

## Scattering rates versus moments: Alternative Grad equations

Alexander N. Gorban and Iliya V. Karlin\*

*Computing Center, Russian Academy of Sciences, Krasnoyarsk 660036, Russian Federation*

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Scattering rates (moments of collision integral) are treated as independent variables, and as an alternative to moments of the distribution function, to describe the rarefied gas near local equilibrium. A version of the entropy maximum principle is used to derive the Grad-like description in terms of a finite number of scattering rates. The equations are compared to the Grad moment system in the heat nonconductive case. Estimations for hard spheres demonstrate, in particular, some 10% excess of the viscosity coefficient resulting from the scattering rate description, as compared to the Grad moment estimation. [S1063-651X(96)51310-3]

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The classical Grad moment method [1] provides an approximate solution to the Boltzmann equation, and leads to a closed system of equations where hydrodynamic variables  $\rho$ ,  $\mathbf{u}$ , and  $P$  (density, mean flux, and pressure) are coupled to a finite set of nonhydrodynamic variables. The latter are usually the stress tensor  $\sigma$  and the heat flux  $\mathbf{q}$  constituting ten- and thirteen-moment Grad systems. The Grad method was originally introduced for diluted gases to describe regimes beyond the normal solutions [2], but later it was used, in particular, as a prototype of certain phenomenological schemes in nonequilibrium thermodynamics [3]. Recently the Grad equations were used to obtain examples of exact summation of gradient expansions arising in the kinetic theory [4].

However, the moments do not constitute the unique system of nonhydrodynamic variables, and the exact dynamics might be equally expressed in terms of other infinite sets of variables (possibly, of a nonmoment nature). Moreover, as long as one shortens the description to only a finite subset of variables, the advantage of the moment description above other systems is not obvious.

In this Rapid Communication we consider another system of nonhydrodynamic variables, *scattering rates*  $M^w(f)$ :

$$M_{i_1 i_2 i_3}^w(f) = \int \mu_{i_1 i_2 i_3} Q^w(f) d\mathbf{v};$$

$$\mu_{i_1 i_2 i_3} = m v_1^{i_1} v_2^{i_2} v_3^{i_3}, \quad (1)$$

which, by definition, are the moments of the Boltzmann collision integral  $Q^w(f)$ :

$$Q^w(f) = \int w(\mathbf{v}', \mathbf{v}'_1, \mathbf{v}, \mathbf{v}_1) \{ f(\mathbf{v}') f(\mathbf{v}'_1) - f(\mathbf{v}) f(\mathbf{v}_1) \} d\mathbf{v}' d\mathbf{v}'_1 d\mathbf{v}_1.$$

Here  $w$  is the probability density of a change of the velocities,  $(\mathbf{v}, \mathbf{v}_1) \rightarrow (\mathbf{v}', \mathbf{v}'_1)$ , of the two particles after their encounter, and  $w$  is defined by a model of pair interactions. The

description in terms of the scattering rates  $M^w$  (1) is alternative to the usually treated description in terms of the moments  $M$ :  $M_{i_1 i_2 i_3}(f) = \int \mu_{i_1 i_2 i_3} f d\mathbf{v}$ .

A reason to consider scattering rates instead of the moments is that  $M^w$  (1) reflect features of the interactions because of the  $w$  incorporated in their definition, while the moments do not. For this reason we can expect that, in general, a description with a *finite* number of scattering rates will be more informative than a description provided by the same number of their moment counterparts.

To come to the Grad-like equations in terms of the scattering rates, we have to complete the following two steps:

(i) To derive a hierarchy of transport equations for  $\rho$ ,  $\mathbf{u}$ ,  $P$ , and  $M_{i_1 i_2 i_3}^w$  in a neighborhood of the local Maxwell states  $f_0(\rho, \mathbf{u}, P)$ .

(ii) To truncate this hierarchy, and to come to a closed set of equations with respect to  $\rho$ ,  $\mathbf{u}$ ,  $P$ , and a finite number of scattering rates.

In the step (i), we derive a description with an infinite number of variables, which is formally equivalent both to the Boltzmann equation near the local equilibrium, and to the description with an infinite number of moments. The approximation comes into play in the step (ii) where we reduce the description to a finite number of variables. The difference between the moment and the alternative description occurs at this point.

The program (i) and (ii) is similar to what is done in the Grad method [1], with the only exception (and this is important) that we should always use scattering rates as independent variables and not to expand them into series in moments. Consequently, we will use a method of a closure in the step (ii) that does not refer to the moment expansions. Major steps of the computation will be presented below.

To complete the step (i), we represent  $f$  as  $f_0(1 + \varphi)$ , where  $f_0$  is the local Maxwellian, and we linearize the scattering rates (1) with respect to  $\varphi$ :

$$\Delta M_{i_1 i_2 i_3}^w(\varphi) = \int \Delta \mu_{i_1 i_2 i_3}^w f_0 \varphi d\mathbf{v};$$

$$\Delta \mu_{i_1 i_2 i_3}^w = L^w(\mu_{i_1 i_2 i_3}). \quad (2)$$

Here  $L^w$  is the usual linearized collision integral, divided by  $f_0$ . Though  $\Delta M^w$  are linear in  $\varphi$ , they are not moments

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\*Present address: Department of Mathematical Physics, University of Ulm, Ulm, D-89069 Germany.

because their microscopic densities,  $\Delta\mu^w$ , are not velocity polynomials for a general case of  $w$ .

It is not difficult to derive the corresponding hierarchy of transport equations for variables  $\Delta M_{i_1 i_2 i_3}^w$ ,  $\rho$ ,  $\mathbf{u}$ , and  $P$  (we will further refer to this hierarchy as the alternative chain): one has to calculate the time derivative of the scattering rates (1) due to the Boltzmann equation, in the linear approximation (2), and to complete the system with the five known balance equations for the hydrodynamic moments (scattering rates of the hydrodynamic moments are equal to zero due to conservation laws). The structure of the alternative chain is quite similar to that of the usual moment transport chain, and for this reason we do not reproduce it here (details of calculations can be found in [5]). One should only keep in mind that the stress tensor and the heat flux vector in the balance equations for  $\mathbf{u}$  and  $P$  are not independent variables anymore, and they are expressed in terms of  $\Delta M_{i_1 i_2 i_3}^w$ ,  $\rho$ ,  $\mathbf{u}$ , and  $P$ .

To truncate the alternative chain [step (ii)], we have, first, to choose a finite set of ‘‘essential’’ scattering rates (2), and second, to obtain the distribution functions that depend parametrically only on  $\rho$ ,  $\mathbf{u}$ ,  $P$ , and on the chosen set of scattering rates. We will restrict our consideration to a single non-hydrodynamic variable,  $\sigma_{ij}^w$ , which is the counterpart of the stress tensor  $\sigma_{ij}$ . This choice corresponds to the polynomial  $mv_i v_j$  in the expressions (1) and (2), and the resulting equations will be alternative to the ten-moment Grad system [6]. For a spherically symmetric interaction, the expression for  $\sigma_{ij}^w$  may be written as

$$\sigma_{ij}^w(\varphi) = \int \Delta\mu_{ij}^w f_0 \varphi d\mathbf{v};$$

$$\Delta\mu_{ij}^w = L^w(mv_i v_j) = \frac{P}{\eta_0^w(T)} S^w(c^2) \left\{ c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right\}. \quad (3)$$

Here  $\eta_0^w(T)$  is the first Sonine polynomial approximation of the Chapman-Enskog viscosity coefficient (VC) [2], and, as usual,  $\mathbf{c} = \sqrt{m/2kT}(\mathbf{v} - \mathbf{u})$ . The scalar dimensionless function  $S^w$  depends only on  $c^2$ , and its form depends on the choice of interaction  $w$ .

Next, we find the functions  $f^*(\rho, \mathbf{u}, P, \sigma_{ij}^w) = f_0(\rho, \mathbf{u}, P) [1 + \varphi^*(\rho, \mathbf{u}, P, \sigma_{ij}^w)]$  which maximize the Boltzmann entropy  $S(f)$  in a neighborhood of  $f_0$  (the quadratic approximation to the entropy is valid within the accuracy of our consideration), for fixed values of  $\sigma_{ij}^w$ . That is,  $\varphi^*$  is a solution to the following conditional variational problem:

$$\Delta S(\varphi) = -\frac{k_B}{2} \int f_0 \varphi^2 d\mathbf{v} \rightarrow \max,$$

$$(i) \int \Delta\mu_{ij}^w f_0 \varphi d\mathbf{v} = \sigma_{ij}^w; \quad (ii) \int \{1, \mathbf{v}, v^2\} f_0 \varphi d\mathbf{v} = 0. \quad (4)$$

The second (homogeneous) condition in Eq. (4) reflects that a deviation  $\varphi$  from the state  $f_0$  is due only to nonhydrodynamic degrees of freedom, and it is straightforwardly satisfied for  $\Delta\mu_{ij}^w$  (3).

Notice, that if we turn to the usual moment description, then condition (i) in Eq. (4) would fix the stress tensor  $\sigma_{ij}$

instead of its scattering counterpart  $\sigma_{ij}^w$ . Then the resulting function  $f^*(\rho, \mathbf{u}, P, \sigma_{ij}^w)$  will be exactly the ten-moment Grad approximation. It can be shown that a choice of any finite set of higher moments as the constraint (i) in Eq. (4) results in the corresponding Grad approximation. In that sense our method of constructing  $f^*$  is a direct generalization of the Grad method onto the alternative description.

The Lagrange multipliers method gives straightforwardly the solution to the problem (4). After the alternative chain is closed with the functions  $f^*(\rho, \mathbf{u}, P, \sigma_{ij}^w)$ , the step (ii) is completed, and we arrive at a set of equations with respect to the variables  $\rho$ ,  $\mathbf{u}$ ,  $P$ , and  $\sigma_{ij}^w$ . Switching to the variable  $\zeta_{ij} = n^{-1} \sigma_{ij}^w$ , we have

$$\partial_t n + \partial_i (n u_i) = 0; \quad (5a)$$

$$\rho(\partial_i u_k + u_i \partial_i u_k) + \partial_k P + \partial_i \left\{ \frac{\eta_0^w(T) n}{2 r^w P} \zeta_{ik} \right\} = 0; \quad (5b)$$

$$\frac{3}{2} (\partial_t P + u_i \partial_i P) + \frac{5}{2} P \partial_i u_i + \left\{ \frac{\eta_0^w(T) n}{2 r^w P} \zeta_{ik} \right\} \partial_i u_k = 0; \quad (5c)$$

$$\begin{aligned} & \partial_t \zeta_{ik} + \partial_s (u_s \zeta_{ik}) + \left\{ \zeta_{ks} \partial_s u_i + \zeta_{is} \partial_s u_k - \frac{2}{3} \delta_{ik} \zeta_{rs} \partial_s u_r \right\} \\ & + \left\{ \gamma^w - \frac{2\beta^w}{r^w} \right\} \zeta_{ik} \partial_s u_s - \frac{P^2}{\eta_0^w(T) n} \left( \partial_i u_k + \partial_k u_i \right. \\ & \left. - \frac{2}{3} \delta_{ik} \partial_s u_s \right) - \frac{\alpha^w P}{r^w \eta_0^w(T)} \zeta_{ik} = 0. \end{aligned} \quad (5d)$$

Here  $\partial_t = \partial/\partial t$ ,  $\partial_i = \partial/\partial x_i$ , summation in two repeated indices is assumed, and the coefficients  $r^w$ ,  $\beta^w$ , and  $\alpha^w$  are defined with the aid of the function  $S^w$  (3) as follows:

$$r^w = \frac{8}{15\sqrt{\pi}} \int_0^\infty e^{-c^2} c^6 [S^w(c^2)]^2 dc; \quad (6)$$

$$\beta^w = \frac{8}{15\sqrt{\pi}} \int_0^\infty e^{-c^2} c^6 S^w(c^2) \frac{dS^w(c^2)}{d(c^2)} dc;$$

$$\alpha^w = \frac{8}{15\sqrt{\pi}} \int_0^\infty e^{-c^2} c^6 S^w(c^2) R^w(c^2) dc.$$

The function  $R^w(c^2)$  in the last expression is defined due to the action of the operator  $L^w$  on the function  $S^w(c^2) (c_i c_j - \frac{1}{3} \delta_{ij} c^2)$ :

$$\frac{P}{\eta_0^w} R^w(c^2) \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right) = L^w \left[ S^w(c^2) \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right) \right]. \quad (7)$$

Finally, the parameter  $\gamma^w$  in Eq. (5) reflects the temperature dependence of the VC:

$$\gamma^w = \frac{2}{3} \left[ 1 - \frac{T}{\eta_0^w(T)} \left( \frac{d\eta_0^w(T)}{dT} \right) \right].$$

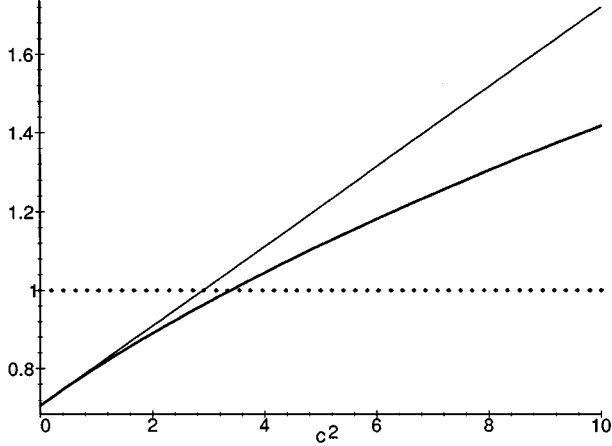


FIG. 1. Approximations for hard spheres: bold line, function  $S^{HS}$ ; solid line, approximation  $S_a^{HS}$ ; dotted line, Grad moment approximation.

The set of ten equations (5) is alternative to the ten-moment Grad equations.

The first observation to be made is that for Maxwellian molecules we have  $S^{MM} \equiv 1$ , and  $\eta_0^{MM} \propto T$ ; thus  $\gamma^{MM} = \beta^{MM} = 0$ ,  $r^{MM} = \alpha^{MM} = \frac{1}{2}$ , and Eq. (5) becomes the ten-moment Grad system under a simple change of variables  $\lambda \zeta_{ij} = \sigma_{ij}$ , where  $\lambda$  is the proportionality coefficient in the temperature dependence of  $\eta_0^{MM}$ .

These properties (the function  $S^w$  is a constant, and the VC is proportional to  $T$ ) are true only for Maxwellian molecules. For all other interactions, the function  $S^w$  is not identical to 1, and the VC  $\eta_0^w(T)$  is not proportional to  $T$ . Thus, the shortened alternative description is not equivalent indeed to the Grad moment description. In particular, for hard spheres, the exact expression for the function  $S^{HS}$  (3) reads

$$S^{HS} = \frac{5\sqrt{2}}{16} \int_0^1 \exp(-c^2 t^2) (1-t^4) [c^2(1-t^2) + 2] dt, \quad \eta_0^{HS} \propto \sqrt{T}. \quad (8)$$

Thus,  $\gamma^{HS} = \frac{1}{3}$ , and  $\beta^{HS}/r^{HS} \approx 0.07$ , and the equation for the function  $\zeta_{ik}$  (5d) contains a nonlinear term,

$$\theta^{HS} \zeta_{ik} \partial_s u_s, \quad (9)$$

where  $\theta^{HS} \approx 0.19$ . This term is missed in the Grad ten-moment equation.

Finally, let us evaluate the VC which results from the alternative description (5). Following Grad's arguments [1], we see that, if the relaxation of  $\zeta_{ik}$  is fast compared to the hydrodynamic variables, then the two last terms in the equation for  $\zeta_{ik}$  (5) become dominant, and the equation for  $\mathbf{u}$  casts into the standard Navier-Stokes form with an effective VC  $\eta_{\text{eff}}^w$ :

$$\eta_{\text{eff}}^w = \frac{1}{2\alpha^w} \eta_0^w. \quad (10)$$

TABLE I. Second virial coefficient for hard spheres.

	$B_{\text{expt}}$	$B_0$	$B_{\text{eff}}$
Argon	8.4	60.9	50.5
Helium	10.8	21.9	18.2
Nitrogen	168	66.5	55.2

For Maxwellian molecules, we easily derive that the coefficient  $\alpha^w$  in Eq. (10) is equal to  $\frac{1}{2}$ . Thus, as one expects, the effective VC (10) is equal to the Grad value, which, in turn, is equal to the exact value in the frames of the Chapman-Enskog method for this model.

For all interactions that are different from the Maxwellian molecules, the VC  $\eta_{\text{eff}}^w$  (10) is not equal to  $\eta_0^w$ . For hard spheres, in particular, a computation of the VC (10) requires information about the function  $R^{HS}$  (7). This is achieved upon a substitution of the function  $S^{HS}$  (8) into Eq. (7). Further, we have to compute the action of the operator  $L^{HS}$  on the function  $S^{HS}(c; c_j - \frac{1}{3}\delta_{ij}c^2)$ , which is rather complicated. However, the VC  $\eta_{\text{eff}}^{HS}$  can be relatively easily estimated by using a function  $S_a^{HS} = (1/\sqrt{2})(1 + \frac{1}{7}c^2)$ , instead of the function  $S^{HS}$ , in Eq. (7). Indeed, the function  $S_a^{HS}$  is tangent to the function  $S^{HS}$  at  $c^2=0$ , and is its majorant (see Fig. 1). Substituting  $S_a^{HS}$  into Eq. (7), and computing the action of the collision integral, we find the approximation  $R_a^{HS}$ ; thereafter we evaluate the integral  $\alpha^{HS}$  (6), and finally come to the following expression:

$$\eta_{\text{eff}}^{HS} \geq \frac{75}{67} \frac{264}{237} \eta_0^{HS} \approx 1.12 \eta_0^{HS}. \quad (11)$$

Thus, for hard spheres, the description in terms of scattering rates results in the VC of more than 10% higher than in the Grad moment description.

A discussion of the results concerns the following two items.

(i) Having two descriptions that are not equivalent which were obtained within one method, we may ask, which is more relevant? A simple test is to compare characteristic times of an approach to hydrodynamic regime. We have  $\tau_G \sim \eta_0^{HS}/P$  for ten-moment description, and  $\tau_a \sim \eta_{\text{eff}}^{HS}/P$  for alternative description. As  $\tau_a > \tau_G$ , we see that scattering rate decays slower than the corresponding moment; hence, at least for rigid spheres, alternative description is more relevant. For Maxwellian molecules both the descriptions are, of course, equivalent.

(ii) The VC  $\eta_{\text{eff}}^{HS}$  (11) has the same temperature dependence as  $\eta_0^{HS}$ , and also the same dependence on a scaling parameter (a diameter of the sphere). In [7], "sizes" of molecules are presented, assuming that a molecule is represented with an equivalent sphere and VC is estimated as  $\eta_0^{HS}$ . Since our estimation of VC differs only by a dimensionless factor from  $\eta_0^{HS}$ , it is straightforward to conclude that effective sizes of molecules will be reduced by the factor  $b$ , where

$$b = \sqrt{\eta_0^{HS}/\eta_{\text{eff}}^{HS}} \approx 0.94.$$

Further, it is well known that sizes of molecules estimated via viscosity in [7] disagree with the estimation via the virial

expansion of the equation of state. In particular, in [8] the measured second virial coefficient  $B_{\text{exp}}$  was compared with the calculated  $B_0$ , in which the diameter of the sphere was taken from the viscosity data. The reduction of the diameter by factor  $b$  gives  $B_{\text{eff}} = b^3 B_0$ . The values  $B_{\text{exp}}$  and  $B_0$  [8] are compared with  $B_{\text{eff}}$  in Table I for three gases at  $T = 500$  K. The results for argon and helium are better for  $B_{\text{eff}}$ , while for nitrogen  $B_{\text{eff}}$  is worse than  $B_0$ . However, both  $B_0$  and  $B_{\text{eff}}$  are far from the experimental values.

Hard spheres is, of course, an oversimplified model of interaction, and the comparison presented does not allow for a decision between  $\eta_0^{HS}$  and  $\eta_{\text{eff}}^{HS}$ . Nevertheless, this simple example illustrates to what extent the correction to the VC can affect a comparison with experiment. Indeed, as is well known, the first-order Sonine polynomial computation for the Lennard-Jones (LJ) potential gives a very good fit of the temperature dependence of the VC for all noble gases [9], subject to a proper choice of the two unknown scaling pa-

rameters of the LJ potential [10]. We may expect that a dimensionless correction of the VC for the LJ potential might be of the same order as above for rigid spheres. However, the functional character of the temperature dependence will not be affected, and a fit will be obtained subject to a different choice of the molecular parameters of the LJ potential.

There remains, however, a general question how the estimation of the VC (10) responds to the exact value [2,11]. Since the analysis performed above does not immediately appeal to the exact Chapman-Enskog expressions just mentioned, this question remains open for a further work.

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- [1] H. Grad, *Comm. Pure Appl. Math.* **2**, 331 (1949).  
 [2] S. Chapman and T. Cowling, *Mathematical Theory of Non-uniform Gases* (University Press, Cambridge, 1970).  
 [3] D. Jou, J. Casas-Vázquez, and G. Lebon, *Rep. Progr. Phys.* **51**, 1104 (1988); D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics* (Springer, Berlin, 1993).  
 [4] A. Gorban and I. Karlin, *Phys. Rev. Lett.* **77**, 282 (1996).  
 [5] A. Gorban and I. Karlin, *New Methods for Solving the Boltzmann Equations* (AMSE Press, Tassin, 1994).  
 [6] To get the alternative to the thirteen-moment Grad equations, one should take into account the scattering counterpart of the heat flux,  $q_i^w = m \int v_i (v^2/2) Q^{v4w}(f) d\mathbf{v}$ .  
 [7] S. Chapman and T. Cowling, Ref. [2], pp. 228–229.  
 [8] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 5.  
 [9] J. Dorfman and H. van Beijeren, in *Statistical Mechanics B*, edited by B. Berne (Plenum, New York, 1977), p. 113.  
 [10] A comparison of molecular parameters of the LJ potential, as derived from the viscosity data, to those obtained from independent sources, can be found elsewhere, e.g., S. Chapman and T. Cowling in Ref. [2], p. 237.  
 [11] P. Résibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).