

Thermodynamic potentials and extremum principles for a Boltzmann gas

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IN THIS PAPER, a thermodynamic interpretation of the kinetic theory and Boltzmann's equation is explicitly obtained; the nonequilibrium thermodynamic space consists of the nonnegative distribution functions. Beginning from a molecular expression for entropy in the form of Boltzmann's H functional, the systematic construction of thermodynamic potentials is demonstrated for gaseous systems beyond local equilibrium ("not infinitesimally near to equilibrium"). Since the nonequilibrium thermodynamic space provides natural comparison states for the principles of maximum entropy or minimum energy, a simple criterion for the choice of gas-state variables can be given which shows that the maximization of the Legendre transforms of entropy is logically equivalent to the minimization of the Legendre transforms of energy. This criterion is sought after in such a way that the concepts of temperature and pressure need no reformulation out of equilibrium. After these preparations, the technique of functional differentiation is used to derive the generalized Gibbs equation (relation) for Boltzmann's entropy. Finally, the paper presents an analysis of how the functional representation of this equation relates to the method of moments.

1. Introduction

IN GIBBSIAN THERMOSTATICS [1–3], one postulates that all macroscopic properties of a thermodynamic system are contained in a fundamental equation representing either the entropy or the energy as a function of additive conserved quantities. Thus in both the entropy and energy representations the extensive parameters play the roles of mathematically independent variables, whereas the intensive parameters are introduced in a systematic manner as derivatives of the fundamental equation. The energy-language fundamental equation can be taken as the basic relation on which the Legendre transformation is performed. Such Legendre transforms of the energy are usually called thermodynamic potentials. Another set of thermodynamic functions (Massieu's functions) can be obtained by performing the Legendre transformations on the entropy rather than on the energy. In the entropy representation the entropy is maximum for constant energy, and from this it follows that each Legendre transform of the entropy is maximum for constant values of the transformed (intensive) variables. Similarly, in the energy representation the energy is minimum for constant entropy, and from this it follows that each Legendre transform of the energy is minimum for constant values of the transformed (intensive) variables.

However, it has been known for a long time that the consistent development of these ideas is contingent on the solution of a methodological problem of Gibbsian thermostatics illustrated by the following paradox: how are we to give a precise meaning to the statement that entropy is maximum for constant energy, whereas

entropy is defined only for systems in equilibrium? Many authors have grappled with this dilemma until a partial solution was found in terms of the composite system. The basic purpose of this paper is to present a simple alternative solution. Based on the kinetic theory of rarefied gases, we approach the question by means of a molecular expression for entropy in the form of Boltzmann's H functional. As we shall soon see, the introduction of nonequilibrium distribution functions enables us to define comparison states for the extremum principles and thus to solve the aforementioned paradox.

Our method is, in fact, quite straightforward. We provide a thermodynamic interpretation of the kinetic theory in which the nonequilibrium states of the gas are described by means of the nonnegative distribution functions f . This description can be used in various ways to introduce also other variables. For example, an interesting alternative is to use the specific volume v , the internal energy density ε , and an appropriately defined phase-space function G , and then to express Boltzmann's entropy h (per unit mass) in terms of (v, ε, G) rather than f . These two descriptions appear on an equal footing, and we can choose either one to suit the problem at hand.

If we choose (v, ε, G) , we will be able to exhibit the decomposition of Boltzmann's entropy h into two physically different parts:

$$(1.1) \quad h(v, \varepsilon, G) = h_E(v, \varepsilon) + \Delta(G).$$

The first part, denoted for brevity by h_E , represents the thermostatic entropy (which is a function of v and ε), while the second part, denoted by Δ , gives the functional contribution to h independent of (v, ε) and vanishing at equilibrium; Δ depends only on G . The resulting expression (1.1) for h is such that the derivatives of h with respect to v and ε are the same functions as in equilibrium, and Gibbsian thermostatics is not to be viewed simply as a first approximation to the full description of the system, but, instead, as an exact theory valid for a suitably chosen parametrization of the space of nonequilibrium states. The motivation for the introduction of Eq. (1.1) may be understood in terms of our desire to insure that the entropy maximum principle will go over into an energy minimum principle on inversion of $h = h(v, \varepsilon, G)$ with respect to ε : $\varepsilon = \varepsilon(v, h, G)$. The extremum principles in the Legendre transformed representations are then proved to be logically equivalent to the maximization of the entropy or to the minimization of the energy.

Mathematically, the nonequilibrium method presented in this paper is parallel to the equilibrium method of CALLEN [2], but has the following feature distinguishing it from that encountered in thermostatics: when the system is removed from equilibrium, the theory of Legendre transforms and thermodynamic potentials depends very much on the choice of variables in terms of which it has to characterize the state of a system. Clearly, if one is interested only in the discussion of the equilibrium case, one knows full well what the "right" variables are

and these sorts of complications may be avoided altogether. For the general case, however, the optimum definition of state variables is not a trivial problem. As a matter of fact, one will be unable to obtain any successful theory of thermodynamic potentials unless one formulates some adequate criterion for the choice of state variables. In our approach we introduce this criterion in such a way that the concepts of temperature and pressure need no reformulation out of equilibrium and the extremum principles are valid for the Legendre transforms of entropy and energy.

If the space of nonequilibrium states carries a structure of a finite-dimensional manifold, the entropy maximum principle allows one to draw upon results from the critical point theory, as formulated by MORSE [4]. Using this theory, it is possible to find a coordinate system for the manifold of nonequilibrium states such that the specific entropy can exactly be written as a sum of two physically different terms [5–7]: the first term represents the thermostatic entropy (which is a function of conserved variables), while the second term is given by a quadratic form depending only on nonequilibrium variables. Due to the existence of this particularly simple representation of the specific entropy, one easily arrives at the natural definitions of temperature, pressure, and thermodynamic potentials for systems “not infinitesimally near to equilibrium.” However, there does not as yet exist a kinetic-theory framework in which these and similar problems may be addressed in a very satisfactory way. Thus, the underlying philosophy here is not to formulate a completely systematic extension of the aforementioned results to the general infinite-dimensional case, or even to propose some modification of Morse’s lemma. Rather, the objective is to exploit the specific properties of a classical rarefied gas of massive particles and to obtain the required coordinatization of the space of nonequilibrium states by direct guessing.

Another remark is also in order. For fixed values of v and ε , $h(v, \varepsilon, \bullet)$ denotes a functional, that is, a function whose argument is G . Consequently, any derivation of the Gibbs relation for h is necessarily based on the technique of functional differentiation. It can be most simply conceived of as a straightforward generalization of the concept of partial derivative. The foregoing functional justification of the existence of thermodynamic potentials for gaseous systems beyond local equilibrium is different from the method of moments [8]. Formally, *this method gives the same Gibbs relation* for the Boltzmann entropy density h as in the technique of functional differentiation; but its precise definition and mathematical status are complex, and lose direct physical meaning because the Hermite expansions of G and $\ln(1 + G)$ are applied at the outset of the analysis. Furthermore, there are difficulties in proving the existence and convergence of various series involved. Nevertheless, to understand the conceptual problems associated with this method, we decide to present an explanation of how the moment representation of entropy relates to our formalism.

The layout of this paper is as follows. In Secs. 2 and 3, we describe the properties of nonequilibrium thermodynamic potentials. In Secs. 4 and 5, the status

of the method of moments is examined *vis-a-vis* the technique of functional differentiation. Section 6 is for discussion and conclusion. Some auxiliary material is included as Appendices A and B.

2. The relation between Boltzmann's entropy and mass density

2.1. Preliminaries

The kinetic theory describes the state of a gas by the distribution function $f(x, c, t)$ defined, according to Boltzmann, in such a way that $f(x, c, t) d^N c$ is the number density of molecules at the point x and at the time t that have velocities in the "volume" element $d^N c$ around c ; N is the dimension of the vector space to which c belongs. The distribution function obeys the kinetic equation of the form

$$(2.1) \quad \partial_t f + c \cdot \partial_x f = J(f),$$

where $J(f)$ is the collision term.

In the kinetic theory of rarefied gases, local entropy S (per unit volume) is sometimes required, and it is locally defined by the functional expression

$$(2.2) \quad S(f) := -k_B \int f \ln(\mathbb{C}f) d^N c,$$

where

$$(2.3) \quad \mathbb{C} := (2\pi\hbar m^{-1})^N$$

and where m is the molecular mass and k_B and $2\pi\hbar$ are constants of Boltzmann and Planck, respectively. Differentiating S with respect to time and using Eq. (2.1) yield the entropy balance equation

$$(2.4) \quad \dot{h} = -\frac{1}{\varrho}(\partial \cdot \Phi) + \sigma$$

in which

$$(2.5) \quad \begin{aligned} h &:= S/\varrho, \\ \varrho &:= m \int f d^N c, \\ \Phi &:= -k_B \int \bar{c} f \ln(\mathbb{C}f) d^N c, \\ \sigma &:= -(k_B/\varrho) \int J(f) \ln(\mathbb{C}f) d^N c, \\ \bar{c} &:= c - u, \\ u &:= (m/\varrho) \int c f d^N c. \end{aligned}$$

Here and henceforth, $\partial := \partial_x$ and an overdot indicates the substantial time derivative defined by $\dot{A} := \partial_t A + u \cdot \partial_x A$. Interpreting Eqs. (2.5), h is the specific entropy, ϱ is the mass density, Φ is the entropy flux, σ is the nonnegative entropy production, \bar{c} is the peculiar velocity, and u is the macroscopic velocity.

2.2. The direct Legendre transform of Boltzmann's entropy

In order to compare and contrast the predictions of various theories of thermodynamic potentials, we begin our discussion by introducing the standard Legendre transform of Boltzmann's entropy. Given a clear statement as to what this transform is, one should be in a much better position to understand what the alternative method of Sec. 3 really entails. Since Boltzmann's entropy is a functional of f , the variation of $S(f)$ can be written as

$$(2.6) \quad \delta S = \int \lambda \delta f d^N c,$$

where

$$(2.7) \quad \lambda(c) := \delta S / \delta f(c) = -k_B [1 + \ln(\mathbb{C}f)].$$

In Eq. (2.7) the dependence of λ on x and t is not shown explicitly in order to make the resulting formulas shorter. The relation (2.7) can be solved uniquely for f in the form

$$(2.8) \quad f = \frac{1}{\mathbb{C}} \exp\left(-1 - \frac{\lambda}{k_B}\right).$$

We define the Legendre transform of $S(f)$ as

$$(2.9) \quad F(\lambda) := S(f) - \int \lambda f d^N c.$$

In view of the kinetic-theory definition (2.2) of S , we then find from Eqs. (2.5)₂, (2.7), and (2.9) that F is proportional to the mass density ϱ :

$$(2.10) \quad F = (k_B/m)\varrho.$$

The variation of $F(\lambda)$ as a functional of λ is given by

$$(2.11) \quad \delta F = - \int f \delta \lambda d^N c,$$

where

$$(2.12) \quad f(c) = -\delta F / \delta \lambda(c).$$

The equivalence of $F = F(\lambda)$ with $S = S(f)$ is evident from the fact that the latter can be regained from the former. The relation is dual in the sense that the inverse and direct relations have the same form, except for a sign in the equation of the Legendre transformation.

Following these lines, a *formal* theory of nonequilibrium potentials can easily be founded parallel to the theory of equilibrium thermodynamics, but in such a method of dealing with S there does not appear to be a way that the “nonequilibrium inverse temperature” $1/T$ and the “thermodynamic pressure” p could be associated with the derivatives of $h = S/\rho$ with respect to the specific internal energy ε (per unit mass) and the specific volume $v = 1/\rho$:

$$(2.13) \quad \frac{1}{T} = \frac{\partial h}{\partial \varepsilon}, \quad p/T = \frac{\partial h}{\partial v}.$$

Thus another way of dealing with Boltzmann’s entropy must be proposed, and in Sec. 3 a calculation is made to *prove* that the generalized Gibbs formulas (2.13) are valid *only* for a suitably chosen parametrization of the space of nonequilibrium states.

The problem has to do with the freedom of choosing independent variables in terms of which we could describe the nonequilibrium state of a Boltzmann gas. If, instead of considering the “fundamental equation” $S = S(f)$ with f as independent “variable,” we had replaced f by (v, ε, G) and then considered v , ε , and G as new independent variables⁽¹⁾, we could have defined another set of thermodynamic potentials by performing the Legendre transformations on $h = h(v, \varepsilon, G)$ rather than on $S = S(f)$. The corollary of this observation is as follows: the kinetic theory in itself does not provide a precise definition of what one means by the Legendre transform of Boltzmann’s entropy, and some additional specifications are still necessary to make this definition precise. They are formulated in the text below.

3. Further Legendre transformations

3.1. A Maxwellian molecular density

To carry on the intended analysis of the aforementioned questions, it is useful to define a few mathematical quantities. First, we define the specific internal energy ε and the reduced peculiar velocity κ by

$$(3.1) \quad \varepsilon := (m/2\rho) \int |\bar{c}|^2 f d^N c$$

and

$$(3.2) \quad \kappa := \alpha \bar{c},$$

⁽¹⁾ See Sec. 3.1 for the definition of v , ε and G .

where

$$(3.3) \quad \alpha := (N/2\varepsilon)^{1/2}.$$

Inspection shows that κ is dimensionless. With the specific internal energy and the reduced peculiar velocity so defined, we now construct f_M as follows:

$$(3.4) \quad f_M(x, \kappa, t) := [\varrho(x, t)/m][\alpha(x, t)]^N \Omega(\kappa),$$

where ϱ is the mass density of Eq. (2.5)₂ and $\Omega(\kappa)$ is given by

$$(3.5) \quad \Omega(\kappa) := \left(\frac{1}{2\pi}\right)^{N/2} \exp\left(-\frac{1}{2}|\kappa|^2\right).$$

Such an f_M is called a Maxwellian molecular density.

As a measure of the deviation of f from f_M we suggest

$$(3.6) \quad G := \frac{1}{f_M} (f - f_M).$$

The natural, independent variables of this function are x , κ , and t ; thus $G = G(x, \kappa, t)$. The same remark concerns f_M . However, for simplicity, the dependence of f_M and G on x and t will not be shown explicitly. Hence we have for f

$$(3.7) \quad f(x, c, t) = f_M(\kappa) [1 + G(\kappa)].$$

Also, in virtue of the definitions of $(\varrho, u, \varepsilon)$, we immediately see that

$$(3.8) \quad \int \Omega G G d^N \kappa = 0,$$

where

$$(3.8') \quad G := 1, \quad \kappa, \quad |\kappa|^2.$$

To summarize, even though f_M does not satisfy the Boltzmann equation (2.1), we can always write f in the form (3.7) and thus uniquely represent f in terms of ϱ , u , ε , and G . This representation and the relations (3.8) are exact and are automatically assured if the distribution function f obeys the following conditions:

$$(3.9) \quad \int |c|^n f d^N c < \infty, \quad n = 0, \dots, 3.$$

The use of these conditions introduces a natural class of distribution functions which are considered to prove the existence of the equations of balance of ϱ , u and ε .

3.2. A canonical form of Boltzmann's entropy

If we substitute the decomposition (3.7) into Eq. (2.2), then by Eqs. (3.4) and (3.8) we obtain for $h = S/\varrho$

$$(3.10) \quad h(v, \varepsilon, G) = h_E(v, \varepsilon) + \Delta(G),$$

where $v = 1/\varrho$ and

$$(3.11) \quad \begin{aligned} h_E(v, \varepsilon) &:= \frac{N}{2}(k_B/m) - (k_B/m) \ln \left[\mathbb{C} \frac{1}{mv} \left(\frac{N}{4\pi\varepsilon} \right)^{N/2} \right], \\ \Delta(G) &:= -(k_B/m) \int \Omega(1+G) \ln(1+G) d^N \kappa. \end{aligned}$$

The separation of h in Eq. (3.10) into h_E and Δ has a clear physical significance: h_E represents the thermostatic entropy (which is a function of v and ε), while Δ gives the functional contribution to h independent of (v, ε) and vanishing at equilibrium. This result shows that the change of dynamical variables, namely, the transition from f to (v, ε, G) , enables one to obtain a particularly useful parametrization of the space of nonequilibrium states. Indeed, on applying such a parametrization, one can easily prove that $\partial h/\partial v$ and $\partial h/\partial \varepsilon$ are the same functions of v and ε as in equilibrium. Precisely speaking, the infinitesimal variation δh and the substantial time derivative of h assume the form

$$(3.12) \quad \begin{aligned} \delta h &= (p/T)\delta v + \frac{1}{T}\delta \varepsilon + \int \Theta \delta G d^N \kappa, \\ \dot{h} &= (p/T)\dot{v} + \frac{1}{T}\dot{\varepsilon} + \int \Theta \dot{G} d^N \kappa, \end{aligned}$$

where $\dot{G}(x, \kappa, t) := (\partial_t + u \cdot \partial_x)G(x, \kappa, t)$, δG is the infinitesimal variation of G consistent with the constraints (3.8) and the obvious inequality $G > -1^{(2)}$, and

$$(3.13) \quad \begin{aligned} p/T &:= \frac{\partial h}{\partial v} = \partial h_E/\partial v = k_B(\varrho/m), \\ \frac{1}{T} &:= \frac{\partial h}{\partial \varepsilon} = \partial h_E/\partial \varepsilon = Nk_B/2m\varepsilon, \\ \Theta(\kappa) &:= \delta h/\delta G(\kappa) = \delta \Delta/\delta G(\kappa) = -(k_B/m)\Omega[1 + \ln(1+G)]. \end{aligned}$$

We shall refer to Eqs. (3.12) as the generalized Gibbs relations (equations).

From Eqs. (3.10) and (3.12)₁ it follows that we can determine h and δh without knowing the particular kinetic process occurring, and without regard to the time

⁽²⁾ It is not difficult to prove the existence of such variations δG of G . In this context, we wish to note that δG is a function of x, κ , and t .

and the place. In other words, the values of the specific entropy and its variation are ascertained from the information which is static and universal. This information consists in the form of the dependence of h upon v , ε , and G . Clearly, the relation (3.12)₂ is a direct consequence of Eq. (3.12)₁. However, this relation is not “static” and “universal,” because it holds only for those distribution functions which are solutions of Boltzmann’s equation.

In the theory of Boltzmann, the temperature T is regarded as but another name for the expected kinetic energy of relative motion; thus

$$(3.14) \quad T = \frac{2m\varepsilon}{Nk_B}.$$

Moreover, if we let $p = (2/N)\varrho\varepsilon$ denote the mean pressure, then from Eq. (3.14) it follows that the “ideal gas law” holds for every condition of the gas:

$$(3.15) \quad p = (\varrho/m)k_B T.$$

Another way to define T and p is through Eqs. (3.13)₁ and (3.13)₂; both methods lead to the same result.

We are now in a position to discuss certain problems regarding the structure of an expression for the entropy flux Φ . Examination of Eqs. (2.5)₃ and (3.7) makes it readily apparent that Φ can exactly be written as

$$(3.16) \quad \Phi = (q/T) - (k_B\varrho/m\alpha) \int \kappa\Omega(1 + G) \ln(1 + G) d^N\kappa,$$

where α is defined by Eq. (3.3) and q is the heat flux:

$$(3.17) \quad q := \frac{m}{2} \int |\bar{c}|^2 \bar{c} f d^N c.$$

Our analysis here shows how the quantity q/T enters the general expression for Φ naturally. By Eq. (3.16) we see, however, that not only net heating flux gives rise to δ . The above calculations also show that if we are to define the entropy flux Φ on the basis of kinetic theory, then it is necessary to identify the “nonequilibrium temperature” T with $2m\varepsilon/Nk_B$. Of course, for gas flows sufficiently near to local equilibrium in the sense that f differs little from the corresponding f_M , we can linearize the integral part of Eq. (3.16) with respect to G and so conclude from the constraints (3.8) that Φ approximately equals q/T . No such approximations are possible, however, in the nonlinear case.

One final word concerning the results just obtained. Given the natural condition (3.9) of Sec. 3.1, we have shown that use of the decomposition $f = F_M(1 + G)$ in Eqs. (2.5)₁ and (2.5)₃ yields the specific entropy h in Eq. (3.10) and the entropy flux Φ in Eq. (3.16) in terms of v , ε , and G . Consequently, within the framework set up here, the formula (3.16) emerges in confirmation to the thermodynamic

principles, and an extended Gibbs-relation-like one-form (3.12)₂ is consistent with the entropy law as characterized by Eq. (2.4). The obvious reason for this consistency is the fact that Eqs. (3.10), (3.12), and (3.16) are identities. Of course, we can also test our results directly by substituting these identities and an appropriate expression for the entropy production σ into Eq. (2.4). The details of this somewhat elaborate programme will not be presented, however, because a hint of what to expect may be obtained from considerations of Sec. 5.

3.3. The extremum principles

We easily conclude from Eqs. (3.8), (3.10), (3.11), and the inequality

$$(3.18) \quad (1 + G) \ln(1 + G) - G \geq 0$$

that of all states (v, ε, G) with given values of v and ε , the equilibrium state $(v, \varepsilon, 0)$ has the greatest specific entropy h (*the entropy maximum principle*):

$$(3.19) \quad h(v, \varepsilon, G) \leq h_E(v, \varepsilon).$$

Here h equals h_E if and only if $G = 0$.

As a further systematic step, it is plausible to express ε in terms of v , h , and G . In fact, by solving Eq. (3.10) for the specific internal energy ε we find that

$$(3.20) \quad \varepsilon(v, h, G) = \frac{N}{4\pi} \left(\frac{\mathbb{C}}{mv} \right)^{2/N} \exp \left\{ \frac{2m}{Nk_B} [h - \Delta(G)] - 1 \right\}.$$

Then, beginning from $\Delta \leq 0$, we see that among all states (v, h, G) having the same values of v and h , the equilibrium state $(v, h, 0)$ gives ε its smallest value (*the energy minimum principle*). Moreover, we have

$$(3.21) \quad p = -\frac{\partial \varepsilon}{\partial v}, \quad T = \frac{\partial \varepsilon}{\partial h},$$

$$\Theta(\kappa) = -\frac{1}{T} [\delta \varepsilon / \delta G(\kappa)].$$

Hence

$$(3.22) \quad \dot{\varepsilon} = -p \dot{v} + T \dot{h} - T \int \Theta \dot{G} d^N \kappa.$$

Clearly, this result is consistent with Eq. (3.12)₂.

The specific free energy

$$(3.23) \quad \varphi(v, T, G) := \varepsilon(T) - Th(v, \varepsilon(T), G)$$

$$= (k_B T / m) \ln \left[\mathbb{C} \frac{1}{mv} \left(\frac{m}{2\pi k_B T} \right)^{N/2} \right] - T \Delta(G)$$

is that partial Legendre transform of ε which replaces the entropy h by the temperature T as independent variable. The substantial time derivative $\dot{\varphi}$ is

$$(3.24) \quad \dot{\varphi} = -p\dot{v} - h\dot{T} - T \int \Theta \dot{G} d^N \kappa.$$

In addition, from Eq. (3.23) it follows that the equilibrium state $(v, T, 0)$ minimizes the specific free energy φ , not absolutely, but over the space of states (v, T, G) with given values of v and T (*the free-energy minimum principle*).

Now, we define the specific enthalpy H and the Gibbs function Q as $H := \varepsilon + vp$ and $Q := \varepsilon - Th + vp$, respectively. The specific enthalpy H is that partial Legendre transform of ε which replaces the specific volume v by the pressure p as independent variable. The Gibbs function Q in turn is the Legendre transform of ε which simultaneously replaces the specific entropy h by the temperature T and the specific volume v by the pressure p as independent variables. The physical meaning of these nonequilibrium thermodynamic potentials is apparent from the differential expressions obtained on using Eq. (3.22):

$$(3.25) \quad \dot{H} = v\dot{p} + T\dot{h} - T \int \Theta \dot{G} d^N \kappa,$$

$$(3.26) \quad \dot{Q} = v\dot{p} - h\dot{T} - T \int \Theta \dot{G} d^N \kappa.$$

Moreover, from

$$(3.27) \quad H = H(p, h, G) = \frac{(N + 2)}{4\pi} \left(\frac{2\pi}{m} \mathbb{C}p \right)^{2/(N+2)} \times \exp \left\{ \frac{2m}{(N + 2)k_B} [h - \Delta(G)] - \frac{N}{N + 2} \right\}$$

one can prove that among all states (p, h, G) having the same values of p and h , the equilibrium state $(p, h, 0)$ gives H its smallest value (*the enthalpy minimum principle*). Similarly, using

$$(3.28) \quad Q = Q(p, T, G) = (k_B T/m) + (k_B T/m) \ln \left[\mathbb{C}(p/k_B T) \left(\frac{m}{2\pi k_B T} \right)^{N/2} \right] - T \Delta(G),$$

one concludes that the equilibrium state $(p, T, 0)$ minimizes the Gibbs function Q , not absolutely, but over the space of states (p, T, G) with given values of p and T (*the Gibbs-function minimum principle*).

The total Legendre transform of ε is defined by

$$(3.29) \quad \begin{aligned} \mathcal{E}(p, T, \Theta) &:= Th - vp - T \int \Theta G d^N \kappa - \varepsilon \\ &= -(k_B T/m) \ln \left[\mathbb{C}(p/k_B T) \left(\frac{m}{2\pi k_B T} \right)^{N/2} \right] + T \int \Theta d^N \kappa. \end{aligned}$$

A glance at Eq.(3.13)₃ shows that the equilibrium value Θ_E of Θ is $\Theta_E = -(k_B/m)\Omega$. Also, with Eq. (3.8) for $G = 1$ and the inequality $\ln(1 + G) - G \leq 0$, we find that

$$(3.30) \quad \int (\Theta - \Theta_E) d^N \kappa \geq 0.$$

Hence

$$(3.31) \quad \mathcal{E}(p, T, \Theta) \geq \mathcal{E}(p, T, \Theta_E),$$

the equality holding if and only if $\Theta = \Theta_E$. The substantial time derivative of \mathcal{E} assumes the form

$$(3.32) \quad (\mathcal{E})^\cdot = -v \dot{p} + h \dot{T} - \int G(T\Theta)^\cdot d^N \kappa.$$

Another set of functions (Massieu’s functions) can be defined by performing the Legendre transformations on $h(v, \varepsilon, G)$ rather than on $\varepsilon(v, h, G)$. As the theory of these functions is very much analogous to that already made familiar, we will not discuss this theory further here; specifically, we will not derive the maximum principles for the Massieu functions⁽³⁾.

4. The method of moments

To study the consequences of using the method of moments, we introduce the Hilbert space \mathcal{H} in which the scalar product $\langle \omega_1, \omega_2 \rangle$ is defined by

$$(4.1) \quad \langle \omega_1, \omega_2 \rangle := \int \Omega(\kappa) \omega_1(\kappa) \omega_2(\kappa) d^N \kappa.$$

We can determine the exact moment representations of h and \dot{h} if we assume that $1 + G$, $\ln(1 + G)$, and \dot{G} are elements of \mathcal{H} . Then by use of the *complete set* of tensor Hermite polynomials $B^n(\kappa)$, $n = 0, 1, \dots, \infty$, it is possible to represent $1 + G$, $\ln(1 + G)$, and \dot{G} by the expansions [9]

$$(4.2) \quad \begin{aligned} 1 + G &= Y := \sum_{n=0}^{\infty} \frac{1}{n!} b^n \cdot B^n, \\ \ln(1 + G) &= \sum_{n=0}^{\infty} X^n \cdot B^n, \\ \dot{G} &= \sum_{n=2}^{\infty} \frac{1}{n!} \dot{b}^n \cdot B^n, \end{aligned}$$

⁽³⁾ Of course, we can also derive the minimum principles, this being purely a matter of convention in the choice of the sign of the function.

where b^n and X^n are the expansion coefficients and the symbol \cdot denotes the inner product of the tensors involved. Clearly, because of the constraints (3.8), we have

$$(4.3) \quad b^0 = 1, \quad b^1 = 0, \quad \text{Tr } b^2 = 0,$$

where Tr is the trace operator. The above series converge in the sense of the norm in \mathcal{H} . However, to express X^n in terms of b^n , we must first assume that the series Y converges both pointwise for each κ and in the sense of \mathcal{H} and then substitute Eq. (4.2)₁ into

$$(4.4) \quad X^n = \frac{1}{n!} \int \Omega B^n \ln(1 + G) d^N \kappa.$$

Here we remark that if the above conditions are not satisfied, then the moment representations of h and \dot{h} described below are not expected to exist. This gives us necessary information about what is and is not possible. In the recent analysis [10] presented by EU [see, e.g., his equations (2.30) and (2.33)], an explicit assumption was made that the expansion Y in Eq. (4.2)₁ converges to $1 + G$ in the sense of means and that this rather weak condition is sufficient to see the method of moments in action (i.e., to express X^n in terms of b^n). The pointwise convergence of Y just deduced clearly suggests it to the contrary.

From Eqs. (3.10)–(3.13) and (4.2) plus the orthogonality properties of Hermite polynomials [9], the moment representations of h and \dot{h} are as follows:

$$(4.5) \quad h = h_E - (k_B/m) \sum_{n=0}^{\infty} X^n \cdot b^n,$$

$$(4.6) \quad \dot{h} = (p/T) \dot{v} + \frac{1}{T} \dot{\varepsilon} - (k_B/m) \sum_{n=2}^{\infty} X^n \cdot \dot{b}^n.$$

Consistency⁽⁴⁾ between Eqs. (4.5) and (4.6) follows directly from the considerations of Appendix B [cf. Eqs. (B.2)₆ and (B.3)₆]. We can similarly analyze the kinetic-theory expression for the entropy flux Φ . In fact, putting the expansions (4.2)₁ and (4.2)₂ into Eq. (3.16), we find that [cf. also Eq. (B.7) in Appendix B]

$$(4.7) \quad \Phi = (q/T) - (k_B \rho / m \alpha) \sum_{n=1}^{\infty} (X^n \cdot b^{n+1} + n X^n \cdot b^{n-1}),$$

where the heat flux q is related to $\text{Tr } b^3$ by

$$(4.8) \quad \text{Tr } b^3 = \frac{2}{\rho} \left(\frac{N}{2\varepsilon} \right)^{3/2} q.$$

⁽⁴⁾ The series in Eqs. (4.5)–(4.7) converge absolutely if $1 + G$, $\kappa(1 + G)$, \dot{G} , and $\ln(1 + G)$ are elements of \mathcal{H} .

However, we have to worry about the convergence of the series in Eq. (4.7); this may require consideration of the situation in which also $\kappa(1+G)$ is an element of \mathcal{H} . From the viewpoint of the present paper, the method of moments is a formal and sophisticated way of deriving the generalized Gibbs relation (3.12)₂ for the specific Boltzmann entropy h . In Secs. 2 and 3, we have seen that there are simpler and more natural ways of deriving this relation. One obvious reason for this is that, with the technique of functional differentiation, we can draw *definite* and *exact* conclusions about the existence of Eqs. (3.12) without making any explicit or implicit reference to \mathcal{H} . This is crucial because representative and physically important cases are known [11] in which solutions of the kinetic equation do not exist in the Hilbert space chosen: $G \notin \mathcal{H}$. This fact detracts much from the usefulness of Hermite expansions (and of various *ad hoc* truncation and projection procedures) at the level of the *nonlinear* Boltzmann or Boltzmann-like equations.

We recall that the nonnegative entropy production σ is given by Eq. (2.5)₄ and conclude from Eqs. (3.7) and (4.2)₂ that

$$(4.9) \quad \sigma = -(k_B/m) \sum_{n=0}^{\infty} X^n \cdot P^n,$$

where

$$(4.10) \quad P^n := (m/\varrho) \int B^n J(f) d^N c$$

and where

$$(4.11) \quad P^0 = 0, \quad P^1 = 0, \quad \text{Tr } P^2 = 0.$$

The exact and/or tractable moment representations of P^n are not expected to exist, except in the case of Maxwellian molecules.

In Sec. 5 we shall verify that if we use the formulas (4.5), (4.7), and (4.9) in the balance equation (2.4) for h , then this balance equation will be automatically satisfied, at least formally. Before doing so, however, it is necessary to derive the evolution equations for ϱ , u , ε , and b^n .

The equations of balance of ϱ , u , and ε are easily obtained from the Boltzmann equation under the natural assumption that f falls off sufficiently rapidly for large values of c :

$$(4.12) \quad \begin{aligned} \dot{\varrho} &= -\varrho(\partial \cdot u), \\ \dot{u} &= -\frac{1}{\varrho} \left[\partial \cdot (pI + \omega) \right], \\ \dot{\varepsilon} &= -\frac{1}{\varrho} (\partial \cdot q) - \frac{1}{\varrho} (pI + \omega) \cdot L. \end{aligned}$$

The abbreviated symbol I stands for the unit tensor of a Euclidean vector space \mathbb{E} ($\dim \mathbb{E} = N$), L is the spatial gradient of u ($L := \partial u$), and ω is the stress deviator defined by

$$(4.13) \quad \omega := m \int \left(\bar{c} \otimes \bar{c} - \frac{1}{N} |\bar{c}|^2 I \right) f d^N c.$$

This stress deviator is proportional to b^2 :

$$(4.14) \quad b^2 = \frac{N}{2\rho\varepsilon} \omega.$$

By use of the notation introduced in Appendix A we obtain from

$$(4.15) \quad b^n = \frac{m}{\rho} \int B^n f d^N c$$

and the Boltzmann equation (under usual assumptions) the following result:

$$(4.16) \quad \dot{b}^n = Z^n + P^n,$$

where

$$(4.16') \quad \begin{aligned} Z^n &:= -\frac{1}{\alpha} \left(\partial \cdot b^{n+1} + n \partial \vee b^{n-1} \right) - \frac{1}{\alpha \rho} \left(\rho' \cdot b^{n+1} + n \rho' \vee b^{n-1} \right) \\ &\quad - n \alpha (\dot{u} \vee b^{n-1}) - n \left[L \cup b^n + (n-1) L \vee b^{n-2} \right] \\ &\quad - \frac{\alpha}{N} \left[(n+1) \varepsilon' \cdot \psi^{n+1} + n(n-1) \varepsilon' \vee \psi^{n-1} \right] - \frac{n \dot{\varepsilon}}{2\varepsilon} \psi^n, \\ \rho' &:= \partial \rho, \quad \varepsilon' := \partial \varepsilon, \\ \psi^n &:= b^n + (n-1) I \vee b^{n-2}, \\ b^{-3} &:= 0, \quad b^{-2} := 0, \quad b^{-1} := 0, \\ n &= 0, 1, \dots, \infty. \end{aligned}$$

This is the desired system of equations for the coefficients b^n in the expansion (4.2)₁ of $1 + G$. Inspection shows that Eqs. (4.16) are automatically satisfied if n equals 0 or 1, because of Eqs. (4.12); moreover, $(\text{Tr } b^2)' = \text{Tr } \dot{b}^2 = \text{tr } Z^2 = \text{tr } P^2 = 0$. Another remark is also in order. To obtain a manageable system of “extended” differential equations, the infinite set of moments has to be truncated and some procedures for expressing P^n in terms of b^n must be proposed. However, to the best of our knowledge, it still remains an open question whether such a truncation procedure is consistent with kinetic theory.

The manner in which these calculations form the first step in the formal derivation of $\dot{h} = -\rho^{-1}(\partial \cdot \Phi) + \sigma$ from Eqs. (4.5), (4.7), and (4.9), will become clear in the text below.

5. Consistency between the generalized Gibbs relation and the entropy law

First of all, there is no question that Eqs. (3.12) and (4.6) are consistent with the entropy law (2.4) because these equations are identities. Nevertheless, since this point has been a subject of debate [12–14] in the past, here the internal consistency of the formalism will be demonstrated from still another viewpoint. To achieve the objective in mind, we first substitute Eqs. (4.7) and (4.9) into the entropy law (2.4) and then establish the following identity by using Eqs. (3.3), (4.8), (4.12), (4.14), (4.16), and the definitions of various quantities involved:

$$(5.1) \quad \dot{h} = (p/T)\dot{v} + \frac{1}{T}\dot{\varepsilon} - (k_B/m)\sum_{n=2}^{\infty} X^n \cdot \dot{b}^n + (k_B/m\varrho T)C_h,$$

where

$$(5.2) \quad \begin{aligned} C_h &:= \sum_{n=1}^{\infty} \left[T(\partial \cdot \vartheta_n) + \varrho T(X^n \cdot Z^n) + (b^n \cdot \chi^n) \right], \\ \vartheta_n &:= \varrho \alpha^{-1} \left[X^n \cdot b^{n+1} + n X^n \cdot b^{n-1} \right], \\ \chi^2 &:= \varrho T L, \quad \chi^3 := \frac{\alpha}{N} \varrho T (I \vee \varepsilon'), \\ \chi^n &:= 0 \quad \text{for } n \neq 2, 3. \end{aligned}$$

The expansion in Eq. (5.2)₁ starts from $n = 1$, because $\vartheta_0 = 0$ and $\vartheta_n \neq 0$ when $n > 0$. Combining Eqs. (4.6) and (5.1), we obtain

$$(5.3) \quad C_h = 0.$$

We call this equation the *consistency condition* because its role in essence is that of a guarantor of the generalized Gibbs relation (4.6) for entropy change. In order to demonstrate the internal consistency of the formalism, it is thus stimulating to show that Eq. (5.3) holds for all conditions of the Boltzmann gas.

Now, we shall prove that C_h can indeed be set equal to zero without encountering any internal contradiction. This proof generalizes to N -dimensional systems the conclusion⁽⁵⁾ formulated directly before Eq. (4.18) in [12]. A straightforward application of Eqs. (3.3), (4.16), (5.2), (B.2)₁, and (B.3)₁ yields

$$(5.4) \quad \frac{1}{\varrho T} C_h = -\alpha(\dot{u} \cdot \mathcal{D}_1) - \frac{\dot{\varepsilon}}{2\varepsilon} \mathcal{D}_2 - \frac{\alpha}{N}(\varepsilon' \cdot \mathcal{D}_3) - L \cdot \mathcal{D}_4 + \frac{1}{\alpha} \mathcal{D}_5,$$

⁽⁵⁾ The notation in [12] slightly differs from ours as follows: ours \Rightarrow his; $N \Rightarrow 1$; $k_B \Rightarrow 1$; $m \Rightarrow 1$; $c \Rightarrow \lambda$; $\bar{c} \Rightarrow \bar{\lambda}$; $\partial \Rightarrow \nabla$; $\varepsilon \Rightarrow e$; $\dot{A} \Rightarrow d_t A$; $\psi^n \Rightarrow \alpha \varrho^{-1} \psi^{n-1}$; $X^0 \Rightarrow T^{-1}(\mu - T\nu)$; $X^n \Rightarrow -T^{-1} X^n$ for $n \neq 0$; $\vartheta_n \Rightarrow -T^{-1}(X^n \cdot \psi^n)$; $\chi^2 \Rightarrow 0$; $\chi^3 \Rightarrow -\chi^3$. Similar comparisons of our consistency condition $C_h = 0$ (specialized to the case $N = 1$) with the corresponding equation (25) of [14] are not possible, however, because in this equation the meaning of the symbol \sum_n is not clearly explained.

where the objects $\mathcal{D}_1, \dots, \mathcal{D}_5$ are defined by Eqs. (B.2). However, from the considerations of Appendix B it follows that $\mathcal{D}_k = 0$ when $k = 1, \dots, 5$. This completes the proof of Eq. (5.3). The validity of $C_h = 0$ and hence of Eq. (4.6) is also obvious on the intuitive ground.

Thus contrary to the suggestion made in the literature [14], there does appear to be a way that the terms in Eq. (5.2)₁ cancel each other so neatly that $C_h = 0$ when Eqs. (4.2) and (4.4) hold; in other words, when the complete set is taken for $B^n(\kappa)$. This implies the second conclusion: there is no kinetic-theory foundation for including the *compensation function* (or the *calortropy*) in the thermodynamic description of Boltzmann's gas, as it is done in the so-called revised version of the modified moment method [13] or in its possible further corrections (see especially the discussion on p. 7177 after Eq. (3.30) in [10]). Such is indeed the case because the generalized Gibbs relation (4.6) holds for the entropy density h itself, and not for the compensation function which appears to be extraneous and redundant. The same observation concerns the notion of calortropy. To be more precise, substitution of the formula (4.2)₂ into Eq. (3.1) in [10] yields the conclusion that the calortropy does not differ from Boltzmann's entropy.

The gist of the point made by the present analysis is that the information contained in the generalized Gibbs relation formally does not contract as the level of description is passed from the phase-space level (3.12) to that at the moment level [cf. Eq. (4.6)], since the passage essentially involves a complete set of Hermite polynomials. Moreover, after expressing X^n in terms of b^n , as is formally always possible [cf., e.g., our analysis directly after Eq. (4.3)], the Boltzmann entropy h becomes a state function in a space spanned by the "thermodynamic" variables $\mathcal{E} := \{v, \varepsilon, b^n \mid n = 2, 3, \dots, \infty\}$, and thus one can think of \dot{h} as being an exact differential in \mathcal{E} . On the basis of such results, it is possible to infer that, as was already found in earlier work [12], a thermodynamic interpretation of kinetic theory may be erected on Boltzmann's entropy alone, i.e., without the necessity [10, 13] of referring to the "concepts" of compensation function and calortropy. However, the method of moments is surely not very useful in practice. This method obscures the real situation: it suggests that there is something very special about the way the theory of thermodynamic potentials is related to Hermite expansions, whereas in reality this is not so. A deductive mathematical way for exhibiting the generalized Gibbs relation has been proposed in Sec. 3 and is clearly linked to the technique of functional differentiation.

6. Discussion and conclusion

We have found a set of thermodynamic potentials for the description of a Boltzmann gas. We have obtained the extremum principles for these potentials, and examined their physical meaning in the simplest case (a one-component gas).

The basis for the initial analysis was Boltzmann's entropy which is a functional of the single particle distribution function, not of the fields. This entropy was then divided into two parts, that associated with the local distribution (and hence yielding a standard function of conserved variables) plus the remainder. Using the technique of functional differentiation, we have proved that if the independent gas-state variables are (v, ε, G) , the quantities $Nk_B/2m\varepsilon$ and $2\rho\varepsilon/N$, which everybody would write down as the only natural concepts in the situation of a classical rarefied gas, exactly correspond to the "nonequilibrium inverse temperature" $1/T$ and the "thermodynamic pressure" p as defined by investigating the partial derivatives of Boltzmann's entropy $h(v, \varepsilon, G)$ with respect to v and ε .

Comparison with the usual approach shows that we can obtain the same results as usual but in a much more transparent way, because in the standard approach (the method of moments) the existence of thermodynamic potentials depends on the convergence of the following series:

$$(6.1) \quad \mathfrak{Z}(x, t) := \sum_{n=0}^{\infty} X^n(x, t) \cdot b^n(x, t),$$

where (x, t) is an arbitrary space-time point. On the other hand, in order to use the method of moments to draw valuable conclusions about the "thermodynamic branch" [12] of solutions of Boltzmann's equation, it would be necessary to have not only the convergence of \mathfrak{Z} for arbitrary space-time points but also some information about uniformity (in space-time) of convergence; the existence theorems for Boltzmann's equation give no indication that there will be any such uniformity. Furthermore, the divergence of Y [cf. Eq. (4.2)₁] in certain important cases makes uniformity of convergence problematical. For a discussion of these divergences, see, for example, [11].

The situation is different, however, with the formalism of Sec. 3, for its equations give rise to the exact theory of thermodynamic potentials independent of any *ad hoc* assumptions and artificial constructions. To summarize, the technique of functional differentiation is an adequate tool to study the mathematical and physical status of the generalized Gibbs relation at the level of Boltzmann's equation. The point of this discussion is that instead of concentrating on the formal Hermite expansion (4.6) of \dot{h} , with the ambiguities that implies, we can deal directly with Eqs. (3.12).

At first sight, it seems that while the questions/problems posed here apply for general systems, their answers/resolutions must be limited to classical rarefied gases. *But this is not the case.* In fact, we have already verified that our ideas are quite universal and can be extended in a number of directions, one of them being the analysis of mixtures and quantum Bose-Einstein or Fermi-Dirac nonequilibrium ideal gases. However, since these extensions are not altogether trivial or immediate, they will be treated in a separate paper.

Appendix A. Some useful abbreviations

To make the resulting formulas shorter, in this paper we have introduced essentially the same notation as in [15–17]. Let \mathbb{E} be a Euclidean vector space ($\dim \mathbb{E} = N$). Choose an orthonormal basis $\{e_1, \dots, e_N\}$ in \mathbb{E} and set $e_{r_1 \dots r_\alpha} := e_{r_1} \otimes \dots \otimes e_{r_\alpha}$.

1. The action of the symmetrizer Π on a tensor M^α of degree α is given by

$$(A.1) \quad \Pi M^\alpha := \sum_{r_1 \dots r_\alpha = 1}^N M_{(r_1 \dots r_\alpha)}^\alpha e_{r_1 \dots r_\alpha},$$

where the coefficients $M_{r_1 \dots r_\alpha}^\alpha$ are components of M^α with respect to $\{e_{r_1 \dots r_\alpha}\}$ and parentheses enclosing a set of α indices represent symmetrization of these indices, i.e., the sum over $\alpha!$ permutations of the indices, divided by $\alpha!$

2. Suppose that M^α and M^β are the tensors of degrees α and β , respectively. Then the equality

$$(A.2) \quad M^\alpha \vee M^\beta := \Pi (M^\alpha \otimes M^\beta)$$

defines the symmetric tensor product of M^α and M^β .

3. The action of \cup on M^α and M^β is characterized by

$$(A.3) \quad M^\alpha \cup M^\beta := \Pi \operatorname{Tr}_{(1, \alpha + 1)} (M^\alpha \otimes M^\beta),$$

where $\operatorname{Tr}_{(1, \alpha + 1)}$ is the trace operator with respect to the pair $(1, \alpha + 1)$.

4. Let us suppose that $\nu := \min(\alpha, \beta)$. Then in contracting M^α with M^β the ν -fold contraction is denoted by \cdot . The tensor $M^\alpha \cdot M^\beta$ of degree $\alpha + \beta - 2\nu$ is usually termed the inner tensor product of M^α and M^β . However, if M^α and M^β are not totally symmetric tensors, then some convention as to which of the 2ν indices are to be contracted, must be followed when doing the contraction. In this context, see the precise definition of $M^\alpha \cdot M^\beta$ in Appendix A of [17].

5. Suppose that M^α and \overline{M}^α are the tensors of degree α . Then the action of \square on M^α and \overline{M}^α is described by

$$(A.4) \quad M^\alpha \square \overline{M}^\alpha := \sum_{r, s = 1}^N [(e_r \cdot M^\alpha) \cdot (e_s \cdot \overline{M}^\alpha)] e_r \otimes e_s.$$

6. The effect of ∂ on a tensor field M^α is given by

$$(A.5) \quad \partial M^\alpha := \sum_{r = 1}^N e_r \otimes \partial_r M^\alpha$$

with $\partial_r := \partial / \partial x^r$.

7. The action of $\partial \cdot$ on a tensor field M^α is defined by

$$(A.6) \quad \partial \cdot M^\alpha := \text{Tr}_{(1, \alpha+1)} (\partial M^\alpha).$$

8. The effect of $\partial \vee$ on a tensor field M^α is characterized by

$$(A.7) \quad \partial \vee M^\alpha := \Pi(\partial M^\alpha).$$

Appendix B. Auxiliary formal properties of b^n and X^n

The effect of $\bar{\partial}$ on a function $\Lambda(\kappa)$ or a tensor field $M^n(\kappa)$ of degree n is given by

$$(B.1) \quad \begin{aligned} \bar{\partial} \Lambda &:= \sum_{r=1}^N (\bar{\partial}_r \Lambda) e_r, \\ \bar{\partial} M^n &:= \sum_{r=1}^N e_r \otimes \bar{\partial}_r M^n, \end{aligned}$$

where $\bar{\partial}_r := \partial / \partial \kappa^r$.

The objects \mathcal{D}_k , $k = 1, \dots, 6$, are defined by

$$(B.2) \quad \begin{aligned} \mathcal{D}_1 &:= \sum_{n=1}^{\infty} n X^n \cdot b^{n-1}, \\ \mathcal{D}_2 &:= \sum_{n=2}^{\infty} n X^n \cdot \psi^n, \\ \mathcal{D}_3 &:= -\text{Tr} b^3 + \sum_{n=1}^{\infty} [(n+1) X^n \cdot \psi^{n+1} + n(n-1) X^n \cdot \psi^{n-1} - X^n \cdot b^{n+1}], \\ \mathcal{D}_4 &:= -b^2 + \sum_{n=1}^{\infty} n [b^n \square X^n + (n-1) X^n \cdot b^{n-2}], \\ \mathcal{D}_5 &:= \sum_{n=1}^{\infty} [(\partial X^n) \cdot b^{n+1} + n(\partial \cdot X^n) \cdot b^{n-1}], \\ \mathcal{D}_6 &:= \sum_{n=0}^{\infty} \dot{X}^n \cdot b^n, \end{aligned}$$

where, of course, $\partial = \partial_x$.

It is only a matter of labor to prove that

$$\begin{aligned}
 \mathcal{D}_1 &= \frac{m}{\alpha^N \varrho} \int f \bar{\partial} [\ln(1 + G)] d^N \kappa = 0, \\
 \mathcal{D}_2 &= \frac{m}{\alpha^N \varrho} \int f \left\{ \kappa \cdot \bar{\partial} [\ln(1 + G)] \right\} d^N \kappa = 0, \\
 \mathcal{D}_3 &= \frac{m}{\alpha^N \varrho} \int f \kappa \left\{ N + 2 - |\kappa|^2 + \kappa \cdot \bar{\partial} [\ln(1 + G)] \right\} d^N \kappa = 0, \\
 \mathcal{D}_4 &= \frac{m}{\alpha^N \varrho} \int f \left\{ I - \kappa \otimes \kappa + \kappa \otimes \bar{\partial} [\ln(1 + G)] \right\} d^N \kappa = 0, \\
 \mathcal{D}_5 &= \frac{m}{\alpha^N \varrho} \int f \left\{ \kappa \cdot \partial [\ln(1 + G)] \right\} d^N \kappa = 0, \\
 \mathcal{D}_6 &= \frac{m}{\alpha^N \varrho} \int f \left[\ln(1 + G) \right]' d^N \kappa = 0,
 \end{aligned}
 \tag{B.3}$$

where $[\ln(1 + G)]'$ is the substantial time derivative of $\ln(1 + G)$. In these equations, f and G are functions of x , κ , and t .

The proof that the series \mathcal{D}_k , $k = 1, \dots, 6$, can indeed be represented by the above *vanishing* integrals, is based on Eqs. (2.5)₅, (3.2), (4.2)₂, (4.15), and the following identities [15, 16] for Hermite polynomials $B^n(\kappa)$ [9]:

$$\begin{aligned}
 \kappa \otimes B^n(\kappa) &= B^{n+1}(\kappa) + n \sum_{r=1}^N e_r \otimes \left[e_r \vee B^{n-1}(\kappa) \right], \\
 \bar{\partial} B^n &= n \sum_{r=1}^N e_r \otimes \left(e_r \vee B^{n-1} \right), \\
 n(n + 1) \left[M^n \cdot (I \vee B^{n-1}) \right] &= 2n \left(M^n \cdot B^{n-1} \right) + n(n - 1) \left[(\text{Tr } M^n) \cdot B^{n-1} \right],
 \end{aligned}
 \tag{B.4}$$

where M^n is an arbitrary symmetric tensor of degree n .

The series in Eqs. (B.2) exist and are absolutely convergent if $1 + G$, $[\ln(1 + G)]'$, $\bar{\partial} \ln(1 + G)$, $\kappa \otimes \bar{\partial} \ln(1 + G)$, $\kappa \otimes \partial \ln(1 + G)$, and $\kappa \otimes \kappa \otimes \bar{\partial} \ln(1 + G)$ are elements of \mathcal{H} . Clearly, as usual, we must also assume that we can exchange the integral over c or κ with the derivative ∂_x ; these assumptions are necessary in order to derive the evolution equations (4.16) for b^n . If these postulates are not satisfied, the method of moments fails to exist.

Using the identity

$$\frac{m}{\alpha^N \varrho} f = \Omega(1 + G)
 \tag{B.5}$$

and integrating by parts, we easily conclude from the constraints (3.8) that the integrals in Eqs. (B.3) vanish; thus

$$\mathcal{D}_k = 0
 \tag{B.6}$$

when $k = 1, \dots, 6$. This observation completes the proof of Eq. (5.3).

A one-dimensional version of these calculations is represented by Eqs. (4.14) in [12]; see also the comments at the bottom of p.359 in that paper. *All the essential ingredients for the proof of the consistency condition (5.3) were thus given seven years ago.*

From $\mathcal{D}_1 = 0$ it follows that Eq. (4.7) simplifies to

$$(B.7) \quad \Phi = (q/T) - (k_B \rho / m \alpha) \sum_{n=1}^{\infty} X^n \cdot b^{n+1}.$$

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Received September 25, 1995.