Analysis of the Evans and Baranyai Variational Principle in Dilute Gases

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A variational principle for thermostated nonequilibrium steady states recently proposed by Evans and Baranyai [Phys. Rev. Lett. **67**, 2597 (1991)] is analyzed by means of a model kinetic equation for dilute gases. It is shown that the principle does not apply exactly, although deviations from it are small, especially when the gradients are not very large.

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Far from equilibrium systems have turned out very difficult to study, and there is not a general theory for them. Recently, Evans and Baranyai (EB) [1] have proposed a variational principle that generalizes the well-established principle of minimum entropy production for near equilibrium situations [2]. The EB principle states that the rate of decrease of the volume of phase space, subject to the externally imposed constraints, is a local minimum. Although restricted to thermostated steady states, the hypothesis has important physical implications, since it provides a criterion to characterize far from equilibrium steady states in physical systems. On the other hand, there is no reason to expect that similar principles hold for other nonequilibrium states. Evans and Baranyai do not give any proof of their generalization, but they compare its predictions with molecular dynamics simulation of a dense fluid under uniform shear flow. In the range of shear rates considered, they get a remarkable agreement [1].

The purpose here is to investigate the validity of the EB principle using kinetic theory methods. This requires being able to get explicit expressions for the properties of a system that is far from equilibrium, which is a formidable problem, except in some limiting cases. One such limit is a low density simple gas, for which all the physically relevant information is contained in the one-particle distribution function $f(\mathbf{r},\mathbf{v};t)$. As in Ref. [1], we consider the gas in uniform shear flow. This state is characterized by uniform temperature T (defined as proportional to the mean kinetic energy) and density n, and a local velocity field given by $u_i(\mathbf{r}) = a_{ij}r_j, a_{ij} = a\delta_{ix}\delta_{jy}$, where a is the constant shear rate. Besides, each particle in the system is subject to a nonconservative external force $\mathbf{F}$ with components

$$F_i = -\alpha V_i - \beta V_i^3 \quad (i = x, y, z) , \tag{1}$$

where $\mathbf{V} = \mathbf{v} - \mathbf{u}$ is the peculiar velocity of the particle. The first term on the right-hand side of Eq. (1) plays the role of a "drag" force and is introduced to control viscous heating. Thus, the parameter α is adjusted to maintain the stationarity of the state (constant temperature). As in Ref. [1], the second term (which is absent in the case of the unconstrained shear flow) is introduced to explore the verification of the EB principle. The parameter β is adjusted to obtain a prescribed value of the fourth moment

$$K_4 = \int d\mathbf{V}(V_x^4 + V_y^4 + V_z^4)f . \tag{2}$$

Therefore, both α and β are functions of a and K_4. Alternatively, one can consider $\alpha(a,\beta)$ and $K_4(a,\beta)$, and this is the point of view adopted in this Letter.

The EB variational principle refers to the average of the phase-space compression factor Λ [3] that for our system is given by

$$\Lambda(a,\beta) = -\left(\alpha + \frac{3k_BT}{m}\beta\right) . \tag{3}$$

We have omitted a constant factor that is irrelevant for our discussion. According to the principle, Λ must have a maximum in absence of constraints on K_4, i.e., at $\beta = 0$. Therefore, the mathematical expression for the EB principle is

$$\lambda(a) \equiv \left.\frac{\partial\Lambda}{\partial\beta}\right|_{\beta=0} = 0 . \tag{4}$$

This is equivalent to saying that in the thermostated steady state, with given values of T, n, and a, Λ is a local maximum with respect to variations in K_4. The principle is formulated in a more general way, including the variation of all the endogeneous variables of the system, but we restrict ourselves to K_4, as is done in Ref. [1].

Our aim in the following is to calculate $\lambda(a)$ for a dilute gas. As long as $\lambda(a) \neq 0$, the EB principle is not exactly verified. Thus, λ can be physically interpreted as a measure of the degree of validity of the principle. Since the Boltzmann equation is too difficult to solve in far from equilibrium situations, we consider instead the kinetic equation proposed by Bhatnagar, Gross, and Krook (BGK) [4] as a model of the Boltzmann equation. The reliability of the BGK equation has been shown in the last few years, since it leads to moment solutions of the same structure as those obtained from the Boltzmann equation in several nonequilibrium states [5]. In the case of (unconstrained) uniform shear flow, the shear viscosity and the viscometric functions obtained from the BGK equation coincide exactly with those obtained from the Boltzmann equation for Maxwell molecules to every order in the shear rate. For hard spheres, the BGK results agree extremely well with Monte Carlo simulations of the Boltzmann equation for large shear rates [6]. The steady BGK equation for the problem reads [7]

$$-aV_y\frac{\partial f}{\partial V_x}-\frac{1}{m}\frac{\partial}{\partial V_i}\left(\alpha V_i+\beta V_i^3\right)f=-\zeta(f-f_{\rm LE})\ , \quad (5)$$

where $f_{\rm LE}$ is the local equilibrium distribution function and ζ is an average collision frequency independent of velocity, but generally is a functional of f through the density and the temperature. Hereafter, we choose units so that $\zeta=1$, $n=1$, $m=1$, and $2k_BT=1$. We introduce the moments

$$M_{k_1,k_2,k_3}=\int d\mathbf{V}V_x^{k_1}V_y^{k_2}V_z^{k_3}f\ , \quad (6)$$

and obtain from Eq. (5) the following hierarchy:

$$-M_{k_1,k_2,k_3}+M^{\rm LE}_{k_1,k_2,k_3}=ak_1M_{k_1-1,k_2+1,k_3}+\alpha(k_1+k_2+k_3)M_{k_1,k_2,k_3}$$
$$+\beta(k_1M_{k_1+2,k_2,k_3}+k_2M_{k_1,k_2+2,k_3}+k_3M_{k_1,k_2,k_3+2})\ , \quad (7)$$

where

$$M^{\rm LE}_{k_1,k_2,k_3}=\pi^{-3/2}\Gamma\left(\frac{k_1+1}{2}\right)\Gamma\left(\frac{k_2+1}{2}\right)\Gamma\left(\frac{k_3+1}{2}\right) \quad (8)$$

if k_1, k_2, and k_3 are even, being zero otherwise. In Eq. (7) it is assumed that M is identically zero when any of its indices is negative. For arbitrary β, the above hierarchy is not closed and cannot be solved. However, in order to evaluate λ, only small values of β need to be considered. Consequently, we carry out an expansion in powers of β by writing $\alpha=\alpha_0+\alpha_1\beta+\cdots$ and $M_{k_1,k_2,k_3}=M^{(0)}_{k_1,k_2,k_3}+M^{(1)}_{k_1,k_2,k_3}\beta+\cdots$, where the coefficients are nonlinear functions of the shear rate a. Inserting these expansions into Eq. (7) one gets a set of hierarchies that can be recursively solved. The result is

$$M^{(\ell)}_{k_1,k_2,k_3}=\sum_{q=0}^{k_1}(-a)^q[\alpha_0(k_1+k_2+k_3)+1]^{-(q+1)}\frac{k_1!}{(k_1-q)!}N^{(\ell)}_{k_1-q,k_2+q,k_3} \quad (9)$$

with $N^{(0)}_{k_1,k_2,k_3}=M^{\rm LE}_{k_1,k_2,k_3}$ and

$$N^{(\ell)}_{k_1,k_2,k_3}=-k_1M^{(\ell-1)}_{k_1+2,k_2,k_3}-k_2M^{(\ell-1)}_{k_1,k_2+2,k_3}-k_3M^{(\ell-1)}_{k_1,k_2,k_3+2}-(k_1+k_2+k_3)\sum_{\ell'=1}^{\ell}\alpha_{\ell'}M^{(\ell-\ell')}_{k_1,k_2,k_3}\ ,\quad \ell\geq 1\ . \quad (10)$$

The expression for the zeroth order moments $M^{(0)}$ has already been derived previously by using a different method [8]. Now, the coefficients α_ℓ can be obtained from the consistency condition $M_{200}+M_{020}+M_{002}=\frac{3}{2}$ that implies $M^{(0)}_{200}+M^{(0)}_{020}+M^{(0)}_{002}=\frac{3}{2}$ and $M^{(\ell)}_{200}+M^{(\ell)}_{020}+M^{(\ell)}_{002}=0$ for $\ell\geq 1$. Finally, substitution of the β expansion into the definition of Λ, Eq. (3), yields

$$\Lambda=-\alpha_0+\lambda\beta-\alpha_2\beta^2+\cdots\ , \quad (11)$$

where α_0 is the real root of the cubic equation

$$3\alpha_0(1+2\alpha_0)^2=a^2\ , \quad (12)$$

and

$$\lambda\equiv-(\alpha_1+\tfrac{3}{2})=3\alpha_0^2\frac{1728\alpha_0^5+2128\alpha_0^4+1664\alpha_0^3+920\alpha_0^2+272\alpha_0+31}{(1+6\alpha_0)(1+4\alpha_0)^5}\ . \quad (13)$$

We have also obtained the explicit expression for α_2, but it is omitted here. Equation (13) shows that λ is not zero in our description. However, for small shear rates, $\alpha_0\approx\frac{1}{3}a^2$, so that $\lambda\approx\frac{31}{3}a^4$ and, consequently, Λ has a maximum at $\beta=0$ when only terms up to third order in the shear rate (super-Burnett order) are retained. Equation (11) can be used to get an estimate of the value $\widetilde{\beta}$ at which Λ has a maximum. In the limit $a\to 0$, $\alpha_2=6$ and one gets $\widetilde{\beta}=\lambda/2\alpha_2\approx\frac{31}{36}a^4$. The value of $\widetilde{\beta}$ turns out to be small also for moderate shear rates. For instance, $\widetilde{\beta}\simeq 0.01$ at $a=1$.

It is interesting to study the behavior of the shear viscosity η as a function of β. The shear viscosity is the most relevant physical quantity and is related to the momentum flux existing in the system. Using the definition $\eta=-2M_{110}/a$ and the above results, it is a simple matter to obtain the first few terms in the expansion $\eta=\eta_0+\eta_1\beta+\eta_2\beta^2+\cdots$. One gets

$$\eta_0=(1+2\alpha_0)^{-2}\ , \quad (14)$$

$$\eta_1 = \frac{2(1+4\alpha_0)^2[2\lambda(1+4\alpha_0)^2 + 3\alpha_0(3+10\alpha_0)] - 27\alpha_0(1+2\alpha_0)^4}{(1+4\alpha_0)^4(1+2\alpha_0)^3} . \quad (15)$$

The explicit expression of η_2 is omitted here. Their small shear rate behavior is $\eta_0 \approx 1$, $\eta_1 \approx -3a^2$, and $\eta_2 \approx 3$. It follows that η has a minimum at $\beta = 0$ up to first order in the shear rate (Navier-Stokes order). Therefore, it could also be considered as a candidate for an approximate variational principle. Nevertheless, the failure of η to be stationary at $\beta = 0$ for $a \neq 0$ is more evident than that of Λ, since $\eta_1 \sim a^2$, while $\lambda \sim a^4$. On the other hand, the dependence of the shear viscosity on β is very small. Let us consider the relative difference $\Delta\eta/\eta_0 = (\eta_1\widetilde{\beta} + \eta_2\widetilde{\beta}^2)/\eta_0$ between the unconstrained shear viscosity and the one corresponding to the value $\beta = \widetilde{\beta}$. In the limit of small shear rates, $\Delta\eta/\eta_0 \approx -\frac{31}{12}a^6$, while $\Delta\eta/\eta_0 < 0.007$ for $a < 1$.

In Fig. 1 we show λ and η_1 as functions of the shear rate. While λ monotonically increases with a, η_1 presents a minimum around $a \simeq 0.2$. For shear rates up to $a \simeq 0.25$, for which the shear viscosity is about 8% smaller than its limiting zero shear rate value, λ is smaller than 0.03. Therefore, the EB principle can be considered as a quite accurate approximation in this region. For larger values of a, the discrepancies are more noticeable. Figure 2 shows the shear rate dependence of both $K_4^{(0)}$ and the ratio $-K_4^{(1)}/K_4^{(0)}$. It is seen that $K_4^{(0)}$ monotonically increases with a, while Evans and Baranyai [1] observed a monotonic decay in their simulation. This difference is probably due to high density effects, which are negligible in the regime of dilute gases. On the other hand, $K_4^{(1)}$ is always negative and, therefore, K_4 decreases with β at a given shear rate, which is in agreement with the results of Ref. [1].

The dependence of the approximate phase-space compression factor $\Lambda = -\alpha_0 + \lambda\beta - \alpha_2\beta^2$ on both a and β is shown in Fig. 3. Although the value $\widetilde{\beta}$ at which Λ has a maximum is always close to $\beta = 0$, for $a \geq 0.5$ it is clearly located at a value $\beta > 0$. Let us point out that the range of shear rates considered in Figs. 1–3 is comparable to the one considered in Ref. [1].

In summary, we have analyzed the EB variational principle for the phase-space compression factor in the context of the nonlinear BGK equation for dilute gases. Our results indicate that the principle is not exactly verified, although it can be considered as a good approximation, especially for not too large shear rates. More specifically, it becomes exact when only terms up to third order in the shear rate (super-Burnett order) need to be retained. Since the results presented here have been derived from the BGK model, it could be that the disagreement with the EB principle is due to inadequacies of the model. Nevertheless, we expect that similar conclusions could be drawn out from the Boltzmann equation. This conjecture is supported by recent results [5,6].

The search for a variational principle characterizing far from equilibrium steady states, as the principle of maximum entropy does with equilibrium states and the principle of minimum entropy production does with near equilibrium states, is a fundamental and long standing problem in statistical mechanics. In this context, we conclude that the EB principle for thermostated states is a nontrivial extension of the principle of minimum entropy production and thus represents a significant step forward. Finally, we expect that analysis based on kinetic theory will stimulate careful simulations in order to progress in the characterization of nonequilibrium states.

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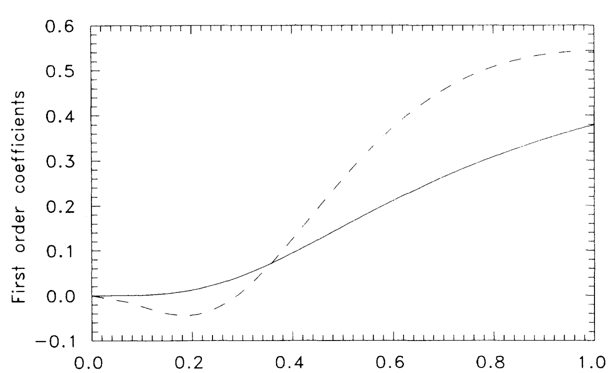

FIG. 1. Shear rate dependence of the first order coefficients λ (solid line) and η_1 (dashed line).

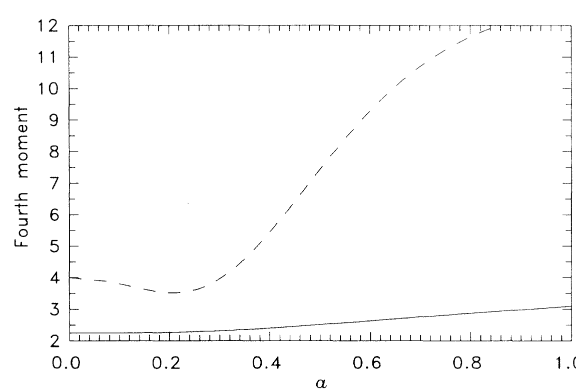

FIG. 2. Shear rate dependence of the unconstrained fourth moment $K_4^{(0)}$ (solid line) and of the ratio $-K_4^{(1)}/K_4^{(0)}$ (dashed line).

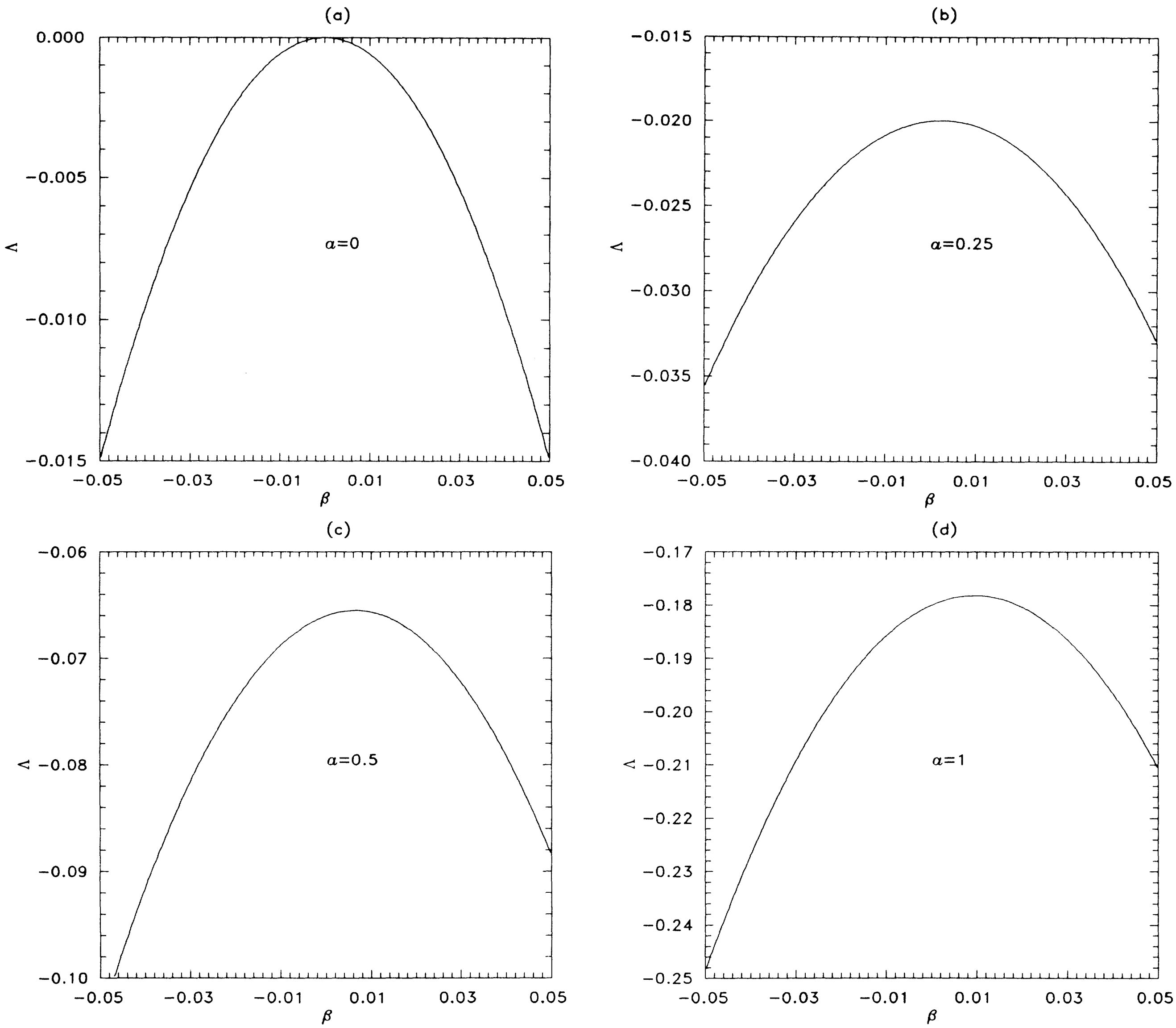

FIG. 3. The phase-space compression factor Λ as a function of both a and β.

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