

SHORT-TIME DYNAMICAL BEHAVIOR OF FLUIDS AT THE ATOMIC SCALE

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Summary In this paper we discuss fundamental aspects of the dynamical behaviour of fluids at the atomic scale using Molecular Dynamics simulation. We present time-series analyses of instantaneous temperature and pressure using linear and non-linear methods. Within the framework of the linear analysis methods, power spectra show evidence of a two-regime power-law ($1/f^a$) behaviour with a large exponent at the high frequency region and a smaller exponent at low frequencies. The dependence of exponent a on system density and temperature is discussed. All time-series exhibit essentially the same characteristics for short times (high frequencies). In contrast, at low frequencies, pressure shows a faster loss of memory. Extracted characteristic times are consistent with results obtained from mean square displacements calculations. Rescaled range analysis reveals also a two-regime behavior. In the framework of nonlinear time series analysis, mutual information is employed for the determination of the optimal embedding delay leading to phase space reconstruction.

INTRODUCTION

Molecular dynamics (MD) is a widely used materials simulation method at the atomic level. The equations of motion are solved and successive states of the system in phase space are generated. Using statistical mechanics relations physical quantities such as temperature, pressure, etc., can be obtained as functions of time [1]. Studies of the instantaneous temperature and pressure generated during constant energy MD simulation of a grain boundary of nickel oxide exhibit $1/f^a$ behaviour [2]. $1/f$ noise is also found in other physical systems [3]. In general, the occurrence of $1/f^a$ noise is considered as an indication of system complexity, $a=1$ being the most commonly encountered case in the literature [4]. We report on analyses of instantaneous temperature and pressure generated by constant energy molecular dynamics simulation as the system (average) temperature and density are varied.

MODELLING AND COMPUTATIONAL ASPECTS

The Lennard-Jones (12-6) potential $\phi(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ where r_{ij} denotes the distance between atoms i and j is used throughout this work. The cut-off distance for the interactions was set to 2.5σ . For argon the values of the parameters are $\sigma=3.408\text{\AA}$ and $\epsilon/k_B=119.8\text{ K}$, k_B being the Boltzmann constant. The simulated system contains $N=256$ atoms. At $t=0$, atoms are located on an fcc lattice in a cube with edges parallel to the directions $x:[100]$, $y:[010]$ and $z:[001]$. The dimensions of the computational cell are such that we match the reduced density of the simulated system. Periodic boundary conditions are applied in all directions. Simulations were performed in the microcanonical ensemble and the equations of motion were integrated using Verlet's algorithm. We focus our attention on the analysis of two

time-series: Temperature, defined by $T = \frac{1}{3Nk_B} \sum_{i=1}^N m_i \vec{v}_i^2$ and pressure $P = \frac{N}{V} k_B T - \frac{1}{3V} \sum_{i=1}^N \sum_{j>i}^N r_{ij} \frac{\partial \phi(r_{ij})}{\partial r_{ij}}$, where

r_{ij} stands for the distance between two particles i and j , and v_i denotes the velocity of particle i . Further details can be found in [5]. We report here on MD simulations at various reduced densities ρ^* and temperatures T^* . Equilibration runs of 3×10^4 steps were performed before starting production runs. Each production run was 10^{-10} s long and all relevant quantities were saved every 10^{-14} s.

RESULTS

Linear methods: Spectral and Rescaled Range Analysis

Spectral analysis reveals that T and P exhibit a two-regime $1/f^a$ power-law behavior with small exponent a for low frequencies and larger values for high frequencies (see figure 1a). For temperature we have a high frequency regime with a large exponent indicating strong memory effects and a low-frequency regime where the power-law exponent is smaller indicating rapid loss of memory. Pressure behaves similarly at high frequencies, but at low frequencies it is characterized by exponents close to zero indicating faster loss of memory. The high frequency exponents for both T and P are insensitive to the system density variation while the low-frequency exponents become smaller as density increases. As the system temperature increases the values of a are in general smaller indicating weakening memory effects.

Rescaled range analysis (Hurst test) confirms the presence of a two-regime behaviour with strong memory effects at small times (high frequencies) and weaker memory effects at large times (see figure 1b). Pressure loses memory faster than temperature at long time intervals.

The two-regime behaviour reflects the two types of motion that atoms perform: vibrations around a given location and diffusive motion among such sites. Typical atomic trajectories are shown in figure 1c. For short times, Mean Square

Displacement (MSD) calculations show a parabolic dependence on time practically the same for all fluid densities. It is interesting to note that the maximum time that this behaviour is observed is around 2×10^{-13} s which corresponds to a frequency about 5×10^{12} Hz which, in turn, is the lower limit of the high-frequency zone in the power spectra.

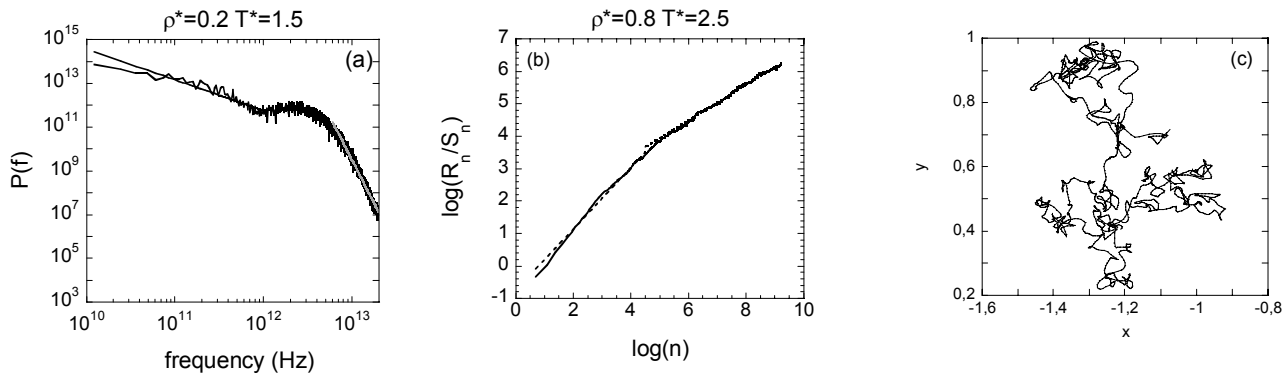


Figure 1. a) power spectrum of temperature time series at $\rho^*=0.2$, $T^*=1.5$ b) rescaled range analysis results of pressure time series at $\rho^*=0.8$, $T^*=2.5$ c) Typical atomic trajectory at $T^*=1.5$, $\rho^*=0.8$ (projection on the x-y plane).

Non-Linear tools: Average Mutual Information

The average mutual information, I , is defined as

$$I = - \sum_{ij} p_{ij}(\tau) \ln(p_{ij}(\tau) / p_i p_j)$$

p_i is the probability to find a value in the i -th interval, and $p_{ij}(\tau)$ is the joint probability that an observation falls into the i -th interval and time τ later falls into the j -th. Mutual information takes into account nonlinear correlations between successive measurements of a given quantity. If $I(\tau)$ has a marked minimum at $\tau = \tau_d$, then it is argued that τ_d is a reasonable choice of time delay for embedding in phase space reconstruction [6]. Note in figure 2 that the minimum is observed in the vicinity of $\tau = 1.5 \cdot 2 \times 10^{-13}$ s which is close to the characteristic time deduced from MSD. As we can see in figure 2 for the temperature time series at a given density, as system temperature increases $I(\tau)$ falls faster, which means that correlation, i.e., memory is lost faster. A similar behaviour is observed for pressure but we do not observe a clear minimum of $I(\tau)$. For a given system temperature correlations are lost faster as system density increases. These observations are not only in agreement with the results of power spectrum and rescaled range analysis but they provide the appropriate input for phase space reconstruction of both T and P time series.

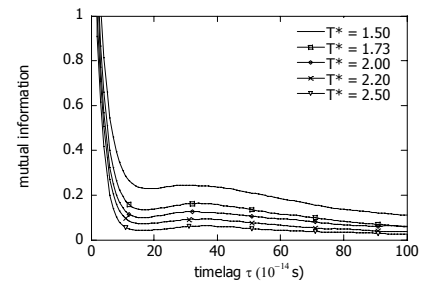


Figure 2. Mutual information of temperature time series at $\rho^*=0.2$

CONCLUSIONS

Spectral and rescaled range analyses of T and P time series indicate two-regime power-law behaviour. For temperature, we have a high frequency regime with a large exponent indicating strong memory effects and a low-frequency regime where the power-law exponent is smaller indicating rapid loss of memory. For high frequencies, pressure behaves similarly. In contrast, at low frequencies, pressure is characterized by exponents close to zero indicating even faster loss of memory. The high frequency exponents are insensitive to density variation while the low-frequency exponents become smaller as density increases. As the system temperature increases the values of the power spectrum exponents are in general smaller indicating that increasing temperature weakens memory effects. Characteristic times based on MSD calculations are found to be in agreement with characteristic times extracted from the time series analysis. Nonlinear correlation measures based on mutual information have been proved very useful in determining delay times for embedding in phase space reconstruction of P and T time series.

Acknowledgements

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