепла розглянуто в наближенні лінійного ходу температури. Виведено прості аналітичні оцінки для тиску, внутрішньої енергії та ентропії. Проаналізовано стисливості й теплоємності. Показано, що результат для ентропії узгоджується з другим началом термодинаміки. Уведено наближення зміщення лінійного ходу температури, покликане врахувати вищі температурні ґрадієнти.