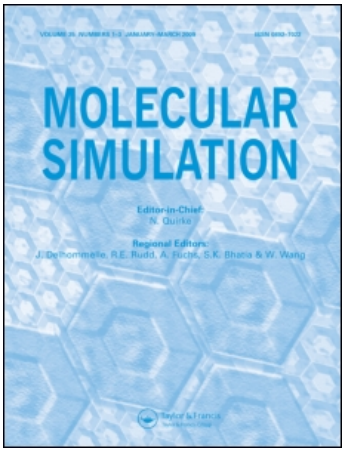

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Dynamics of Driven Systems from Newtonian to Athermal Limits

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Dynamics of Driven Systems from Newtonian to Athermal Limits

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The dynamics and properties of driven flowing systems are examined using non-equilibrium molecular dynamics (NEMD) simulations in conjunction with an energy landscape analysis. The systems are analyzed as a function of temperature and driving rate, and span the range from high temperature/low driving rate to low temperature/high driving rate. In the high temperature/low driving rate limit the dynamics are due to thermally activated transitions, while in the low temperature/high driving rate limit the dynamics are due to the external driving force. The purpose of this investigation is to link the properties of flowing thermal system (e.g. liquids and colloids) to flowing athermal systems (e.g. foams and granular materials).

Keywords: Tanning; Thermal and athermal systems; Shear flow; Energy landscapes

INTRODUCTION

Flowing systems are of obvious importance in a very wide range of situations, and this wide range of situations leads to a very different flow phenomena. For example, the flowing system may be composed of small molecules, polymers, colloidal particles, larger particles (granular materials), or foams. In some of these systems thermal motion makes important contributions to the system dynamics (e.g. molecular and colloidal liquids), while in athermal systems thermal motion is negligible (e.g. foams, granular materials and glasses).

The similarities between the dynamics of thermal systems and driven athermal systems have been an area of much recent activity [1,2]. A driving force can cause particle dynamics in athermal systems, while either thermal motion or a driving force can cause particle dynamics in thermal systems. When the driving force or temperature is reduced, thermal and athermal systems undergo jamming transitions that are characterized by the cessation of particle dynamics and flow.

The present investigation will use the energy landscape picture to address flow in thermal and athermal systems. The energy landscape govern the dynamics of the system, in that the gradient of the energy landscape determines the force on the particles, which in turn determine the dynamics [3,4,5]. When the temperature is low, the particles follow the gradient of the energy landscape to a local energy minimum, and the particles vibrate about this energy minimum until thermal motion leads the system over a saddle point to another energy minimum. As the temperature increases, the rate of transitions between energy minima increase, and at high temperatures the system moves relatively freely over the energy landscape. Changes in temperature not only change the rate of transitions between energy minima, but also the type of energy minima visited by the system. As the temperature decreases, the system visits regions of the energy landscape with deeper (lower-energy) energy minima [6].

COMPUTATIONAL METHODS

The system examined here is the widely-used binary (80–20%) Lennard–Jones mixture that prevents crystallization [7]. The Lennard–Jones parameters are ε_{ij} and σ_{ij} for interactions between atoms of type i and type j, where $\varepsilon_{22} = 0.5\varepsilon_{11}$, $\sigma_{22} = 0.88\sigma_{11}$, $\varepsilon_{12} = 1.5\varepsilon_{11}$ and $\sigma_{12} = 0.8\sigma_{11}$; the interactions are truncated at the distance of $2.5\sigma_{ij}$ (and shifted with respect to energy such that the energy is continuous).

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All of the atoms have the mass m. The following units are used throughout the paper: ε_{11} for energy, σ_{11} for length, and ε_{11}/k_B for temperature. The simulations are carried out for $N = 500$ atoms at the density $\rho = 1.2$.

Two types of simulations are carried out. First, simulations are carried out to determine the effects of shear on the energy landscape. More specifically, these simulations determine how energy minima change with applied shear strain. These simulations are carried out by incrementing the shear strain in very small steps, with energy minimizations carried out after each step. These simulations begin with an instantaneous configuration obtained from a molecular dynamics simulation at finite temperature.

Second, non-equilibrium molecular dynamics (NEMD) simulations are used to determined properties at temperature T and shear rate γ. The NEMD simulations are based on the sllod equations of motion with Less–Edwards boundary conditions and a Gaussian thermostat [8]. The simulations are run for 1–10 million NEMD steps with a time step of 0.01. An energy landscape analysis is used to characterize the region of the energy landscape visited by the system in the NEMD simulations. Energy minima visited by the systems are found with energy minimizations that begin from instantaneous configurations during the NEMD trajectory (these minimizations do not affect the NEMD trajectory); these energy minimizations are carried out at time intervals of 10–100.

RESULTS

First, we present the equilibrium properties of the system (obtained from NEMD simulations with a shear rate of zero). Equilibrium results for the average energy of the energy minima visited are shown in Fig. 1 as a function of temperature. Below

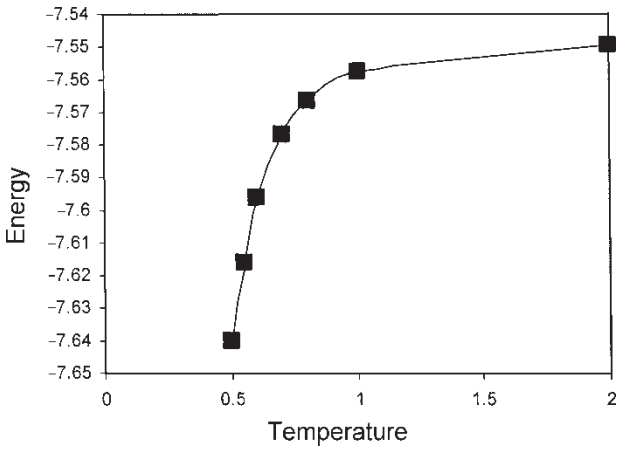

FIGURE 1 Average energy of the energy minima visited by the system during equilibrium molecular dynamics simulations.

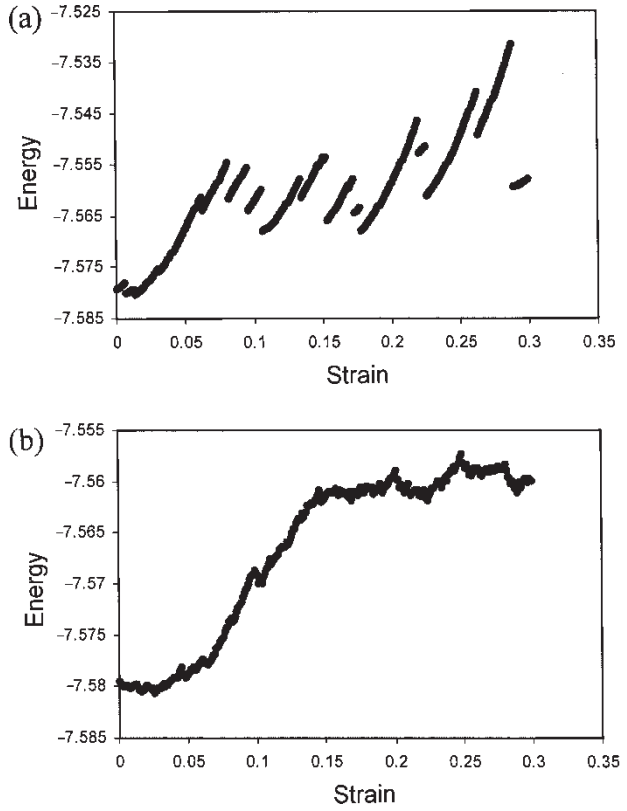

FIGURE 2 Energy of energy minima as shear strain is applied to the system (a) Results for one configuration; (b) ensemble average of results.

the glass transition temperature (approximately $T = 0.45$), equilibrium results cannot be obtained. These results are in agreement with previous simulation results by others, which show that a liquid visits different regions of the energy landscape as the temperature is reduced [6,9].

We now examine the changes in energy minima as the system is strained. We begin with configurations obtained from the equilibrium molecular dynamics simulations discussed above, at $T = 0.7$. The change in the energy at the energy minimum with shear strain is shown in Fig. 2a, for one particular starting configuration. The energy of the energy minimum usually increases continuously with strain. However, the energy increases are punctuated by discontinuous energy drops.

As we have shown previously, these changes of energy with strain are due to distortions of the energy landscape shown schematically in Fig. 3.[10,11] The important aspect of these landscape distortions are the strain-induced disappearances of energy minima; if the energy minimum that the system is in disappears, then the system will be forced to an alternate energy minimum, which leads to the discontinuous drops in energy evident in Fig. 2a. To prove that the landscape distortions shown in Fig. 3 do in fact occur, we showed that the following

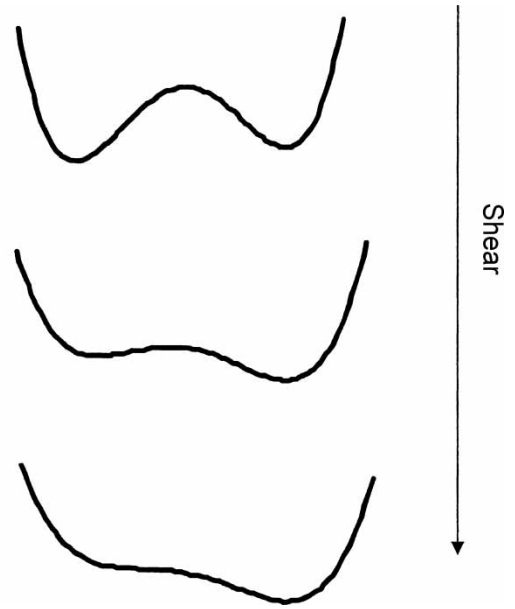

FIGURE 3 Schematic of the shear-induced distortions of the energy landscape.

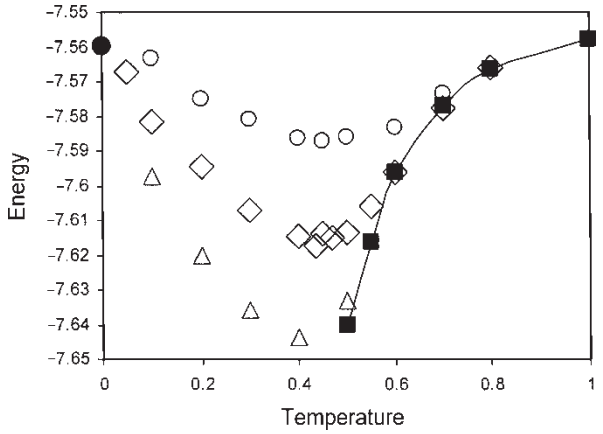

FIGURE 4 Average energy of the energy minima visited by the system. Filled squares: equilibrium molecular dynamics; Filled circle: steady state result from energy landscape analysis at zero temperature (see Fig. 2b); Open circles: NEMD, $\gamma = 0.01$; Open diamonds: NEMD, $\gamma = 0.001$; Open squares: NEMD, $\gamma = 0.0001$.

changes occur as the shear strain is incremented: (1) The curvature of the energy minimum along one dimension (i.e. a normal mode eigenvalue) decreases to zero; (2) The height of an energy barrier from this energy minimum decreases to zero; (3) The curvature of this energy barrier increases to zero; and (4) The distance between the energy minimum and the energy barrier decreases to zero [10,11].

The results for the *average* energy at the energy minimum as a function of shear strain are shown in Fig. 2b (the results in Fig. 2b are the average for an ensemble of starting configurations, while the results shown in Fig. 2a are for one particular starting configuration; all starting configurations in the ensemble are obtained from molecular dynamics simulations at $T = 0.7$). These results show that shear causes the system to leave the region of the energy landscape that the system visits at $T = 0.7$, as characterized by the energy of the energy minima. For strains greater than approximately 15%, the system reaches a steady state in the average energy of the energy minima visited; this steady state is independent of the history of the system (i.e. the temperature at which the initial configurations were obtained).

Finally, NEMD simulations are carried out at various temperature and shear rates. The results for the average energy of the energy minima visited are shown in Fig. 4, as a function of temperature and shear rate. At high temperature, the finite shear rare results coincide with the equilibrium (zero shear rate) results; note that higher temperatures are necessary for the higher shear rate results to coincide with the equilibrium results. At low temperature, the finite shear rate results extrapolate towards the steady state result from the energy landscape analysis (discussed above).

DISCUSSION

The energy landscape picture leads to a unified description of the dynamics of driven systems, from the Newtonian limit (i.e. the zero-shear rate limit) to the athermal limit. Strain distorts the energy landscape, as shown schematically in Fig. 3. The nature of the dynamics of the system under strain depends on the relative magnitudes of three timescales: τ_{thermal}, τ_{strain}, and τ_{intra}. The timescale τ_{thermal} is for thermally activated transitions between energy minima, and τ_{thermal} increases as the temperature decreases. The timescale τ_{strain} is the timescale over which the strain is applied, and τ_{strain} is controlled by the rate at which the system is driven. The third timescale, τ_{intra}, is the timescale for dynamics within an energy minimum; τ_{intra} is one of the order of the vibrational frequencies, and in most cases is much faster than the other timescales.

Three dynamic regimes can be identified, depending on the relative magnitudes of τ_{strain} and τ_{thermal} (for τ_{intra} much faster than τ_{strain} and τ_{thermal}):

i. $\tau_{\text{strain}} \gg \tau_{\text{thermal}}$: In this limit thermally activated events occur much faster than the rate at which strain is applied. The system therefore maintains its equilibrium distribution among the energy minima as the strain is applied, as shown schematically in Fig. 5a. The equilibrium results shown in Fig. 4 correspond to this limit. The finite shear rate results in Fig. 4 approach this limit at high temperatures, because τ_{thermal} decreases with increasing temperature; note that higher temperatures are necessary for the higher shear rate results to reach this limit,

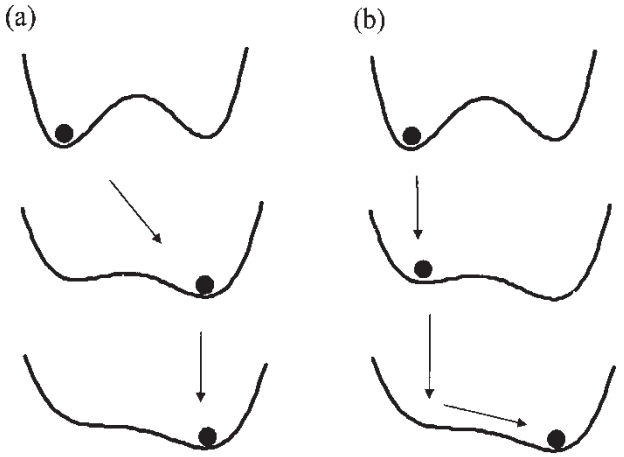

FIGURE 5 Schematic of the limiting types of dynamics under shear. (a) $\tau_{strain} \gg \tau_{thermal}$ (Newtonian limit). (b) $\tau_{strain} \ll \tau_{thermal}$ (athermal limit).

because $\tau_{strain} \sim 1/\gamma$. This limit can be referred to the Newtonian limit, because in this limit the viscosity is Newtonian (i.e. independent of shear rate).

ii. $\tau_{strain} \ll \tau_{thermal}$: This limit is the athermal limit, in which thermally activated events occur much more slowly than the rate at which strain is applied. The nature of the dynamics in this limit is shown in Fig. 5b: The system remains at an energy minimum until the energy minimum disappears due to strain-induced distortions, after which the system then relaxes to another energy minimum. The steady state result from the energy landscape analysis shown in Fig. 4 corresponds to this limit. The finite shear rate results in Fig. 4 approach this limit at low temperatures, because $\tau_{thermal}$ increases with decreasing temperature.

iii. $\tau_{strain} \sim \tau_{thermal}$: In this timescale regime, thermally activated events occur, but the dynamics is modified significantly by the changes in the barrier heights that occur on the same timescale.

CONCLUSION

The nature of the dynamics of driven systems depends on the relative timescales for the rate of driving and the rate of thermally activated process. A unified picture of these dynamics, that spans the range of the relative timescales, can be developed from the energy landscape formalism. When the timescale for thermally activated processes is much smaller than the timescale of the driving, the system is able to maintain its equilibrium properties while being driven; this regime is characteristic of Newtonian liquids. In contrast, when the timescale for thermally activated processes is much greater than the timescale of the driving, the system is far out of equilibrium and it enters a steady state in which the dynamics arise from strain-induced disappearances of energy minima; this regime is characteristic of driven athermal systems.

Acknowledgements

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