On the validity of a variational principle for multicomponent systems

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The validity of a variational principle for nonequilibrium steady states proposed by Evans and Baranyai [Phys. Rev. Lett. **67**, 2597 (1991)] is investigated in the case of a dilute binary mixture described by the well-known Groos–Krook kinetic model. We construct a perturbation solution around the unconstrained shear flow state and evaluate the phase-space compression factor, the temperature ratios, and the nonlinear shear viscosity up to the first-order approximation. All these quantities are nonlinear functions of the shear rate and the parameters of the mixture (particle masses, concentrations, and force constants). It is shown that this principle does not hold exactly, although deviations from it are small in some situations for not very large shear rates. The calculations presented here extend previous results derived for a single dilute gas. © *1997 American Institute of Physics.* [S0021-9606(97)50231-5]

I. INTRODUCTION

The development of a general theory for far from equilibrium states is a fundamental and long standing problem in statistical mechanics. Only in the case of near equilibrium states does the well-established principle of minimum entropy production[1] provide a criterion to characterize such situations. Beyond the linear regime, where local thermodynamic equilibrium is broken down, much less is known and the search for a general principle still remains open. A few years ago, Evans and Baranyai (EB)[2] proposed a nonlinear generalization of the minimum entropy production principle. The EB principle states that, subject to the externally imposed constraints, the rate of change of the volume of space phase is a local minimum. Evans and Baranyai did not give any proof of their principle, but provided support for the conjecture on the basis of computer-simulation data for a thermostatted *single* fluid under uniform shear flow. The EB principle has also been shown to be related to a well-known macroscopic nonequilibrium entropy definition.[3] Afterward, Brey, Santos, and Garzó found that exact solutions of the BGK[4] and Boltzmann[5] equations did not *exactly* verify the principle. More specifically, and in the case of the nonlinear Boltzmann equation,[5] the EB principle holds only in the first order of the shear rate so that it has the same range of validity as the minimum entropy production principle. Nevertheless, so far all numerical studies[6] carried out using nonequilibrium molecular dynamics simulations have confirmed that this principle is at least a good approximation.

Very recently, Baranyai and Cummings[7] proposed a new molecular dynamics algorithm capable of modeling phase coexistence between two nonequilibrium steady state phases, which can be constituted by different components. In order to test their algorithm, they use the EB variational principle and apply their results to simple model mixtures. Given that this principle has only been analyzed in the case of a single gas, it is a subject of interest to investigate its range of validity for multicomponent systems. This is the main goal of this paper, in which we will consider a binary mixture in the low density regime. It must be emphasized that the extension of our previous results[4,5] to mixtures is not trivial at all since now the properties of the system not only depend on the shear rate, but also on parameters characterizing the mixture, such as the mass ratios, the molar fractions, and/or the size ratios. Unfortunately, due to the complexity of the problem, the task cannot be carried out analytically using the Boltzmann equation. For this reason, here we start from the well-known Gross–Krook (GK) kinetic model for a binary mixture.[8] The reliability of the GK model in the case of (unconstrained) uniform shear flow has been recently shown.[9]

The plan of the paper is as follows. In Sec. II we give a brief summary of the results obtained from the GK equation for uniform shear flow. Section III is concerned with analysis of the EB principle. By performing a perturbation expansion around the uniform shear flow, we obtain explicit expressions for the phase-space compression factor, the temperature ratio, and the shear viscosity coefficient up to first order in the expansion parameter. These quantities are nonlinear functions of the shear rate and parameters of the mixture (mass ratio, concentration ratio, and force constant ratios). Analysis again shows that the EB variational principle is *not* verified far from equilibrium, although it can be seen as a good approximation in several limit cases for not too large shear rates. In Sec. IV, we close the paper with some concluding remarks.

II. UNIFORM SHEAR FLOW FOR A BINARY MIXTURE

Let us consider a dilute binary mixture. In terms of the velocity distribution function $f_s(\mathbf{r},\mathbf{v};t)$ of species $s(s \equiv 1,2)$, the number density and mean velocity of species s are defined, respectively, as

$$n_s = \int d\mathbf{v} f_s, \tag{1}$$

$$\mathbf{u}_s = \frac{1}{n_s} \int d\mathbf{v} \mathbf{v} f_s. \tag{2}$$

These quantities define the total number density $n = n_1 + n_2$ and the flow velocity $\mathbf{u} = (\rho_1\mathbf{u}_1 + \rho_2\mathbf{u}_2)/\rho$, where $\rho_s = m_s n_s$ is the mass density of species s, m_s is the mass of a particle of species s, and $\rho = \rho_1 + \rho_2$ is the total mass density. It is usual to define a local ''temperature'' for each species through

$$\frac{3}{2}\, n_s k_B T_s = \frac{m_s}{2}\int d\mathbf{v}(\mathbf{v} - \mathbf{u}_s)^2 f_s,\tag{3}$$

which is related to the mean kinetic energy of each species. Here, k_B is the Boltzmann constant. From these partial temperatures, the temperature of the mixture T (which is the relevant one at a hydrodynamic level) is

$$n k_B T = \sum_{s=1}^{2}(n_s k_B T_s + \tfrac{1}{3}\rho_s(\mathbf{u}_s - \mathbf{u})^2).\tag{4}$$

In the uniform shear flow state, the only nonzero hydrodynamic gradient corresponds to the x component of the flow velocities along the y direction:

$$u_{s,i} = u_i = a_{ij}r_j, \quad a_{ij} = a\,\delta_{ix}\delta_{jy},\tag{5}$$

a being the constant shear rate. Since no mutual diffusion appears in the system, the only nonequilibrium parameter (which may be arbitrarily large) is the shear rate. The uniform shear flow state is not stationary since the temperature grows in time due to viscous heating. In order to prevent this effect, it is usual in computer experiments to introduce external forces which remove the heat at the same rate as it is produced. The simplest choice (which is based on Gauss' principle of least constraint) is a nonconservative force proportional to the peculiar velocity $V_i = v_i - a_{ij}r_j$, i.e.,[10]

$$\mathbf{F}_s = -m_s\alpha\mathbf{V},\tag{6}$$

where the thermostat parameter α is adjusted to maintain the temperature constant. In addition, the uniform shear flow becomes spatially homogeneous in the frame moving with the flow velocity $\mathbf{u}$. Thus in this frame the velocity distribution function adopts the form $f_s(\mathbf{r},\mathbf{v}) = f_s(\mathbf{V})$.

Exact expressions for the rheological properties (which are related to the second-degree velocity moments) of a binary mixture of Maxwell molecules described by the Boltzmann equation and under uniform shear flow have been recently obtained.[11] Nevertheless, no explicit expressions for higher-degree velocity moments are known. In particular, as we will see below, the fourth-degree moments are necessary to analyze the validity of the EB principle. Consequently, in order to overcome such limitation one needs to resort to simplified kinetic models. Perhaps, in the case of binary mixtures, the most widely used is the model proposed by Gross and Krook (GK).[8] In this model, the Boltzmann collision integrals $J_{rs}[f_r,f_s]$ are replaced by terms of the form

$$J_{rs}^{\text{GK}}[f_r,f_s] = -\nu_{rs}(f_r - f_{rs}),\tag{7}$$

where for the uniform shear flow problem f_{rs} is

$$f_{rs} = n_r\left(\frac{m_r}{2k_B T_{rs}}\right)^{3/2}\exp\left[-\frac{m_r}{2k_B T_{rs}}\mathbf{V}^2\right]\tag{8}$$

with

$$T_{rs} = T_r + 2\frac{m_r m_s}{(m_r + m_s)^2}(T_s - T_r).\tag{9}$$

Here, ν_{rs} is a velocity independent collision frequency given by

$$\nu_{rs} = A n_s\left(\kappa_{rs}\frac{m_r + m_s}{m_r m_s}\right)^{1/2},\tag{10}$$

where $A = 4\pi\times 0.422$. The quantities T_{rs} and ν_{rs} are determined by imposing that the total momentum and energy are conserved and that the first five collisional moments as computed with Eq. (7) be the same as those computed with the exact $J_{rs}[f_r,f_s]$ for Maxwell molecules. Although the GK model can be extended to general repulsive interactions,[12] for the sake of concreteness we will restrict ourselves to Maxwell molecules.

Under the conditions of the shear flow state, the velocity distribution function f_1 verifies the kinetic equation

$$-\frac{\partial}{\partial V_i}(a_{ij}V_j + \alpha V_i)f_1 = -\nu_{11}(f_1 - f_{11}) - \nu_{12}(f_1 - f_{12})\tag{11}$$

and a similar equation holds for f_2. From these coupled equations one may obtain the reduced velocity moments corresponding to each species. They are defined as

$$M_{k,l,m} = \frac{1}{n_1}\left(\frac{2k_B T}{m_1}\right)^{-\frac{1}{2}(k+l+m)}\int d\mathbf{V}V_x^k V_y^l V_z^m f_1(\mathbf{V}),\tag{12}$$

$$N_{k,l,m} = \frac{1}{n_2}\left(\frac{2k_B T}{m_2}\right)^{-\frac{1}{2}(k+l+m)}\int d\mathbf{V}V_x^k V_y^l V_z^m f_2(\mathbf{V}).\tag{13}$$

Very recently, explicit expressions of these moments have been obtained.[9] The only nonvanishing moments correspond to $k+l$ and m even, in which case one gets

$$M_{k,l,m} = \pi^{-3/2}\sum_{q=0}^{k}\frac{k!}{(k-q)!}(-a)^q$$
$$\times[\nu_1 + (k+l+m)\alpha]^{-(1+q)}$$
$$\times C_{k-q}C_{l+q}C_m[\nu_{11}\chi_1^{(k+l+m)/2} + \nu_{12}\chi_{12}^{(k+l+m)/2}],\tag{14}$$

where $C_k = \Gamma((k+1)/2)$,

$$\chi_1 \equiv \frac{T_1}{T} = \left[1 + \frac{3\alpha(\nu_1 + 2\alpha)^2 - a^2\nu_1}{M\nu_{12}(1+\delta)[3(\nu_1 + 2\alpha)^2 + 2a^2]}\right]^{-1},\tag{15}$$

$\nu_1 = \nu_{11} + \nu_{12}$, $\nu_{11} = w_{11}^{1/2}(\delta/(1+\delta))\sqrt{2/(1+\mu)}$, $\nu_{12} = 1/(1+\delta)$, $M \equiv \mu/(1+\mu)^2$, and $\chi_{12} \equiv T_{12}/T = \chi_1 + 2M(1+\delta)(1-\chi_1)$. In these expressions, $\mu \equiv m_1/m_2$ is the mass ratio, $\delta \equiv n_1/n_2$ is the concentration ratio, and $w_{11} \equiv \kappa_{11}/\kappa_{12}$. The thermostat parameter α is the largest root of a sixth-degree algebraic equation with coefficients depending on the parameters of the problem (see the Appendix).[9] Notice that in Eq. (14) we have taken $\tau = (n_2/n)\nu_{12}^{-1}$ as the time unit so

that a, α, and the collision frequencies ν_{rs} are now dimensionless quantities. Henceforth, we will take this time unit in our calculations. The moments $N_{k,l,m}$ can be easily obtained from Eq. (14) by the adequate changes: $\mu \leftrightarrow \mu^{-1}$, $\delta \leftrightarrow \delta^{-1}$, $w_{11} \leftrightarrow w_{22}$. The shear rate dependence of the second-degree moments[9] presents a reasonably good agreement with the one obtained from the Boltzmann equation.[11] This fact shows the reliability of the GK model for computing transport properties in a binary mixture far from equilibrium. Since all the velocity moments of the (unconstrained) shear flow problem are known, we are in a condition to investigate the EB principle. This will be done in the next section.

III. ANALYSIS OF THE EB PRINCIPLE IN DILUTE BINARY MIXTURES

Let us assume that we perturb the uniform shear flow described before by introducing an extra nonconservative external force

$$\mathscr{F}_{s,i} = -m_s \beta V_i^3 \quad (s=1,2) \quad (i=x,y,z). \tag{16}$$

This force is introduced to explore the verification of the EB principle. The parameter β is adjusted to get a prescribed value of the fourth moment, which will be taken as the endogenous variable. The EB principle refers to the phase-space compression factor Λ, which in general is proportional to the thermostating multiplicator α. In reduced units it is given by[2]

$$\Lambda(a,\beta) = -(\alpha(a,\beta) + \tfrac{3}{2}\beta). \tag{17}$$

According to the EB principle, Λ must have a maximum in absence of constraints on the endogenous variable, namely, at $\beta=0$. This implies that

$$\lambda(a) \equiv \left(\frac{\partial \Lambda}{\partial \beta} \right)_{\beta=0} = 0, \tag{18}$$

for arbitrary shear rates.

The purpose of this work is to evaluate $\lambda(a)$ from the GK kinetic model. In the constrained shear flow problem, the steady GK equation for f_1 reads

$$-a_{ij}V_j \frac{\partial}{\partial V_i} f_1 - \frac{\partial}{\partial V_i}(\alpha V_i + \beta V_i^3) f_1$$
$$= -\nu_{11}(f_1 - f_{11}) - \nu_{12}(f_1 - f_{12}), \tag{19}$$

while a similar equation applies for f_2. In the following we will focus on the properties of species 1. Multiplying both sides of Eq. (19) by $V_x^k V_y^l V_z^m$ and integrating over the velocity space, one gets the hierarchy

$$R_{k,l,m} - \nu_1 M_{k,l,m} = akM_{k-1,l+1,m} + \alpha(k+l+m)M_{k,l,m}$$
$$+ \beta(kM_{k+2,l,m} + lM_{k,l+2,m}$$
$$+ mM_{k,l,m+2}), \tag{20}$$

where the moments $M_{k,l,m}$ are given by Eq. (14) and we have introduced the quantity

$$R_{k,l,m} = \pi^{-3/2} C_k C_l C_m [\nu_{11} \chi_{11}^{(k+l+m)/2} + \nu_{12} \chi_{12}^{(k+l+m)/2}]. \tag{21}$$

In Eq. (20) it is assumed that $M_{k,l,m}$ is identically zero when any of its indices is negative. For arbitrary values of β, the above hierarchy is not closed and cannot be solved. However, in order to compute $\lambda(a)$ only small values of β need to be considered. Consequently, we shall carry out a perturbation expansion around the unconstrained shear flow state by taking β as the perturbation parameter. Therefore, we write

$$\alpha = \alpha_0 + \beta\alpha_1 + \cdots, \tag{22}$$

$$\chi_s = \chi_s^{(0)} + \beta\chi_s^{(1)} + \cdots, \tag{23}$$

$$M_{k,l,m} = M_{k,l,m}^{(0)} + \beta M_{k,l,m}^{(1)} + \cdots. \tag{24}$$

The coefficients in these expansions are nonlinear functions of the shear rate and the parameters of the mixture. Inserting these expansions into Eq. (20), one gets a set of hierarchies (one for each order in β) that can be recursively solved. Here, we will restrict ourselves to the two first approximations. The zeroth-order approximation corresponds to the shear flow solution described in Sec. II, where the moments $M^{(0)}$ are given by Eq. (14) and α_0 is related to the shear rate through Eq. (A11).

In the first-order approximation, one has the hierarchy:

$$R_{k,l,m}^{(1)} - \nu_1 M_{k,l,m}^{(1)} = akM_{k-1,l+1,m}^{(1)} + \alpha_0(k+l+m)M_{k,l,m}^{(1)}$$
$$+ kM_{k+2,l,m}^{(0)} + lM_{k,l+2,m}^{(0)} + mM_{k,l,m+2}^{(0)}$$
$$+ \alpha_1(k+l+m)M_{k,l,m}^{(0)}, \tag{25}$$

where

$$R_{k,l,m}^{(1)} = \pi^{-3/2} C_k C_l C_m \frac{k+l+m}{2} \left[\nu_{11} \chi_1^{(0)k+l+m/2} \frac{\chi_1^{(1)}}{\chi_1^{(0)}} \right.$$
$$\left. + \nu_{12} \chi_{12}^{(0)k+l+m/2} \frac{\chi_{12}^{(1)}}{\chi_{12}^{(0)}} \right]. \tag{26}$$

The solution of Eq. (25) can be written as

$$M_{k,l,m}^{(1)} = \sum_{q=0}^{k} \frac{k!}{(k-q)!} (-a)^q [\nu_1 + (k+l+m)\alpha_0]^{-(1+q)}$$
$$\times S_{k-q,l+q,m}, \tag{27}$$

where

$$S_{k,l,m} = R_{k,l,m}^{(1)} - kM_{k+2,l,m}^{(0)} - lM_{k,l+2,m}^{(0)} - mM_{k,l,m+2}^{(0)}$$
$$- (k+l+m)\alpha_1 M_{k,l,m}^{(0)}. \tag{28}$$

Equation (28) is still a formal expression as we do not know the shear rate dependence of α_1 and $\chi_1^{(1)}$. These quantities can be obtained from the consistency conditions:

$$\tfrac{3}{2}\chi_1^{(1)} = M_{200}^{(1)} + M_{020}^{(1)} + M_{002}^{(1)}, \tag{29}$$

$$\tfrac{3}{2}\chi_2^{(1)} = N_{200}^{(1)} + N_{020}^{(1)} + N_{002}^{(1)}, \tag{30}$$

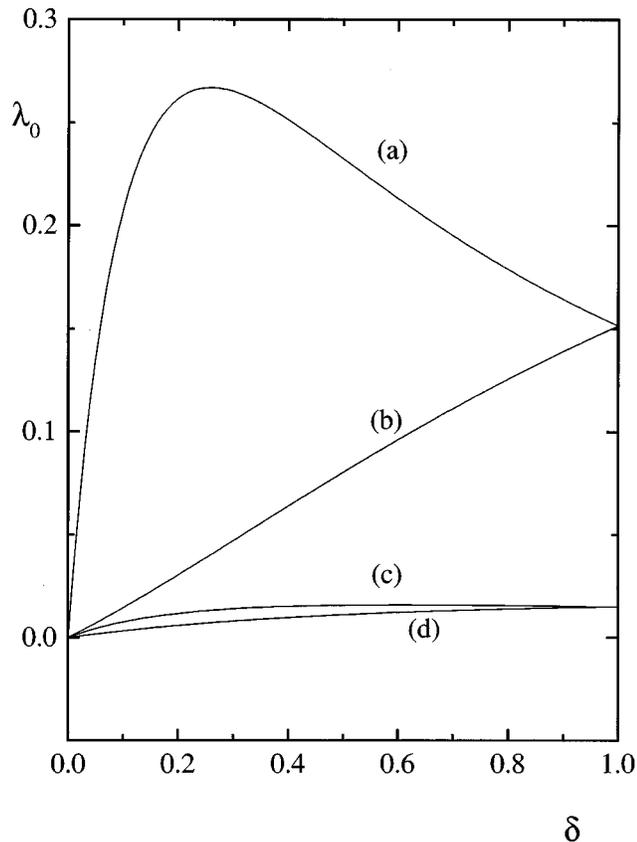$$\delta\chi_1^{(1)} + \chi_2^{(1)} = 0. \tag{31}$$

FIG. 1. Plot of the coefficient λ_0 as a function of the concentration ratio for $w_{11}=w_{22}=1$ and (a) $\mu=0.1$, (b) $\mu=10$, (c) $\mu=0.5$, and (d) $\mu=2$.

FIG. 2. Shear rate dependence of λ for $w_{11}=w_{22}=1$, and several values of δ and μ: (a) $\delta=0.1$, $\mu=0.1$; (b) $\delta=1$, $\mu=2$; (c) $\mu=1$; (d) $\delta=0.1$, $\mu=10$.

The solution of these equations provides, after a tedious but straightforward algebra, an explicit expression for α_1. From it one can compute λ as

$$\lambda = -(\alpha_1 + \tfrac{3}{2}). \tag{32}$$

The expression of α_1 is given in the Appendix in terms of the second- and fourth-degree moments corresponding to $f_1^{(0)}$ and $f_2^{(0)}$. By substituting the shear rate dependence of these recently derived moments,[9] it turns out that λ is different from zero for all nonvanishing values of the shear rate. In particular, in the limit of small shear rates

$$\lambda \approx \frac{2\delta}{\nu_1^2 \nu_2^2} \frac{(\nu_1 - \nu_2)^2}{(1+\delta)^2} a^2 \equiv \lambda_0 a^2. \tag{33}$$

Consequently, in general, the EB principle is only verified in the linear regime (Navier–Stokes approximation). Nevertheless, there can be some limit cases for which the Burnett coefficient λ_0 is zero or very small. Thus in the case of mechanically equivalent particles ($\mu=1$, and $\kappa_{11}=\kappa_{22}=\kappa_{12}=1$ so that $\nu_1=\nu_2=1$), $\lambda_0=0$. As a matter of fact, $\lambda \approx (31/3)a^4$, according to the results derived in Ref. 4. Since λ_0 depends in a nontrivial way on the parameters of the mixture, in Fig. 1 we plot this coefficient as a function of the concentration ratio for several values of the mass ratio. For the sake of clarity, we have assumed that $\delta \leqslant 1$ and we have set $w_{11}=w_{22}=1$. The corresponding behavior for $\delta>1$ can be easily inferred. We observe that λ_0 goes to zero
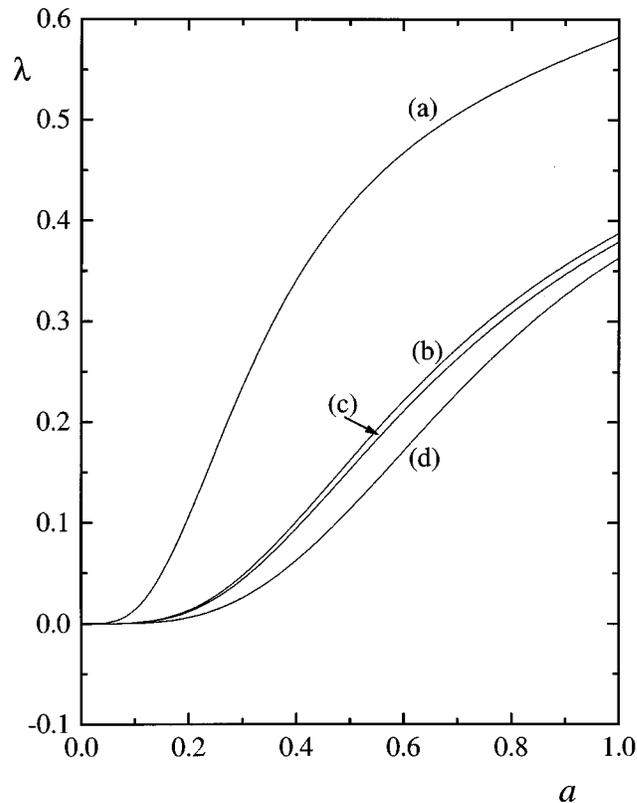
as the mass ratio goes to one and/or as the concentration ratio goes to zero (tracer limit). In addition, at a given value of δ, λ_0 is smaller for $\mu>1$ than for $1/\mu<1$. For instance, at $\delta=0.1$, $\lambda_0 \approx 0.014$ for $\mu=10$, while $\lambda_0 \approx 0.21$ for $\mu=0.1$. The behavior of λ_0 is indicative of what happens for finite shear rates. In Fig. 2, we show λ as a function of the shear rate for several values of μ and δ. In general, this coefficient monotonically increases with a. We see that the accuracy of the EB principle increases as the concentration ratio tends to zero, especially when the tracer particles are heavier than the bath particles. Furthermore, since for $\mu=1$, λ is independent of δ, the above conditions ($\mu>1$ and $\delta\leqslant1$) lead to a deviation from the EB principle smaller than that previously found in the case of identical particles.[4] For instance, for shear rates up to $a \simeq 0.3$ (for which the shear viscosity of the mixture with $\mu=10$ and $\delta=0.1$ is about 1.1 times smaller than its limiting zero shear rate value), λ is smaller than 0.03. In this sense, the EB principle can be considered as an excellent approximation in this region. Obviously, for larger values of a the discrepancies are more significant.

Apart from investigating the EB principle, it is interesting to study the β dependence of the main transport properties of the mixture, namely, the temperature ratios (which is a measure of the failure of the equipartition theorem far from equilibrium) and the nonlinear shear viscosity η. This coefficient is the most relevant physical quantity characterizing the nonequilibrium behavior of the mixture. It is defined as
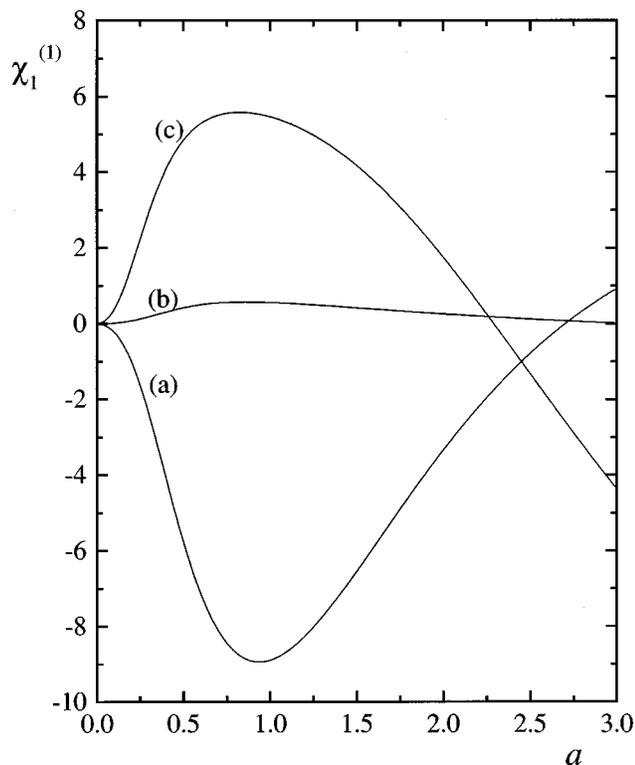
FIG. 3. Shear rate dependence of $\chi_1^{(1)}$ for $w_{11}=w_{22}=1$, $\delta=0.5$ and several values of μ: (a) $\mu=10$; (b) $\mu=0.5$; (c) $\mu=0.1$.

FIG. 4. Shear rate dependence of η_1 for $w_{11}=w_{22}=1$, $\delta=0.5$ and several values of μ: (a) $\mu=0.1$; (b) $\mu=0.5$; (c) $\mu=1$; (d) $\mu=10$.

$$\eta = -\frac{2nk_BT}{\tau a}\frac{1}{1+\delta}(M_{110}\delta+N_{110}). \tag{34}$$

Up to first order in β, both quantities can be written as

$$\chi_1 = \chi_1^{(0)}+\beta\chi_1^{(1)}, \tag{35}$$

$$\eta = \frac{1}{1+\delta}\frac{\nu_1+\delta\nu_2}{\nu_1\nu_2}\frac{nk_BT}{\tau}(\eta_0+\beta\eta_1), \tag{36}$$

where η_0 is the (reduced) unconstrained nonlinear shear viscosity.[9] The explicit expressions of the coefficients $\chi_1^{(1)}$ and η_1 are also given in the Appendix. In Figs. 3 and 4 we plot the shear rate dependence of $\chi_1^{(1)}$ and η_1, respectively, for $\delta=0.5$ and several values of μ. We observe that $\chi_1^{(1)}$ and η_1 do not present a monotonic behavior. In the case of comparable masses, $\chi_1^{(1)}$ is very small and is practically insensitive to the value of the shear rate. On the other hand, the shear rate dependence of η_1 is very similar for all the mass ratios considered, namely, there is a small region of shear rates for which this coefficient decreases with the shear rate while the opposite happens for larger values of a.

IV. CONCLUDING REMARKS

In this paper, we have analyzed a variational principle proposed a few years ago by Evans and Baranyai[2] for characterizing steady states far from equilibrium. The EB principle states that the phase-space compression factor Λ is a local maximum with respect to variations in endogeneous variables. Although this conjecture has not been proved, all
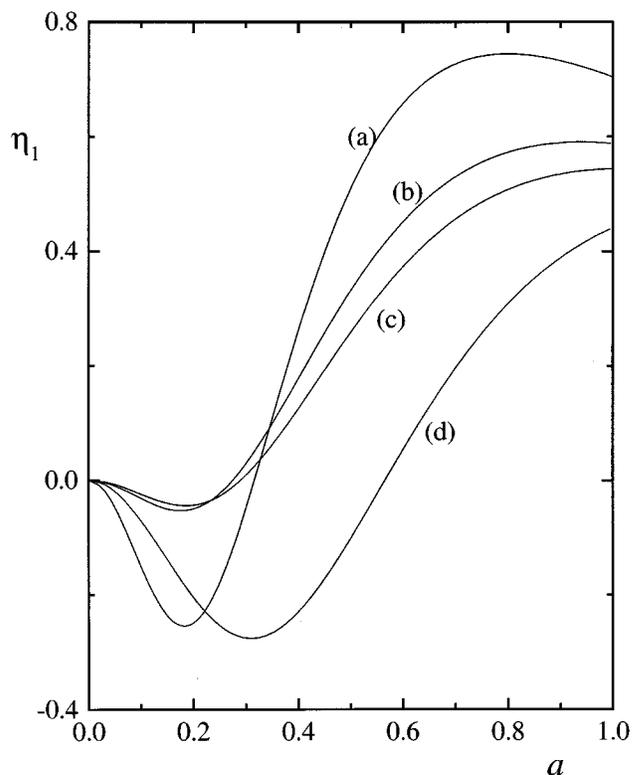
numerical studies performed for single fluids under thermostatted shear flow[6] have supported this principle. In this sense, very recently Baranyai and Cummings[7] have used the principle for testing a new algorithm capable of simulating a two-phase two-component system. Since no theoretical proof of the EB principle for multicomponent systems has been given to date, here we have investigated the range of validity of such principle using kinetic theory methods. This requires the knowledge of explicit expressions for the properties of the mixture that is far from equilibrium, which is an unapproachable problem except in particular cases. One of them is a low density gas. For this reason, we have used the well-known nonlinear GK kinetic model for a dilute binary mixture. The present work extends our previous results derived for a dilute single gas in the context of the BGK[4] and Boltzmann equations.[5]

In order to validate the EB principle, we have considered a dilute binary mixture in a thermostatted shear flow state. In addition, a new external force, characterized by a parameter β, is introduced to fix the fourth moment. The EB principle implies that $\Lambda(a,\beta)$ must have a maximum at $\beta=0$ for arbitrary values of the shear rate a. Since only small values of β need to be considered to check this hypothesis, here we have constructed a perturbation solution of the GK equation in powers of β around the unconstrained shear flow state. The main feature of this expansion is that the successive approximations are nonlinear functions of a and the parameters of the mixture (mass ratio, concentration ratio, and force constant ratios). In the zeroth-order approximation (β

=0), one recovers recent results[9] obtained for a binary mixture under uniform shear flow. The general expressions derived in the first-order solution indicate that, in the same manner as in previous results,[4,5] the EB principle does not apply exactly. Nevertheless, when the shear rate is not very large, this principle may be at least an accurate approximation in some particular situations; more specifically, in systems of like particles and/or in the tracer limit, when the mass of the defect component is larger than that of the excess component. Under these circumstances, the EB principle can be considered as a good approximation and consequently, it provides an excellent criterion for testing molecular dynamics algorithms. Otherwise, the accuracy of this principle in the nonlinear regime is in doubt. Apart from analyzing the EB principle, we have studied the β dependence of the relevant quantities of the mixture: the temperature ratio and the shear viscosity coefficient. We have shown that the effect of β on these properties is more noticeable than on the phase-space compression factor.

Since the results presented here have been obtained from a model kinetic equation, it could be that the disagreement with the EB principle is due to the inadequacies of the model. Nevertheless, and according to the previous results derived for a single dilute gas,[4,5] one expects that similar conclusions could be given from the set of coupled Boltzmann equations. Finally, as Baranyai and Cummings[7] claim, it must be noticed that the thermostats of our theoretical model and of the computer experiments are *slightly* different. The EB principle was proposed for a generalized microcanical ensemble, where, in addition to the volume, internal energy, and number of particles, the external shear rate is also fixed. In our description, since microcanonical and canonical ensembles are identical in the low density regime, we use a constant thermostat variable. However, we think that, at a qualitatively level, this subtlety does not drastically change the main conclusions reported here. Anyway, it is true that the significance of such difference is still an open question.

ACKNOWLEDGMENTS

APPENDIX: EXPLICIT EXPRESSIONS OF SOME QUANTITIES

In this Appendix we list the expressions of the main quantities appearing in the first-order approximation, namely, α_1, $\chi_1^{(1)}$, and η_1. The coefficient α_1 can be written as

$$\alpha_1 = \frac{Aa^4 + Ba^2 + C}{Da^4 + Ea^2 + F}, \tag{A1}$$

where

$$A = \delta(2M - \nu_2)\left[2M_{040}^{(0)} - (2\alpha_0 + \nu_1)\frac{M_{130}^{(0)} + M_{310}^{(0)}}{a}\right]$$
$$+ (2M - \nu_1)\left[2N_{040}^{(0)} - (2\alpha_0 + \nu_2)\frac{N_{130}^{(0)} + N_{310}^{(0)}}{a}\right], \tag{A2}$$

$$B = 2\delta M_{040}^{(0)}G + 2N_{040}^{(0)}H + \delta(2M - \nu_2)(2\alpha_0 + \nu_1)^2 M_{400}^{(0)}$$
$$+ (2M - \nu_1)(2\alpha_0 + \nu_2)^2 N_{400}^{(0)} - 3(\alpha_0 + M)(2\alpha_0 + \nu_1)$$
$$\times (2\alpha_0 + \nu_2)\left[\delta\frac{M_{130}^{(0)} + M_{310}^{(0)}}{a}(2\alpha_0 + \nu_2)\right.$$
$$\left. + \frac{N_{130}^{(0)} + N_{310}^{(0)}}{a}(2\alpha_0 + \nu_1)\right], \tag{A3}$$

$$C = 3(\alpha_0 + M)(2\alpha_0 + \nu_1)^2(2\alpha_0 + \nu_2)^2[\delta(M_{400}^{(0)}$$
$$+ 2M_{040}^{(0)}) + N_{400}^{(0)} + 2N_{040}^{(0)}], \tag{A4}$$

$$D = 2\delta(\nu_2 - 2M)\left[M_{020}^{(0)} - (2\alpha_0 + \nu_1)\frac{M_{110}^{(0)}}{a}\right] + 2(\nu_1$$
$$- 2M)\left[N_{020}^{(0)} - (2\alpha_0 + \nu_2)\frac{N_{110}^{(0)}}{a}\right], \tag{A5}$$

$$E = \delta(\nu_2 - 2M)(2\alpha_0 + \nu_1)^2 M_{200}^{(0)} + (\nu_1 - 2M)$$
$$\times (2\alpha_0 + \nu_2)^2 N_{200}^{(0)} - 2\delta M_{020}^{(0)}G$$
$$- 2N_{020}^{(0)}H + 6(\alpha_0 + M)$$
$$\times (2\alpha_0 + \nu_1)(2\alpha_0 + \nu_2)\left[\delta\frac{M_{110}^{(0)}}{a}(2\alpha_0 + \nu_2) + \frac{N_{110}^{(0)}}{a}\right.$$
$$\left. \times (2\alpha_0 + \nu_1)\right], \tag{A6}$$

$$F = -\tfrac{9}{2}(\alpha_0 + M)(2\alpha_0 + \nu_1)^2(2\alpha_0 + \nu_2)^2(1 + \delta). \tag{A7}$$

Here, we have introduced the quantities

$$G = 12\alpha_0^3 + 4\alpha_0^2(5M + 2\nu_2) + \alpha_0[4M(2\nu_1 + 3\nu_2)$$
$$+ \nu_2(3\nu_2 - 4\nu_1)] + M(2\nu_1^2 + 3\nu_2^2) - \nu_1^2\nu_2, \tag{A8}$$

and H is defined from G by the adequate change of indices ($\nu_1 \leftrightarrow \nu_2$). The coefficients $\chi_1^{(1)}$ and η_1 are given by

$$\chi_1^{(1)} = -\frac{2}{a^2(2M - \nu_1) + 3(\alpha_0 + M)(\nu_1 + 2\alpha_0)^2}$$
$$\times\left[2a^2(M_{040}^{(0)} + \alpha_1 M_{020}^{(0)}) - a(2\alpha_0 + \nu_1)(2\alpha_1 M_{110}^{(0)}\right.$$
$$+ M_{130}^{(0)} + M_{310}^{(0)}) + (2\alpha_0 + \nu_1)^2$$
$$\left.\times\left(\frac{3}{2}\alpha_1\chi_1^{(0)} + 2M_{040}^{(0)} + M_{400}^{(0)}\right)\right], \tag{A9}$$

$$\eta_1 = -\frac{2\nu_1\nu_2}{(\nu_1+\delta\nu_2)(\nu_1+2\alpha_0)^2(\nu_2+2\alpha_0)^2}\left[2\delta(2\alpha_0+\nu_2)^2(\alpha_1 M_{020}^{(0)}+M_{040}^{(0)})+2(2\alpha_0+\nu_1)^2(\alpha_1 N_{020}^{(0)}+N_{040}^{(0)})\right.$$

$$-\frac{2}{a}\delta(2\alpha_0+\nu_2)^2(2\alpha_0+\nu_1)(2\alpha_1 M_{110}^{(0)}+M_{310}^{(0)}+M_{130}^{(0)})-\frac{2}{a}(2\alpha_0+\nu_1)^2(2\alpha_0+\nu_2)$$

$$\times(2\alpha_1 N_{110}^{(0)}+N_{310}^{(0)}+N_{130}^{(0)})+\chi_1^{(1)}\delta(\nu_2-\nu_1)\left[M(4\alpha_0+\nu_1+\nu_2)+\frac{1}{2}(4\alpha_0^2-\nu_1\nu_2)\right]\Bigg]. \tag{A10}$$

When $\mu=1$, $\chi_1^{(1)}=0$, the expressions of α_1 and ν_1 reduce to the ones previously derived from the BGK model.[4] According to Eqs. (A1), (A9), and (A10), the coefficients α_1, $\chi_1^{(1)}$ and η_1 are given in terms of the thermostat α_0 and the unconstrained second-and fourth-degree moments. Expressions of these moments can be easily obtained from Eq. (14) and its corresponding counterpart. As stated in Sec. II, the parameter α_0 can be numerically obtained as a function of the shear rate by solving a sixth-degree algebraic equation. However, from a practical point of view it is convenient to take α_0 as independent variable (instead of a) and express explicitly all the unknowns as functions of α_0. In particular, the relationship between a^2 and α_0 is[9]

$$a^2=-\tfrac{1}{2}(P+\sqrt{P^2-4Q}), \tag{A11}$$

where

$$P=\frac{3}{\nu_1\nu_2(1+\delta)-2M(\delta\nu_1+\nu_2)}\left[4\alpha_0^3(1+\delta)(2M-\nu_1-\nu_2)+4\alpha_0^2[M(\delta\nu_1+\nu_2)-2\nu_1\nu_2(1+\delta)]\right.$$

$$\left.+\alpha_0[2M(\delta\nu_1^2+\nu_2^2)-4M\nu_1\nu_2(1+\delta)-\nu_1\nu_2(\nu_1+\nu_2)(1+\delta)]-M\nu_1\nu_2(\nu_1+\delta\nu_2)\right], \tag{A12}$$

$$Q=\frac{9\alpha_0(1+\delta)(\alpha_0+M)(2\alpha_0+\nu_1)^2(2\alpha_0+\nu_2)^2}{\nu_1\nu_2(1+\delta)-2M(\delta\nu_1+\nu_2)}. \tag{A13}$$

Finally, the behaviors of $\chi_1^{(1)}$ and η_1 in the limit of small shear rates are

$$\chi_1^{(1)}\approx\frac{\nu_1-\nu_2}{2M^2\nu_1^2\nu_2^2(1+\delta)^2}\left[\delta(4M-\nu_2)\nu_1+(4M-\nu_1)\nu_2\right]a^2, \tag{A14}$$

$$\eta_1\approx\frac{1}{\nu_1^3\nu_2^3 M(\nu_1+\delta\nu_2)(1+\delta)^2}\Big\{(1/2M)\delta(\nu_1-\nu_2)^2[\delta(4M-\nu_2)\nu_1+(4M-\nu_1)\nu_2][2(\nu_1+\nu_2)M-\nu_1\nu_2]$$

$$-M(3\delta^3\nu_2^4+\delta^2[\nu_1^2(13\nu_1^2-10\nu_1\nu_2-8\nu_2^2)+\nu_2^2(6\nu_1\nu_2+8\nu_2^2)]+\delta[\nu_1^2(8\nu_1^2+6\nu_1\nu_2)$$

$$-\nu_2^2(8\nu_1^2+10\nu_1\nu_2-13\nu_2^2)]+3\nu_1^4)+2\delta(1+\delta)\nu_1\nu_2(\nu_1-\nu_2)^2(\nu_1+\nu_2)\Big\}a^2. \tag{A15}$$

In these expressions, use has been made of the behaviors

$$\alpha_0\approx\frac{\delta\nu_2+\nu_1}{3(1+\delta)\nu_1\nu_2}a^2, \tag{A16}$$

$$\chi_1^{(0)}\approx\frac{\nu_1-\nu_2}{3M(1+\delta)\nu_1\nu_2}a^2. \tag{A17}$$

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