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The Nonsymmetric Pressure Tensor in Polyatomic Fluids

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Nonequilibrium molecular dynamics calculations are used to show that polyatomic fluids can support antisymmetric stress. In a homogeneous system where the time dependence of vorticity is a step function, it is shown that the rate at which intrinsic angular velocity approaches its steady-state value ($\boldsymbol{\omega} = \frac{1}{2}\nabla \times \mathbf{u}$) is determined by the magnitude of the antisymmetric part of the pressure tensor.

KEY WORDS: Molecular dynamics; antisymmetric pressure tensor; nonequilibrium; angular velocity; vorticity.

1. INTRODUCTION

In this paper we present clear evidence for the existence and hydrodynamic relevance of the antisymmetric component of the pressure tensor. We present the results of nonequilibrium molecular dynamics calculations which show that the tendency in molecular fluids for the local average angular velocity to relax to half the vorticity is governed by the magnitude of the antisymmetric part of the pressure tensor via the vortex viscosity coefficient.

Two sets of model calculations are described. The first set were performed using a realistic five-centered, exp-6 potential representing methane. This model potential developed by Williams(1) using the properties of molecular crystals, has been shown to predict equilibrium and nonequilibrium properties of methane with reasonable accuracy throughout a wide range of dense fluid conditions.(2,3) The potential energy of molecules 1, 2 (assumed to be rigid) takes the usual atom–atom form

$$U_{12} = \sum_{\alpha,\beta} U_{\alpha\beta} \tag{1}$$

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The Williams potential assumes that the potential between atom α in molecule 1 and atom β in molecule 2 is given by

$$U_{\alpha\beta} = A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{\alpha\beta}) + C_{\alpha\beta}/r_{\alpha\beta}^6 \tag{2}$$

where $r_{\alpha\beta}$ is the distance between atoms α, β. The potential parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, and $C_{\alpha\beta}$ together with the reducing parameters are given in Table I.

The second set of calculations were performed for a deliberately artificial diatomic Lennard-Jones potential. The diatomic Lennard-Jones potential is defined by

$$U_{\alpha\beta} = 4\epsilon[(\sigma/r_{\alpha\beta})^{12} - (\sigma/r_{\alpha\beta})^6] \tag{3}$$

The potential parameters were taken from the chlorine potential of Singer *et al.*(4) with a reduced bond length (= bond length/σ) of 0.630. The potential differed from that of Singer *et al.* only in that the reduced inertia tensor was 786.8 times the correct value for chlorine. The reason for deliberately making this change will become obvious later. The potential parameters and reducing units for this diatomic Lennard-Jones potential are given in Table I.

2. THEORY

The first description of the properties of a fluid with a nonsymmetric stress tensor appears to date from the work of Born(5) in 1920. Since that time numerous papers have expanded that work.[2] A brief summary of the macroscopic equations describing transport processes in dense fluids assumed to

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[2] See Refs. 6, as well as the work cited in Refs. 7, 12, and 13.

Table I. Potential Parameters

(A) Methane Interaction	$A_{\alpha\beta}^*$	$B_{\alpha\beta}^*$	$C_{\alpha\beta}^*$
$C \cdots C$	218,024.0	14.436	−0.4278
$C \cdots H$	38,744.0	14.717	−0.1084
$H \cdots H$	9,260.0	14.997	−0.0274

Reducing parameters for methane are $\sigma = 4.01$ Å, $\epsilon/k = 142.87$ K, m = molecular weight of methane = 16.043 AMU. Thus $A_{\alpha\beta}^* = A_{\alpha\beta}/\epsilon$, $B_{\alpha\beta}^* = B_{\alpha\beta}\sigma$, $C_{\alpha\beta}^* = C_{\alpha\beta}/\sigma^6$. The reduced CH bond length is 0.2559.

(B) Model diatomic

The reducing parameters are $\sigma = 3.332$ Å, ϵ/k = 178.3 K, m = 70.91 AMU

Reduced bond length $R^* = 0.63$

Reduced inertia tensor = 78.11 = 786.8 times the actual value for chlorine(4) be composed of rigid molecules obeying classical dynamics has been given by Evans and Streett.(7) That paper also gives statistical mechanical expressions for the various force/flux tensors. The pressure tensor P is defined in the usual way, relating the infinitesimal force $\mathbf{dF}$ due to nonconvective influences across the area $\mathbf{dA}$

$$\mathbf{dF} = -\mathsf{P}^T \cdot \mathbf{dA} \tag{4}$$

The superscript T denotes the transpose, which in general can be different from the tensor itself. If the local momentum density is $\rho\mathbf{u}$ and the local intrinsic angular momentum density is $\rho\mathbf{S} \equiv \rho\Theta\boldsymbol{\omega}$, where $\boldsymbol{\omega}$ is the local average angular velocity, one obtains in the usual way continuity equations for linear momentum and intrinsic angular momentum

$$\rho\, \mathbf{du}/dt + \nabla \cdot \mathsf{P} = \mathbf{0} \tag{5}$$

and

$$\rho\, d\mathbf{S}/dt + \nabla \cdot \mathsf{Q} + 2\mathbf{P}^d = \mathbf{0} \tag{6}$$

In Eq. (6) $\mathbf{P}^d$ is the vector dual of the antisymmetric part of the pressure tensor, and Q, the couple tensor, is the torque anolog of the pressure tensor. It is defined by the torque $\mathbf{d\Gamma}$ about $\mathbf{x}$ due to nonconvective influences across a surface $\mathbf{dA}$ located at $\mathbf{x}$,

$$\mathbf{d\Gamma} = -\mathsf{Q}^T \cdot \mathbf{dA} \tag{7}$$

From the form of Eq. (6) we see that intrinsic angular momentum is not conserved when the pressure tensor is nonsymmetric. In that circumstance the antisymmetric part of the pressure tensor governs the rate of exchange between the orbital, $\rho\mathbf{x} \times \mathbf{u}$, and intrinsic angular momentum densities.

If fluid properties are assumed to be isotropic, then for small departures from equilibrium the antisymmetric part of pressure tensor $\mathbf{P}^d$ satisfies the constitutive relation

$$\mathbf{P}^d = -\eta_r(\nabla \times \mathbf{u} - 2\boldsymbol{\omega}) \tag{8}$$

η_r is called the vortex viscosity and we shall use the term sprain rate to describe the thermodynamic force $\nabla \times \mathbf{u} - 2\boldsymbol{\omega}$.

In our calculations the pressure tensor was calculated from the usual expression

$$\mathsf{P} = \sum_i m(\mathbf{v}_i - \mathbf{u}(\mathbf{x}_i))(\mathbf{v}_i - \mathbf{u}(\mathbf{x}_i)) + \frac{1}{2} \sum_{i \neq j} \mathbf{R}_{ij} \frac{\partial U_{ij}}{\partial \mathbf{X}_i} \tag{9}$$

where $\mathbf{v}_i$, $\mathbf{x}_i$ denote the velocity and position of molecule i, $\mathbf{R}_{ij} = \mathbf{x}_j - \mathbf{x}_i$, and $\mathbf{u}$ is of course the stream velocity. From (9) it can be seen that if noncentral forces are present $\mathsf{P}^T \neq \mathsf{P}$, in general.

3. METHOD

Evans and Streett(7) used equilibrium molecular dynamics to calculate the vortex viscosity of liquid nitrogen. Unfortunately the Kubo–Green time correlation technique that was used(8) is very inefficient for calculating hydrodynamic transport coefficients. This, together with the smallness of vortex viscosity, meant that in spite of the 75,000 time steps, the ratio of vortex viscosity to shear viscosity could only be given as $\eta_r/\eta = 1 \times 10^{-3} \pm 1 \times 10^{-3}$! Although entropy considerations imply that both coefficients are positive, the results of the calculations were *not* inconsistent with the conjecture that vortex viscosity is zero.

The situation is made worse by the fact that, apart from liquid crystals,(11) the single experimental determination of vortex viscosity(13) is subject to fairly large errors. Although the Kubo–Green calculation provided statistically significant evidence for the existence of the time correlation function $\langle \mathbf{P}^d(0)\cdot\mathbf{P}^d(t)\rangle$, the large negative tail of this correlation function at intermediate times meant that the integral of the time correlation function, which is proportional to the zero-frequency vortex viscosity, was essentially zero.

This unsatisfactory state of affairs prompted us to use the more efficient technique of nonequilibrium molecular dynamics to calculate vortex viscosity. The idea behind nonequilibrium molecular dynamics is very simple. Instead of looking at fluctuations in an equilibrium system, one simply uses a "Maxwell demon" to create a nonequilibrium disturbance in the system and then uses either the constitutive relations or the Navier–Stokes equations to calculate the required transport coefficient.

The technique was originally devised by Ashurst and Hoover,(9) who detailed many of the ground rules that need to be observed in using the method. The particular algorithms used here are modifications of the "homogeneous shear algorithm" developed by Ashurst and Hoover to calculate shear viscosity. The details of our modifications and improvements to the technique as applied to shear viscosity have been described elsewhere.(3)

In our first set of calculations we calculated the vortex viscosity of methane using Eq. (8). To establish a steady homogeneous sprain rate, $\nabla \times \mathbf{u} - 2\boldsymbol{\omega}$ was calculated at each time step in the program. In general $\nabla \times \mathbf{u} - 2\boldsymbol{\omega} \neq \mathbf{k}s$, where $\mathbf{k}s$ is the desired sprain rate. To ensure that the observed and desired sprain rates are equal, the angular velocities of every molecule were altered so that, whatever the value of the vorticity, the average angular velocity satisfied the equation

$$\boldsymbol{\omega} = \tfrac{1}{2}[\nabla \times \mathbf{u} - \mathbf{k}s] \tag{10}$$

Because the process is dissipative, thermostats were applied to the translational degrees of freedom so that, in a similar way, the translational temperature at every time step was equal to the desired value. For the sprain rates induced in these calculations the trajectory changes caused by the "Maxwell demon" were relatively small, as evidenced by the fact that in the worst case (the highest sprain rates) the temperature was stable to within 6%.

In other respects the program was the same as the normal equilibrium molecular dynamics program used in Ref. 2 and developed by Evans and Murad.(10) The program uses quaternions to represent orientations, ensuring a singularity-free set of equations of motion. Normal orthogonal periodic boundaries were used.

For the second set of calculations with the diatomic Lennard-Jones potential the homogeneous shear algorithm described in Ref. 3 was employed. Time-varying oblique periodic boundaries were used in conjunction with a least squares procedure to guarantee a homogeneous linear velocity profile

$$\mathbf{u} = \mathbf{a} + \mathbf{b}\mathbf{x} \tag{11}$$

where **a** is a constant (usually zero), **x** denotes position, and **b** is the strain rate tensor

$$\nabla\mathbf{u} = \mathbf{b} = \begin{pmatrix} 0 & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{12}$$

We shall refer to γ as the strain rate. For this set of calculations thermostats were applied to the rotational degrees of freedom. Because the molecules were idealized diatomics, each molecule has one degree of freedom fewer than in methane. Slight changes were therefore necessary to the quaternion equations of motion. The modified equations of motion were

$$d\omega_{pxi}/dt = \Gamma_{pxi/I}, \qquad d\omega_{pyi}/dt = \Gamma_{pyi/I} \tag{13}$$

$$\frac{d}{dt}\begin{pmatrix} \xi \\ \eta \\ \zeta \\ \chi \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} -\zeta & -\chi & \eta & \xi \\ \chi & -\zeta & -\xi & \eta \\ \xi & \eta & \chi & \zeta \\ -\eta & \xi & -\zeta & \chi \end{pmatrix} \cdot \begin{pmatrix} \omega_{px} \\ \omega_{py} \\ 0 \\ 0 \end{pmatrix} \tag{14}$$

In these equations ω_{pxi}, ω_{pyi}, Γ_{pxi}, and Γ_{pyi} are the principal components of angular velocity and torque for molecule i. Here I is the moment of inertia and ξ, η, ζ, and χ are the usual quaternions.(10) This set of six first-order differential equations is the minimum number of equations per molecule that are required for a singularity-free algorithm.

4. Results

Table II shows the results of seven 2000-time-step calculations of the vortex viscosity of methane. For two different state conditions Table II

Table II. Vortex Viscosity Results for CH_4

T^*	ρ^*	$\nabla^* \times \mathbf{u}^* - 2\boldsymbol{\omega}^*$	$\eta_r \times 10^7$	$\eta \times 10^4$ (14)	$\eta_r^* \times 10^4$	Estimated uncertainty, %
2.0	0.7	11.92	3.19	3.49	7.07	10
2.0	0.7	7.94	3.24	3.49	7.20	10
2.0	0.7	4.00	3.92	3.49	8.70	14
2.0	0.7	7.94	—	—	$(8.66 - i1.94)$	[a]
2.0	0.9	11.91	5.99	—	13.3	10
2.0	0.9	7.97	8.10	—	18.2	10
2.0	0.9	3.99	5.72	—	12.7	14

[a] Special calculation at reduced frequency of 20.0.

shows the dependence of the effective vortex viscosity coefficient upon the sprain rate. From the tabulated values we see that at $T^* = 2.0$, $\rho^* = 0.7$ (which corresponds to a temperature and density of 285.7 K, 18.03 moles/liter) $\eta_r^* = 9.0 \pm 1.2 \times 10^{-4}$, while at $T^* = 2.0$, $\rho^* = 0.9$ (corresponding to a density of 23.18 moles/liter) $\eta_r^* = 1.4 \pm 0.2 \times 10^{-3}$.

In contrast with the 75,000-time-step Kubo–Green calculations for nitrogen,(7) these two runs of effectively 6000 time steps yielded results which were, statistically speaking, significantly different from zero. At a reduced density of 0.7 the ratio $\eta_r/\eta = (1.7 \pm 0.16) \times 10^{-3}$. This has the same order of magnitude as the nitrogen calculations.(7) We also see that vortex viscosity is a rapidly increasing function of density. A 30% increase in density is observed to produce 56% increase in vortex viscosity.

Table II also shows the results of a single calculation of the frequency-dependent vortex viscosity. This calculation was performed in a way entirely analogous to the recently developed method for shear viscosity.(3) It can be seen that within estimated uncertainties the real part of the frequency-dependent vortex viscosity is the same as the zero-frequency value. This is in dramatic contrast to the corresponding situation for shear viscosity, where for the same state condition, the ratio of the real part of the shear viscosity at a reduced frequency of 20.0 to the zero-frequency shear viscosity is 0.58.(3) This rapid decrease of shear viscosity with frequency is due to the $t^{-3/2}$ long-time tail. This produces a strong, $\omega^{1/2}$ cusp at zero frequency. Apparently vortex viscosity has a much weaker long-time tail, if it has one at all.

Although the methane calculations demonstrate conclusively that the pressure tensor can be nonsymmetric and that it is a linear function of the sprain rate (within numerical uncertainties), we felt that a check on the hydrodynamic consequences of the nonsymmetric pressure tensor would be desirable. The technique of molecular dynamics places severe limitations on the types of hydrodynamic flow that can be studied.

One of the predictions of the generalized hydrodynamics of polyatomic fluids is that if $\nabla\boldsymbol{\omega}$ is zero, then(7)

$$\frac{d\boldsymbol{\omega}}{dt} = -\frac{2\eta_r}{\rho\Theta}(2\boldsymbol{\omega} - \nabla \times \mathbf{u}) \tag{15}$$

Furthermore, if we prepare a system where $\boldsymbol{\omega} = \mathbf{0}$ at time zero and then we apply a constant vorticity, the intrinsic angular velocity is

$$\boldsymbol{\omega} = \tfrac{1}{2}\nabla \times \mathbf{u}(1 - e^{-t/\tau}) \tag{16}$$

where $\tau = \rho\Theta/4\eta_r$. The periodic boundary conditions used in computer simulations mean that it is impossible to produce a homogeneous flow field where $\nabla \times \mathbf{u}$ is a constant and the other irreducible components of $\nabla\mathbf{u}$ are zero. However, in the homogeneous shear algorithm that was used to compute the shear viscosity of methane,(3) Eq. (12) implies that as well as homogeneous shear $(\nabla^0 u)^s_{xy} = \frac{1}{2}\gamma$ the algorithm induces homogeneous vorticity $\nabla \times \mathbf{u} = -\gamma\mathbf{k}$. Unfortunately, for the strain rates γ that were accessible in Ref. 3, the antisymmetric part of the pressure tensor and the sprain rate were subject to so much noise as to make the vertification of (16) impossible.

To make a more conclusive check on the validity of (16), the following strategy was followed:

(i) Look at a diatomic system with larger anisotropy than methane.

(ii) Increase the inertia tensor of the model diatomic system to values much larger than ones observable in nature.

Although this strategy means that the results are not directly applicable to a particular system in nature, it does allow computational confirmation of the hydrodynamic consequences of the nonsymmetric pressure tensor.

As a result of (i) the computer program ran approximately five times faster than the corresponding methane program, enabling better statistics to be gathered. The increased anisotropy meant that η_r should be much larger than for the corresponding state condition in methane. The effect of increasing the inertia tensor (ii) has two desirable effects. First it counteracts the effect upon the relaxation time of increasing η_r. For Eq. (16) to be valid, τ must be much greater than the decay time of the associated Kubo–Green time correlation function, $\langle \mathbf{P}^d(0)\cdot\mathbf{P}^d(t)\rangle$. If this were not so, a time-dependent vortex viscosity would have to be substituted into (16). Second, increasing the inertia tensor decreases the variance of the local angular velocity. This was the prime reason for the failure to check Eq. (16) in methane. Methane's very small inertia tensor allows statistical fluctuations in the angular velocity which are approximately 80 times greater than the corresponding fluctuations in translational velocity.

Starting from an equilibrium state ($T^* = 1.532$, $\rho^* = 0.4610$, which corresponds to a point midway between the triple and critical points on the coexistence curve⁽⁴⁾), homogeneous shear was imposed, $\gamma^* = 0.559$, for 20,000 time steps. In the usual way the shear viscosity was calculated to be $\eta^* = 2.17 \pm 0.06$. It was observed that after the initial establishment of antisymmetric stress and sprain ($\leqslant 50$ time steps), both quantities were observed to decrease monotonically. Estimates of the vortex viscosity were made at every time step by measuring the ratio of antisymmetric stress to sprain. After averaging over the entire run, vortex viscosity was found to be $\eta_r^* = 0.078 \pm 0.019$.

By substituting this calculated value into (16), the reduced relaxation time was found to be $\tau^* = 76.6$ or 42,560 time steps. This is much longer than the correlation time of the antisymmetric stress time correlation function ($\leqslant 500$ time steps⁽⁷⁾), so that the assumption that η_r is a constant should be quite accurate.

The relaxation time τ^* was also about twice as long as the total duration of the molecular dynamics run. Thus, verification of the exponential decay of the sprain rate was not possible. The slope $d\omega/dt$ at time zero could be calculated and when substituted into (16) provided a second estimate of $\tau^* = 80.4 \pm 4.0$. The two estimates of the sprain rate relaxation time agree within numerical errors, implying that it is the antisymmetric stress that, in the absence of spatial angular velocity gradients, governs the behavior of the intrinsic angular velocity.

5. CONCLUSION

We believe that there are two main conclusions to be drawn from this work. First, a steady-state system can support antisymmetric stress. Second, in the absence of gradients in the intrinsic angular velocity, antisymmetric stress governs the behavior of intrinsic angular velocity. This has been demonstrated by verifying the behavior predicted by Eq. (16) for an admittedly unrealistic system.

For real systems such as chlorine and methane the simple behavior predicted by (16) is probably not observed, because the relaxation time τ is so fast that the use of a constant for vortex viscosity leads to errors. The reason for the use of a very large moment of inertia in our model diatomic was partly to separate the relaxation time scales sufficiently for Eq. (16) to be essentially correct. Even when these time scales are not well separated, antisymmetric stress still determines intrinsic angular velocity, but (16) may not correctly describe the process.

In earlier work we have shown that for an istropic fluid the pressure tensor is symmetric.⁽¹²⁾ That result is supported by the results given here.

During the model diatomic calculations the order parameter was calculated and found to differ significantly from an isotropic tensor. The order parameter for methane was very difficult to calculate since the first nonvanishing order tensor for methane is of hexadecapole rank. In the diatomic the normalized order parameter $\mathbf{S}^{(2)}$ defined by the equation.

$$\mathbf{S}^{(2)} = \sum_i (x_i^2 \mathsf{I} - \mathbf{x}_i\mathbf{x}_i) \Big/ \sum_i (\mathbf{x}_i^2 \mathsf{I} - \mathbf{x}_i\mathbf{x}_i)_{\text{equil}}$$

was found to differ from the isotropic Kronecker delta tensor by terms of the order of 0.025 for a reduced strain rate of 0.56.

From the parity of the sprain rate vector it is easily seen that for the symmetric order tensor defined above, sprain-induced birefringence must be quadratic in the sprain rate [i.e., $\dot{\mathbf{S}}^{(2)} \propto (\nabla \times \mathbf{u} - 2\boldsymbol{\omega})(\nabla \times \mathbf{u} - 2\boldsymbol{\omega})$]. Further investigation of flow-induced birefringence effects is continuing, but it appears that for molecules with anisotropies within the range studied here their effects are comparatively small.

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