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Non-equilibrium phase transition in a binary mixture

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Abstract. – A non-equilibrium phase transition is identified from an exact solution of the Boltzmann equation describing a binary mixture under shear flow in the tracer limit ($n_1/n_2 \ll 1$): there exists a critical value a_c (which depends on the mass ratio m_1/m_2 and the force constant ratios) of the shear rate such that $\lim_{n_1/n_2\to 0} E_1/E = 0$ for $a < a_\mathrm{c}$ (disordered phase), while $\lim_{n_1/n_2\to 0} E_1/E \neq 0$ for $a > a_\mathrm{c}$ (ordered phase), where E_1/E is the relative contribution of the tracer species to the total energy. This phase transition is absent when m_1/m_2 is sufficiently large and/or the strength of the interactions 2-2 is sufficiently larger than that of 1-2.

The study of the properties of tracer particles immersed in a medium is a subject of great interest. For instance, passive tracer particles are used to monitor the characteristics of porous-media flows [1]. The so-called Milne problem, which deals with the diffusion of test particles through a background species, has applications in fields such as radiation-transfer problems [2], neutron transport theory [3], and rarefied-gas dynamics [4]. The diffusion of a tagged particle in a concentrated colloidal suspension can also be regarded essentially as a tracer problem [5].

Since the tracer limit corresponds to a situation in which the molar fraction $x_1 = n_1/n$ of the tracer species is negligible, one expects that the properties of the medium are not affected by the presence of the tracer particles. Let us consider the relative contribution of the tracer particles to the total energy of the system, E_1/E. At equilibrium, equipartition of energy implies that $E_1/E = x_1$, so that E_1/E goes to zero in the tracer limit. Out of equilibrium, the natural expectation is that $E_1/E \sim x_1$ when $x_1 \ll 1$ and, consequently, the contribution of the tracer species to the total energy is negligible. In this letter we present an example of a violation of the above expectation. There exists a *critical* value a_c of the non-equilibrium control parameter a, such that $\lim_{x_1\to 0} E_1/E = 0$ for $a < a_\mathrm{c}$ ("disordered" phase), while $\lim_{x_1\to 0} E_1/E \neq 0$ for $a > a_\mathrm{c}$ ("ordered" phase).

The system considered here consists of a gaseous binary mixture under shear flow. The only hydrodynamic gradient is that of the flow velocity: $\partial u_i/\partial r_j = a\delta_{ix}\delta_{jy}$, a being the constant shear rate, which is the relevant non-equilibrium parameter of the problem. The main transport property is the non-linear shear viscosity η, which is a function of the shear rate and also of the parameters of the mixture, namely the mass ratio $\mu \equiv m_1/m_2$, the molar fraction ratio $\nu \equiv n_1/n_2$, and the size ratio. The energy ratio is also an important property and depends on the same parameters. Very recently, an *exact* solution of the set of two coupled Boltzmann equations has been derived in the case of Maxwell molecules (*i.e.* an interaction potential $V_{rs} = \kappa_{rs} r^{-4}$) [6]. In this work we are going to analyse in detail what happens in the tracer limit ($\nu \to 0$).

In ref. [6] it was proved that the time evolution of the relevant second-degree velocity moments is governed by a linear homogeneous set of 6 coupled first-order differential equations with constant coefficients. The general solution is given in terms of the roots of the sixth-degree characteristic polynomial with coefficients depending on a and $\boldsymbol{\xi} \equiv \{\mu, \nu, \gamma_{11} \equiv [(\kappa_{11}/2\kappa_{12})(1+\mu)]^{1/2}, \gamma_{22} \equiv [(\kappa_{22}/2\kappa_{12})(1+\mu)/\mu]^{1/2}\}$. For long times, the dominant behaviour is described by the two real roots, α and α'. In particular, the energy ratio is of the form

$$\frac{E_1}{E} = \frac{AF(\alpha, a, \boldsymbol{\xi}) + BF(\alpha', a, \boldsymbol{\xi}) \exp[-2(\alpha - \alpha')t]}{A + B\exp[-2(\alpha - \alpha')t]}, \tag{1}$$

where A and B are constants depending on the initial conditions and the function F is the ratio of a 4×4 determinant and a 5×5 determinant, whose explicit expression can be found in the appendix of ref. [6]. After a relaxation time of the order of $|\alpha - \alpha'|^{-1}$, the energy ratio E_1/E reaches a steady-state value $F(\alpha_{\max}, a, \boldsymbol{\xi})$, where $\alpha_{\max}(a, \boldsymbol{\xi}) = \max(\alpha, \alpha')$. As long as $\nu \neq 0$, one has $\alpha \neq \alpha'$ for any value of the shear rate and $\boldsymbol{\xi}$. If $\nu \to 0$, the sixth-degree equation for α and α' decouples into two cubic equations, whose real solutions are $\alpha_0 = \tau_{22}^{-1}\varphi(a\tau_{22})$, $\alpha_0' = [(1+\mu)^2\tau_{12}/2]^{-1}[\varphi(a(1+\mu)^2\tau_{12}/2) - \mu\zeta]$, where $\varphi(x) \equiv \frac{2}{3}\sinh^2[\frac{1}{6}\cosh^{-1}(1+9x^2)]$ and $\zeta \simeq 0.648$. In the above equations, $\tau_{rs} \propto n_s^{-1}[\kappa_{rs}(m_r + m_s)/m_r m_s]^{-1/2}$ is an effective mean free time of a particle of species r for collisions with particles of species s. In particular, $\tau_{12}/\tau_{21} = \nu$ and $\tau_{12}/\tau_{22} = [(2\kappa_{22}/\kappa_{12})\mu/(1+\mu)]^{1/2}$. Henceforth, we take τ_{22} as unit of time. It can be easily seen that, for a given choice of the force constants, $\alpha_{\max} = \alpha_0$ if μ is larger than a certain threshold value $\mu_{\rm th}$, which is the solution of $\tau_{12}(\mu) = 2/(1+\mu)^2$. On the other hand, if $\mu < \mu_{\rm th}$, $\alpha_{\max} = \alpha_0'$ for shear rates larger than a critical value $a_{\rm c}(\mu)$. The μ-dependence of $a_{\rm c}$ is shown in fig. 1 for three choices of the force constants. The critical shear rate goes to infinity both when μ goes to 0 and to $\mu_{\rm th}$. As a consequence, there exists a minimum value for $a_{\rm c}$ that depends on the choice of the force constants. The threshold mass ratio $\mu_{\rm th}$ is smaller than 1 in the three cases of fig. 1, but it can be larger than 1 if κ_{12} is sufficiently larger than κ_{22}.

Let us discuss the physical consequences of the existence of $a_{\rm c}(\mu)$. If $\nu \ll 1$, the function $F(\alpha, a, \boldsymbol{\xi})$ becomes

$$F(\alpha, a, \boldsymbol{\xi}) \approx \nu \frac{D(\alpha, a)}{\Delta_0(\alpha, a) + \Delta_1(\alpha, a)\nu}, \tag{2}$$

where the dependence on μ, γ_{11}, and γ_{22} is implicitly assumed on the right-hand side. The general expressions of D, Δ_0, and Δ_1 are too lengthy to be written down here. For the sake of illustration, we give their expressions for the case $\mu = \frac{1}{2}$ and $\gamma_{11} = \gamma_{22} = 1$:

$$D(\alpha, a) = 2\zeta(2\alpha+1)^2(3\alpha+2\zeta+2)^2 + [6(\alpha-\zeta)^2 - (2\zeta-1)(\zeta-2)]a^2, \tag{3}$$

$$\Delta_0(\alpha, a) = (2\alpha+1)^2[(3\alpha+2\zeta)(3\alpha+2\zeta+2)^2 - 3a^2], \tag{4}$$

$$\Delta_1(\alpha, a) = (2\zeta-1)\Big[2(2\alpha+1)(3\alpha+2\zeta)(3\alpha+2\zeta+2) - a^2\Big(6\alpha+2\zeta+\frac{3}{2}\Big)\Big]. \tag{5}$$

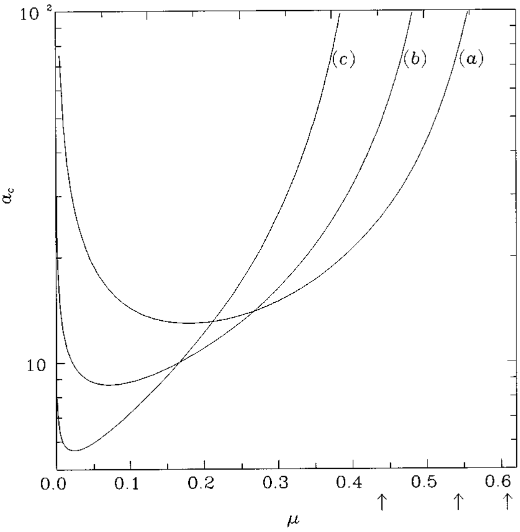

Fig. 1.

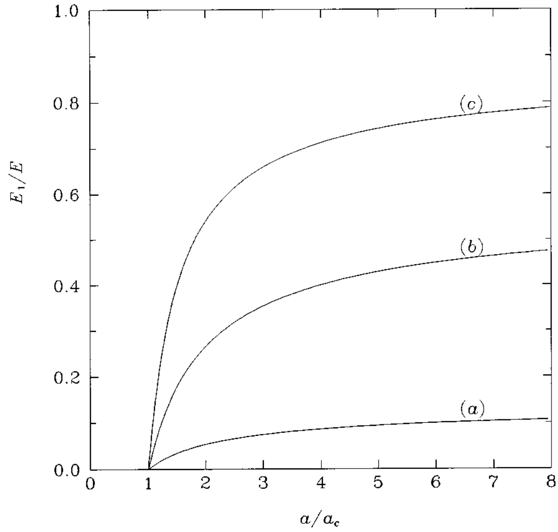

Fig. 2.

Fig. 1. – Plot of a_c as a function of μ for three choices of the force constant ratios: *a*) $\gamma_{22} = 1$, *b*) $\kappa_{12} = \kappa_{22}$, and *c*) $\kappa_{rs} \propto (m_r m_s)^{1/2}$. The arrows indicate the location of the corresponding threshold values $\mu_{\rm th}$.

Fig. 2. – Plot of the order parameter E_1/E *vs.* a/a_c in the tracer limit ($\nu \to 0$) for $\kappa_{11} = \kappa_{12} = \kappa_{22}$ and several values of μ: *a*) $\mu = 0.5$, *b*) $\mu = 0.3$, and *c*) $\mu = 0.1$.

Equations (2)-(5) hold for α as well as for α'. Furthermore, α and α' are still functions of a and ν: $\alpha(a,\nu) \approx \alpha_0(a) + \alpha_1(a)\nu$ and a similar relation for $\alpha'(a,\nu)$ holds. Here we omit the explicit expressions of α_1 and α'_1. By taking the tracer limit in eq. (2), one gets

$$\lim_{\nu\to 0} \frac{1}{\nu} F(\alpha(a,\nu), a, \nu) = \frac{D(\alpha_0(a), a)}{\Delta_0(\alpha_0(a), a)}, \tag{6a}$$

$$\lim_{\nu\to 0} F(\alpha'(a,\nu), a, \nu) = \frac{D(\alpha'_0(a), a)}{\Delta_{01}(a) + \Delta_1(\alpha'_0(a), a)} \equiv F_0(a), \tag{6b}$$

where $\Delta_{01}(a) \equiv \alpha'_1(a)\,(\partial\Delta_0(\alpha,a)/\partial\alpha)\,|_{\alpha=\alpha'_0(a)}$. In eq. (6*b*), use has been made of the fact that $\Delta_0(\alpha'_0(a), a) = 0$. If $\alpha_{\max} = \alpha_0$, the right-hand side of eq. (6*a*) is the temperature ratio T_1/T, where T_1 is a partial "temperature" measuring the mean kinetic energy per tracer particle. This ratio was first obtained in an analysis of tracer diffusion under shear flow [7]. On the other hand, if $\alpha_{\max} = \alpha'_0$, the temperature ratio diverges to infinity and the energy ratio becomes finite. Therefore, $\lim_{\nu\to 0} E_1/E = F_0(a)$ if $\mu < \mu_{\rm th}$ and $a > a_c(\mu)$, being zero otherwise. This shows that a qualitatively different behaviour is found in the tracer limit depending on whether the control parameter a is larger or smaller than a_c. As a approaches a_c from above, $\alpha'_1(a) \sim (a - a_c)^{-1}$, so that $F_0(a) \sim (a - a_c)$. By borrowing the usual terminology of equilibrium phase transitions [8], one can identify the energy ratio E_1/E as an "order" parameter. If $a < a_c(\mu)$, the system evolves in time towards a "disordered" phase, for which $E_1/E = 0$. On the other hand, if $a > a_c(\mu)$, the system tends to an "ordered" phase, where $E_1/E \neq 0$. The phase transition at $a = a_c(\mu)$ only takes place if the mass ratio is smaller than the threshold value $\mu_{\rm th}$. Figure 1 can then be interpreted as a phase diagram: the points lying above the curve $a_c(\mu)$ represent states belonging to an ordered phase. The remaining points correspond to a disordered phase. In fig. 2 we plot the order parameter *vs.* a/a_c for several values of μ in the case $\kappa_{11} = \kappa_{12} = \kappa_{22}$. The fact that the order parameter goes to zero when $a - a_c \to 0^+$ indicates that the transition is of second order. We observe that the order parameter for a given value of $a/a_c > 1$ increases as the mass ratio decreases. For large shear rates, E_1/E tends to the asymptotic value $\{1 + \mu/[1 - (1 + \mu)^2\tau_{12}/2]\}^{-1}$. Thus, the tracer contribution to the total energy can be even larger than that of the excess component.

It is tempting to consider an analogy with the transition in a ferromagnetic system. In this sense, the shear rate a plays the role of the (inverse) temperature, the energy ratio E_1/E plays the role of the magnetization, and the density ratio ν plays the role of the external magnetic field. By exploiting the above analogy, one can define the following critical exponents [8]: $E_1/E \sim \nu^{1/\delta}$, $a = a_c$; $E_1/E \sim (a - a_c)^\beta$, $\nu = 0$; $\partial(E_1/E)/\partial\nu \sim |a - a_c|^{-\gamma}$, $\nu = 0$. Near the critical point, the "equation of state" has the form $E_1/E \approx K(a - a_c) + [K^2(a - a_c)^2 + K'\nu]^{1/2}$, K and K' being positive constants. Consequently, $\delta = 2$, $\beta = 1$, $\gamma = 1$. This equation is consistent with a Landau free energy $\Phi(a - a_c, \nu; E_1/E) = -\nu(E_1/E) - (K/K')(a - a_c)(E_1/E)^2 + (1/3K')(E_1/E)^3$. It is interesting to remark that when $\tau_{12} \geq 2/(1 + \mu)^2$, the critical value a_c becomes infinite and the phase transition disappears. In this case, the system is analogous to a paramagnetic system.

In summary, we have analysed the tracer limit of an exact solution [6] of the Boltzmann equation for a binary mixture of Maxwell molecules under shear flow. This solution applies to arbitrary values of the shear rate a and the parameters of the mixture, namely the molar fraction ratio $\nu \equiv n_1/n_2$, the mass ratio $\mu \equiv m_1/m_2$, and the force constant ratios κ_{22}/κ_{12} and κ_{11}/κ_{12}. Quite surprisingly, the relative contribution of the tracer species to the total properties of the mixture does not tend to zero as $\nu \to 0$ when the system is sufficiently far from equilibrium. That happens for shear rates larger than a *critical* value a_c, which depends on the mass and force constant ratios. The value of a_c becomes infinite if μ and/or κ_{22}/κ_{12} are sufficiently large.

In this problem, the shearing motion induces viscous heating and, consequently, the temperature increases in time. To compensate for this effect, a thermostat external force is usually introduced. It is important to notice that in the special case of Maxwell molecules an exact equivalence between the solutions of the Boltzmann equation with and without a thermostat exists [6]. In order to understand the physical origin of the phenomenon studied in this letter, it is useful to interpret α_0 as the thermostat parameter needed to get a stationary value for the temperature T_2 of the excess component. This parameter scales with the collision frequency τ_{22}^{-1}. The tracer particles are subjected to two competing effects. On the one hand, T_1 tends to increase in time due to viscous heating. On the other hand, the collisions with the excess particles tend to approximate T_1 to T_2. Analogously to α_0, α_0' (that scales with τ_{12}^{-1}) may also be interpreted as the minimum value of the thermostat parameter that is necessary to get a stationary value of T_1. Thus, if $\alpha_0 < \alpha_0'$, T_1/T_2 grows infinitely in time. This situation occurs if $\tau_{12} < 2\tau_{22}/(1 + \mu)^2$ and the shear rate is large enough (*i.e.* $a > a_c$). Although the temperature ratio T_1/T_2 goes to infinity when $\alpha_0 < \alpha_0'$, the *energy* ratio E_1/E_2 reaches a finite value.

The different qualitative behaviour of the system depending on whether $a < a_c$ or $a > a_c$ can be interpreted as a (second-order) non-equilibrium phase transition. Below (above) the critical shear rate, the ordered (disordered) phase is unstable, the relaxation time going to infinity at criticality. In equilibrium critical phenomena [8], the appearance of an order parameter is associated with a broken symmetry. The natural question is: which symmetry is broken in our problem? Near equilibrium, E_1/E scales with ν (when ν is small), so that $\nu^{-1}E_1/E$ is *invariant* under the transformation $\nu \to \lambda\nu$. We may call this invariance property generalized equipartition of energy. This invariance is broken in the ordered phase, since the mean kinetic energy per tracer particle is very much larger than the one corresponding to the excess particles.

Usually, when one studies the tracer limit in the context of the Boltzmann equation, one assumes that the excess component 2 is not disturbed by collisions with particles of the tracer component 1 and that the self-collisions among tracer particles can be neglected [9]. Consequently, the velocity distribution functions f_2 and f_1 obey a closed Boltzmann equation and a Boltzmann-Lorentz equation, respectively. These assumptions are justified by the fact that the mean free times are well separated ($\tau_{11} \gg \tau_{12}$ and $\tau_{21} \gg \tau_{22}$) and implicitly by what we have called generalized equipartition of energy. Nevertheless, although the existence of a critical shear rate a_c can be predicted from a Boltzmann-Lorentz description [7], our results show that for $a > a_\mathrm{c}$ the above equipartition fails and, consequently, collisions of type 1-1 affect f_1 and collisions of type 2-1 affect f_2, despite being much less frequent than collisions of types 1-2 and 2-2, respectively. In this sense, the tracer problem in the ordered phase is essentially as complex as the general one in an arbitrary mixture. The strength of this phenomenon increases as m_1/m_2 or κ_{22}/κ_{12} decrease. Obviously, identical conclusions can be drawn if one considers other quantities of the system, such as the shear viscosity and the viscometric functions. In particular, if one defines an *intrinsic* shear viscosity [10] $[\eta] = \lim_{\nu\to 0}(\eta - \eta_\mathrm{s})/\eta_\mathrm{s}\nu$, where η and η_s are the shear viscosities of the mixture and the solvent, respectively, then $[\eta]$ goes to infinity when $a > a_\mathrm{c}$.

To the best of our knowledge, the phenomenon described here has not been previously reported in the literature. Since it arises from an *exact* solution of the Boltzmann equation for a binary mixture, there is no doubt about its existence. The price paid for having an exact description is the restriction to Maxwell molecules and to the low-density regime. However, we expect that the result is not an artifact but it may appear in dense systems as well as for more general interactions. The transition occurs at shear rates for which non-Newtonian effects are generally very important. For instance, if $\kappa_{11} = \kappa_{12} = \kappa_{22}$ and $m_2 = 10m_1$, the shear viscosity at a_c is about 94% smaller than its Navier-Stokes value. It is worth pointing out that when one does not consider atomic particles but mesoscopic ones, such as colloids or micelles, the shear rates required to observe non-Newtonian effects become attainable in laboratory conditions.

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