Energy and pressure of shearing fluids at different state points

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Nonequilibrium molecular dynamics simulations are reported at different strain rates ($\dot{\gamma}$) and thermodynamic state points for a shearing atomic fluid interacting via a Lennard-Jones potential. Our simulations are performed at the Lennard-Jones triple point, a point midway between the triple point and the critical point, and a high point closer to the critical temperature. We find that, for the mid-point and high point, the energy and hydrostatic pressures have strain-rate dependencies of $\dot{\gamma}^2$, in contrast to the $\dot{\gamma}^{3/2}$ dependencies predicted by mode coupling theory. This analytical dependence is consistent with a Taylor series expansion of these quantities as powers of the strain rate tensor. Only at the triple point does the pressure and energy display a nonanalytical dependence on $\dot{\gamma}^{3/2}$.

In a recent paper [1] we reported on the analytical dependence of the pressure and energy of shearing liquid argon interacting via accurate two- and three-body potentials, as reviewed in detail elsewhere [2]. The pressure was convincingly found to vary as $\dot{\gamma}^2$. Our nonequilibrium molecular dynamics (NEMD) simulations were performed at a state point of $(\rho,T) = (1.034 \, \text{g cm}^{-3}, 135 \, \text{K})$, representative of the liquid phase of argon approximately midway between the critical point and the triple point. Further NEMD simulations on liquid xenon [3] demonstrated even more convincingly the $\dot{\gamma}^2$ dependence of both the pressure and energy. Independent work by Matin, Daivis, and Todd [4] suggested that the nonanalytical variation of the energy and pressure as a function of strain rate may be a peculiarity of the triple point, and that an analytical dependence may be observed at other state points.

NEMD simulations of atomic fluids have been overwhelmingly performed at the triple point. This is because simulations performed at higher liquid densities deliver superior statistical accuracy in all measurable quantities, but also because they have revealed interesting nonanalytical functional forms for the phenomenological constitutive relations, agreeing with predictions based on long-time tail theories [5]. Most work performed at the triple point reports a nonanalytical dependence of the energy and pressure on strain rate, in conformity with the predictions of mode coupling theory [6], i.e.,

$$E(\dot{\gamma}) = E(0) + a\dot{\gamma}^{3/2},$$
$$p(\dot{\gamma}) = p(0) + b\dot{\gamma}^{3/2}. \tag{1}$$

This result is in contrast to what one might expect from expanding the internal energy and pressure tensor as a Taylor series about the thermodynamic driving force, in this case the strain rate tensor, $\nabla \mathbf{u}$. Here $\mathbf{u}$ is the streaming velocity of the fluid. Of course, such an expansion assumes at the outset that both the energy and pressure are analytical functions of

the strain rate. If they are not, then no such expansion is possible [6,7]. For a fluid flowing in the x direction and shearing in the y direction, the strain rate tensor has only one nonzero off-diagonal term,

$$\nabla \mathbf{u} = \begin{pmatrix} \dfrac{\partial u_x}{\partial x} & \dfrac{\partial u_y}{\partial x} & \dfrac{\partial u_z}{\partial x} \\[6pt] \dfrac{\partial u_x}{\partial y} & \dfrac{\partial u_y}{\partial y} & \dfrac{\partial u_z}{\partial y} \\[6pt] \dfrac{\partial u_x}{\partial z} & \dfrac{\partial u_y}{\partial z} & \dfrac{\partial u_z}{\partial z} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{2}$$

where $\dot{\gamma} \equiv \partial u_x / \partial y$.

Now consider expanding the total internal energy of the fluid as a function of $\nabla \mathbf{u}$, and truncating at second order:

$$
\begin{aligned}
E &= E(\nabla \mathbf{u}) \\
&= E(0) + \nabla \mathbf{u} : \left. \frac{\partial E}{\partial (\nabla \mathbf{u})} \right|_{\nabla \mathbf{u} = 0} \\
&\quad + \frac{1}{2}(\nabla \mathbf{u})(\nabla \mathbf{u})(\cdot)^{[4]} \left. \frac{\partial^2 E}{\partial (\nabla \mathbf{u}) \partial (\nabla \mathbf{u})} \right|_{\nabla \mathbf{u} = 0} + \cdots,
\end{aligned} \tag{3}
$$

Here the notation $(\cdot)^{[4]}$ stands for a fourth order contraction between the two fourth rank tensors $(\nabla \mathbf{u})(\nabla \mathbf{u})$ and $[\partial^2 E / \partial (\nabla \mathbf{u}) \partial (\nabla \mathbf{u})]_{\nabla \mathbf{u} = 0}$.

The two partial derivatives in Eq. (3), $[\partial E / \partial (\nabla \mathbf{u})]_{\nabla \mathbf{u} = 0}$ and $[\partial^2 E / \partial (\nabla \mathbf{u}) \partial (\nabla \mathbf{u})]_{\nabla \mathbf{u} = 0}$, are both evaluated at zero applied thermodynamic force, i.e., at equilibrium. It is thus reasonable to assume that just as an equilibrium fluid should be isotropic in space, so too should be the phenomenological coefficient tensors that are descriptive of their material properties. This allows for some simplification of their form. As the first order partial derivative is a second rank isotropic tensor, it can be conveniently expressed as

$$\left. \frac{\partial E}{\partial (\nabla \mathbf{u})} \right|_{\nabla \mathbf{u} = 0} = a\delta_{\alpha\beta} \tag{4}$$

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where a is a constant. Thus, the second term in Eq. (3) can be written as

$$E^{(2)} \equiv \nabla\mathbf{u} : \frac{\partial E}{\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} = \nabla_\beta u_\alpha a \, \delta_{\alpha\beta} = a \nabla_\beta u_\beta = 0. \quad (5)$$

In the above derivation and subsequent derivations, we use the Einstein notation for contraction of tensor indices.

The second order partial derivative in Eq. (3) is a fourth rank isotropic tensor, which may be expanded as a linear combination of the three isotropic fourth rank polar tensors [7–9]:

$$\frac{\partial^2 E}{\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} \equiv B_{\alpha\beta\gamma\delta}$$

$$= b_1 \delta_{\alpha\beta}\delta_{\gamma\delta} + b_2 \delta_{\alpha\gamma}\delta_{\beta\delta} + b_3 \delta_{\alpha\delta}\delta_{\gamma\beta}. \quad (6)$$

Thus the third term in Eq. (3) can be written as

$$E^{(3)} \equiv \frac{1}{2} (\nabla\mathbf{u})(\nabla\mathbf{u})(\cdot)^{[4]} \frac{\partial^2 E}{\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0}$$

$$= \frac{1}{2}(\nabla_\delta u_\gamma)(\nabla_\beta u_\alpha) B_{\alpha\beta\gamma\delta}. \quad (7)$$

Substituting Eq. (6) into Eq. (7), one finds

$$E^{(3)} = \tfrac{1}{2} b_2 \dot{\gamma}^2. \quad (8)$$

Finally, substituting Eqs. (5) and (8) into Eq. (3) gives

$$E(\dot{\gamma}) = E(0) + \tfrac{1}{2} b_2 \dot{\gamma}^2. \quad (9)$$

In a similar manner, we may expand the pressure tensor as a function of powers of the strain rate tensor, and truncate at second order:

$$\mathbf{P} = \mathbf{P}(\nabla\mathbf{u}) = \mathbf{P}(0) + \nabla\mathbf{u} : \frac{\partial \mathbf{P}}{\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0}$$

$$+ \frac{1}{2}(\nabla\mathbf{u})(\nabla\mathbf{u})(\cdot)^{[4]} \frac{\partial^2 \mathbf{P}}{\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} + \cdots$$

$$= p_0\mathbf{1} + \nabla\mathbf{u} : \frac{\partial \mathbf{P}}{\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} + \frac{1}{2}(\nabla\mathbf{u})(\nabla\mathbf{u})$$

$$\times (\cdot)^{[4]} \frac{\partial^2 \mathbf{P}}{\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} + \cdots, \quad (10)$$

Here the unit tensor is defined as $\mathbf{1}$, and the equilibrium hydrostatic pressure is designated as p_0. We further note that now the second term involves a second order contraction of a second rank tensor $(\nabla\mathbf{u})$, with a fourth rank tensor, $[\partial\mathbf{P}/\partial(\nabla\mathbf{u})]_{\nabla\mathbf{u}=0}$. Similarly, the third term represents fourth order contraction of a fourth rank tensor $(\nabla\mathbf{u})(\nabla\mathbf{u})$ with a sixth rank tensor, $[\partial^2\mathbf{P}/\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})]_{\nabla\mathbf{u}=0}$. Both contractions result in second rank tensors, as required.
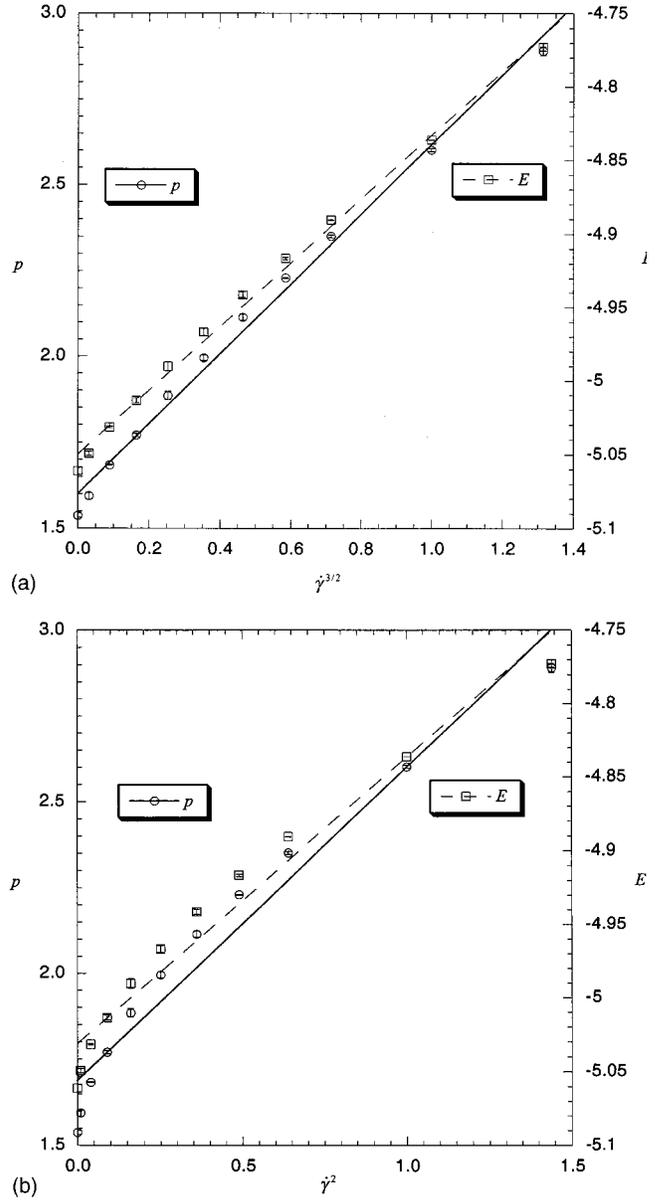

FIG. 1. Reduced pressure and energy as functions of (a) $\dot{\gamma}^{3/2}$ and (b) $\dot{\gamma}^2$ at the Lennard-Jones triple point. AAD's are 1.55% and 0.11% for the pressure and energy, respectively for (a), and 3.78% and 0.30%, respectively, for (b).

Defining the nonequilibrium part of the total pressure as $\mathbf{\Pi} \equiv \mathbf{P} - p_0\mathbf{1}$, we have

$$\mathbf{\Pi} = \nabla\mathbf{u} : \frac{\partial \mathbf{P}}{\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0}$$

$$+ \frac{1}{2}(\nabla\mathbf{u})(\nabla\mathbf{u})(\cdot)^{[4]} \frac{\partial^2 \mathbf{P}}{\partial(\nabla\mathbf{u})\partial(\nabla\mathbf{u})}\bigg|_{\nabla\mathbf{u}=0} + \cdots$$

$$\equiv \mathbf{\Pi}^{(1)} + \mathbf{\Pi}^{(2)} + \cdots. \quad (11)$$

The first order partial derivative is a fourth order isotropic

tensor, expressible as a linear combination of the three iso-tropic fourth rank polar tensors as before:

$$\frac{\partial \mathbf{P}}{\partial(\nabla \mathbf{u})}\Bigg|_{\nabla \mathbf{u}=0} \equiv B_{\alpha\beta\gamma\delta} = b_1 \delta_{\alpha\beta}\delta_{\gamma\delta} + b_2 \delta_{\alpha\gamma}\delta_{\beta\delta} + b_3 \delta_{\alpha\delta}\delta_{\gamma\beta},$$ (12)

Substituting Eq. (12) into Eq. (11), and performing the nec-

essary algebra, leads to the following simplification for the first term:

$$\mathbf{\Pi}^{(1)} = \dot{\gamma} \begin{pmatrix} 0 & b_2 & 0 \\ b_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$ (13)

The second order partial derivative in Eq. (11) is a sixth rank isotropic tensor, so it may be expressed as a linear combination of the 15 independent isotropic sixth rank tensors:

$$\frac{\partial^2 \mathbf{P}}{\partial(\nabla \mathbf{u})\partial(\nabla \mathbf{u})}\Bigg|_{\nabla \mathbf{u}=0} \equiv E_{\alpha\beta\gamma\delta\varepsilon\zeta}$$

$$= e_1 \delta_{\alpha\beta}\delta_{\gamma\varepsilon}\delta_{\delta\zeta} + e_2 \delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\varepsilon\zeta} + e_3 \delta_{\alpha\beta}\delta_{\gamma\zeta}\delta_{\delta\varepsilon} + e_4 \delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\varepsilon\zeta} + e_5 \delta_{\alpha\gamma}\delta_{\beta\varepsilon}\delta_{\delta\zeta} + e_6 \delta_{\alpha\gamma}\delta_{\beta\zeta}\delta_{\varepsilon\delta}$$

$$+ e_7 \delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\varepsilon\zeta} + e_8 \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta} + e_9 \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\varepsilon\gamma} + e_{10} \delta_{\alpha\varepsilon}\delta_{\gamma\delta}\delta_{\beta\zeta} + e_{11} \delta_{\alpha\varepsilon}\delta_{\beta\gamma}\delta_{\delta\zeta} + e_{12} \delta_{\alpha\varepsilon}\delta_{\gamma\zeta}\delta_{\beta\delta}$$

$$+ e_{13} \delta_{\alpha\zeta}\delta_{\gamma\beta}\delta_{\varepsilon\beta} + e_{14} \delta_{\alpha\zeta}\delta_{\beta\gamma}\beta_{\delta\varepsilon} + e_{15} \delta_{\alpha\zeta}\delta_{\gamma\varepsilon}\delta_{\beta\delta}.$$ (14)

Substituting Eq. (14) into Eq. (11), and performing some tedious but straightforward manipulations, lead to

$$\mathbf{\Pi}^{(2)} = \frac{1}{2}\dot{\gamma}^2 \begin{pmatrix} e_4+e_{12}+e_{15} & 0 & 0 \\ 0 & e_4+e_5+e_6 & 0 \\ 0 & 0 & e_4 \end{pmatrix}.$$ (15)

Substituting Eqs. (13) and (15) into Eq. (11) gives

$$\mathbf{\Pi} = \dot{\gamma} \begin{pmatrix} 0 & b_2 & 0 \\ b_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$+ \frac{1}{2}\dot{\gamma}^2 \begin{pmatrix} e_4+e_{12}+e_{15} & 0 & 0 \\ 0 & e_4+e_5+e_6 & 0 \\ 0 & 0 & e_4 \end{pmatrix}.$$ (16)

Thus the hydrostatic pressure is simply determined as

$$p(\dot{\gamma}) \equiv \tfrac{1}{3}\mathrm{Tr}(\mathbf{P})$$

$$= p_0 + \tfrac{1}{3}\mathrm{Tr}(\mathbf{\Pi})$$

$$= p_0 + \tfrac{1}{6}[3e_4+e_5+e_6+e_{12}+e_{15}]\dot{\gamma}^2.$$ (17)

Equations (9) and (17) show that if the energy and pressure are analytical in powers of the strain rate, then their leading terms must be $\dot{\gamma}^2$. While there are terms involving $\dot{\gamma}$ in the pressure tensor expansion, they are off-diagonal terms related to the shear stress. Indeed, the constants b_2 and b_3 are equivalent, and equal in magnitude to the shear viscosity η. Only diagonal terms contribute to the hydrostatic pressure.

Our simulations were conducted on a Lennard-Jones fluid of 500 atoms at three distinct state points: the Lennard-Jones

triple point $(T,\rho)=(0.722,0.8442)$; a point midway between the triple point and the critical point, $(T,\rho)=(0.97,0.61)$; and a high point close to the critical temperature, $(T,\rho)=(1.1,0.643)$. All units quoted are reduced.

The Lennard-Jones 12-6 interatomic potential is given as

$$\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$ (18)

The parameters ε and σ were set at 1, and a cutoff radius of half the box length was chosen.

The NEMD simulations were performed by applying the standard SLLOD equations of motion for planar shear flow [7]. A Gaussian thermostat multiplier [7] was used to keep the kinetic temperature of the fluid constant. The equations of motion were integrated with a fourth order Gear predictor-corrector scheme [10], with a reduced integration time step of 0.001. A nonequilibrium simulation trajectory is typically run for 200 000 time steps. Averages are taken over 4–5 independent trajectories, each starting at a new configuration. To equilibrate the system, each trajectory is first run without a shearing field. After the shearing field is switched on, the first 50 000 time steps of each trajectory are ignored, and the fluid is allowed to relax to a nonequilibrium steady state. Thus every pressure and energy data point represents a total run length of $(4-5)\times 200000=8\times 10^5-1\times 10^6$ time steps.

In Figs. 1(a) and 1(b) we plot the pressure and energy of the fluid at the Lennard-Jones triple point as functions of $\dot{\gamma}^{3/2}$ and $\dot{\gamma}^2$. As expected, the energy and pressure appear to be linear in $\dot{\gamma}^{3/2}$, though a close examination does suggest a slight systematic deviation from linearity. A plot of the pressure and energy as functions of $\dot{\gamma}^2$ gives very poor fits to the data. A comparison of the average absolute deviations
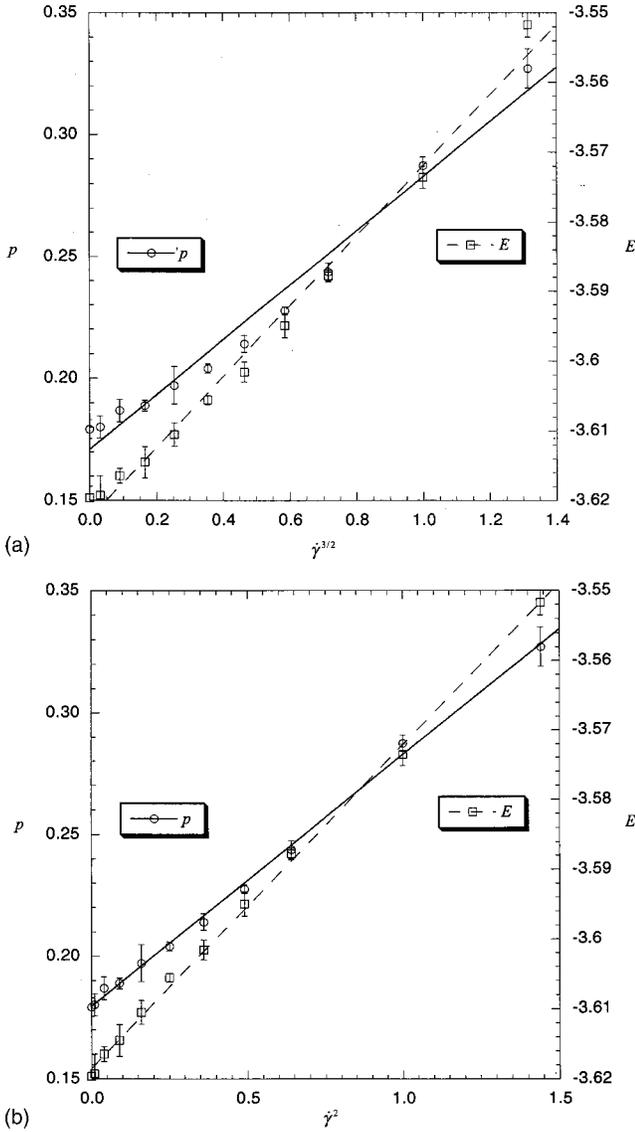
FIG. 2. Reduced pressure and energy as functions of (a) $\dot{\gamma}^{3/2}$ and (b) $\dot{\gamma}^2$ at the midpoint AADs are 2.81% and 0.05% for the pressure and energy, respectively, for (a), and 0.76% and 0.02%, respectively, for (b).
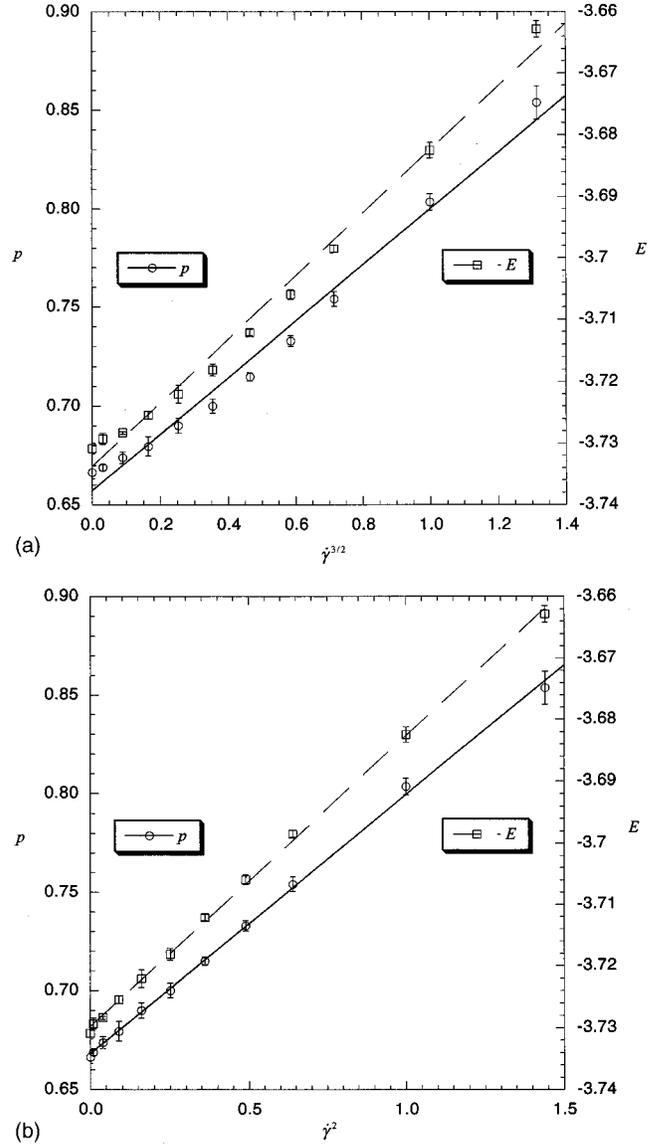

FIG. 3. Reduced pressure and energy as functions of (a) $\dot{\gamma}^{3/2}$ and (b) $\dot{\gamma}^2$ at the high point. AADs are 0.84% and 0.05% for the pressure and energy, respectively, for (a), and 0.19% and 0.01%, respectively, for (b).

(AAD) [11] for both curves demonstrates a 2–3-fold improvement in the quality of the agreement between the data and the $\dot{\gamma}^{3/2}$ fit compared to the $\dot{\gamma}^2$ fit. The lower the value of the AAD, the more faithfully the curve fits the simulation data.

In Figs. 2(a) and 2(b), we plot the pressure and energy of the fluid at the midpoint as functions of $\dot{\gamma}^{3/2}$ and $\dot{\gamma}^2$, respectively. In this case both the pressure and energy show systematic departures from linearity when plotted against $\dot{\gamma}^{3/2}$. However, when plotted against $\dot{\gamma}^2$ the fits are excellent. A comparison of the AAD's for both fits now shows that the $\dot{\gamma}^2$ curves give an almost fourfold improvement over those for $\dot{\gamma}^{3/2}$, reversing the behavior at the triple point. A similar result is also seen for the high-point data in Figs. 3(a) and 3(b). We make no comparisons on the viscosity data, as the statis-

tics are not sufficiently good to check for accurate strain rate dependencies. This work is currently in progress.

Our simulation results show a clear departure from the expected $\dot{\gamma}^{3/2}$ dependence of pressure and energy on strain rate away from the triple point. This result should be true irrespective of the type of intermolecular potential used [1], and is consistent with the suggestion made by Matin, Daivis, and Todd [4] that the $\dot{\gamma}^{3/2}$ dependence may be a peculiarity of fluids close to the triple point. Our simulations away from the triple point suggest an analytical dependence of pressure and energy on the strain rate, the leading term being $\dot{\gamma}^2$, as demonstrated by a Taylor series expansion of both quantities. While our simulations confirm the leading term in these expansions, a deeper understanding of why such a discrepancy

exists between the triple point and other state points remains elusive at this stage.

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