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Generalized fluctuation relation and effective temperatures in a driven fluid

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By numerical simulation of a Lennard-Jones-like liquid driven by a velocity gradient γ we test the fluctuation relation (FR) below the (numerical) glass transition temperature T_g. We show that, in this region, the FR deserves to be generalized introducing a numerical factor $X(T,\gamma)<1$ that defines an "effective temperature" $T_{FR}=T/X$. On the same system we also measure the effective temperature T_{eff}, as defined from the generalized fluctuation-dissipation relation, and find a qualitative agreement between the two different nonequilibrium temperatures.

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The *fluctuation theorem* (FT) concerns the fluctuations of the entropy production rate $\sigma(t)$ in the stationary nonequilibrium states of a *chaotic* driven system. We will set $k_B=1$ and define $\sigma_+\equiv\langle\sigma(t)\rangle$, where $\langle\cdot\rangle$ is the time average in stationary state; if $\sigma_+>0$ the system is out of equilibrium. Defining the variable $p(t)=(\tau\sigma_+)^{-1}\int_t^{t+\tau}ds\sigma(s)$ (such that $\langle p\rangle=1$), its probability distribution function (PDF) $\pi_\tau(p)$, and the large deviations function

$$\zeta_\tau(p)=\tau^{-1}\ln\pi_\tau(p),\quad \zeta(p)=\lim_{\tau\to\infty}\zeta_\tau(p), \tag{1}$$

the FT states that, for $|p|<p^*$ [where p^* is defined by $\lim_{p\to\pm p^*}\zeta(p)=-\infty$], the following relation—also called *Fluctuation Relation* (FR)—must hold:

$$\zeta(p)-\zeta(-p)=p\sigma_+. \tag{2}$$

The validity of this relation was first shown by Evans *et al.* in a numerical simulation of a sheared fluid [1] and subsequently proven for reversible Anosov systems by Gallavotti and Cohen [2]. Gallavotti then showed that, close to equilibrium ($\sigma_+\to 0$), the FR implies the usual fluctuation-dissipation relation (FDR) [3]. In the recent past, the FR has been tested under a wide class of different conditions, and is now believed to be a very general relation for chaotic systems [4–7]; recently, it has been also tested in some experiments [8].

Extending the FT to the case of driven Langevin systems, Kurchan pointed out that "the FR might be violated for those (infinite) driven systems, which in the absence of drive have a slow relaxational dynamics that does not lead them to equilibrium in finite times" [6]. This is (by definition) the case of driven glassy systems. Driven glassy systems have been widely studied by numerical simulations: in [9], a uniform velocity gradient γ was applied on a Lennard-Jones liquid (which manifests glassy behavior below the *glass transition temperature* T_g [10]) at a fixed kinetic temperature T. In presence of the driving force, the system becomes stationary also below T_g, while in the absence of drive, the system is not able to equilibrate with the bath and ages indefinitely. It was shown that below T_g, the FDR does not hold anymore (because in the absence of drive, the system is not able to reach equilibrium below T_g) but can be generalized, for a small driving force, introducing an "effective temperature" T_{eff}—higher than the temperature of the bath—associated with the "slow" modes that in absence of drive are responsible for the glassy behavior [9,11]. The breakdown of the FDR and the close relation between the latter and the FR support the conjecture of Kurchan that the FR also has to be modified below T_g.

A possible generalization of the FR, of the form

$$\zeta(p)-\zeta(-p)=Xp\sigma_+, \tag{3}$$

was proposed in [4] in the context of chaotic dynamical systems. It has also been proposed to define $T_{FR}\equiv T/X$ as the "temperature" in nonequilibrium steady states [12]. A similar generalization has been proposed by many authors in the context of glassy systems, following the reported Kurchan's observation, and some attempts have been made in order to relate T_{FR} with the effective temperature T_{eff} introduced in the generalized FDR [13,14]. Recently, a connection between the generalized FDR and the FR has been derived in a model for the Brownian diffusion of a particle in a nonequilibrium environment [15].

However, up to now numerical studies of the FR have been performed only in the high temperature region ($T\gg T_g$). The aim of this paper is to test the FR *below* T_g in a numerical simulation of a Lennard-Jones-like liquid. We measured $\zeta(p)$ and found that the data are consistent with Eq. (3) with $X<1$, while above T_g one has $X=1$, consistently with what has been found in previous works. We measured also the effective temperature T_{eff} from the generalized FDR and found a good agreement between $T_{FR}=T/X$ and T_{eff}.

The investigated system is a 80/20 binary mixture of $N=66$ particles of equal mass m interacting via a soft sphere potential (SSP) $V_{\alpha\beta}(r)=\epsilon_{\alpha\beta}(\sigma_{\alpha\beta}/r)^{12}$ ($\alpha,\beta\in[A,B]$). This system has been introduced and characterized in equilibrium by De Michele *et al.* [16] as a modification of the standard Lennard-Jones (LJ) Kob-Andersen mixture that is known to avoid crystallization on very long time scales, and hence to be a very good model of glass former; it has been chosen because the SSP can be cut at very short distance

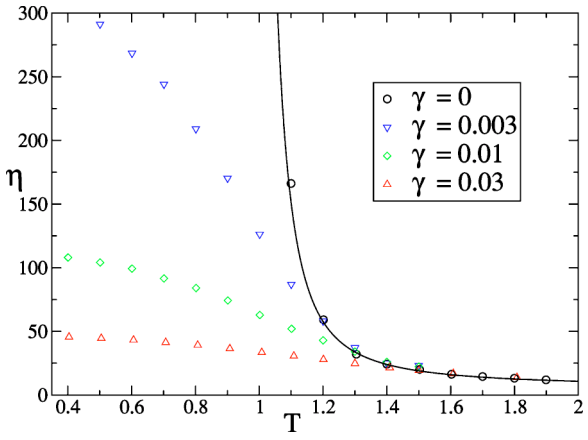

FIG. 1. (Color online) Viscosity as a function of temperature for different values of γ. The continuous line is a fit to a Vogel-Tamman-Fulcher law, $\eta(T)=\eta_0 \exp[AT_0/(T-T_0)]$ with $\eta_0=5.2$, $A=0.99$, $T_0=0.85$. Here and in the following all quantities are reported in LJ units (see text).

($\sim 1.5\sigma_{AA}$) allowing the system to be very small ($N=66$) in order to observe the negative values of p that are required to test Eq. (2). All the quantities are reported in units of m, ϵ_{AA}, and σ_{AA} (LJ units). In these units the integration step is $dt=0.005$. The particles are confined in a cubic box with Lees-Edwards boundary conditions [17] at density $\rho=1.2$. The shear flow is applied to the system along the x direction with a gradient velocity field along the y axis. The molecular dynamics simulation is performed using the Sllod[1] equations of motion [17]

$$\dot{q}_i = \frac{p_i}{m} + \gamma q_{yi}\hat{x}, \quad \dot{p}_i = F_i(q) - \gamma p_{yi}\hat{x} - \alpha p_i, \tag{4}$$

where $F_i(q)=-\partial_{q_i}V(q)$ and α is a Gaussian thermostat that fixes the kinetic energy $\Sigma_i p_i^2/2m=\frac{3}{2}NT$. The entropy production rate is defined as the dissipated power W divided by the kinetic temperature T [18]: $\sigma(p,q)=W(p,q)/T=-\gamma P_{xy}(p,q)/T$, where $P_{xy}(p,q)=\Sigma_i[p_{xi}p_{yi}+q_{yi}F_{xi}(q)]$ is the xy component of the stress tensor [17].

In Fig. 1 we report the viscosity $\eta \equiv \langle P_{xy}\rangle/\gamma$ as a function of the temperature T for different values of the shear rate γ. At $\gamma=0$ the viscosity seems to diverge at a temperature $T_0 \sim 0.85$; however, we are able to equilibrate our system only down to $T\sim 1.1$, that provides an estimate for the glass transition temperature T_g. For $\gamma>0$, the system becomes stationary and the viscosity is finite at all temperatures, even below T_0.

Very long simulation runs (up to 2×10^9 time steps) have been performed to measure the PDF of the entropy production rate along the line $\gamma=0.03$. During the run, $p(t)$ has been measured on subsequent time intervals of duration τ. From this dataset, we constructed the histograms of $\pi_\tau(p)$ and the large deviations function $\zeta_\tau(p)$ defined in Eq. (1). The function $\zeta_\tau(p)$ is observed to converge to its asymptotic value

[1]The label Sllod refers to the relationship with the Dolls tensor algorithm.

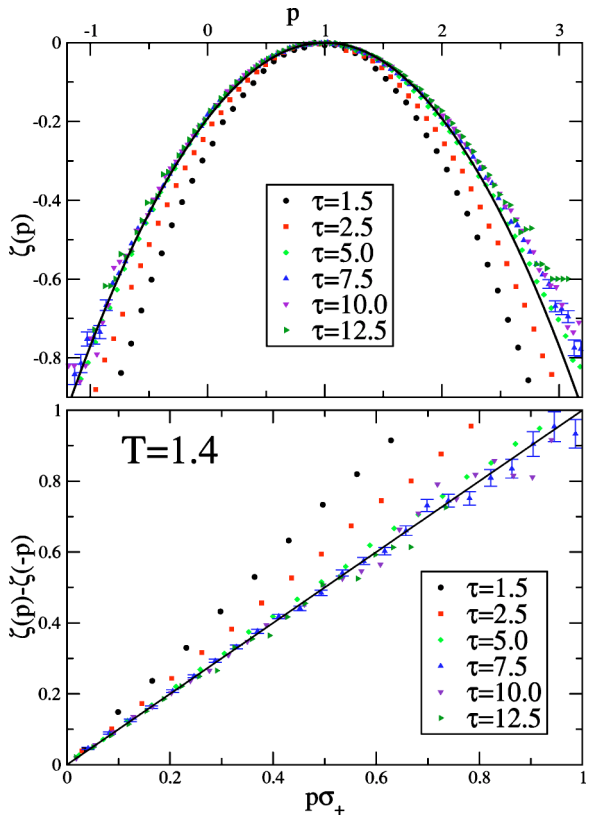

FIG. 2. (Color online) Top: the large deviation function $\zeta_\tau(p)=\tau^{-1}\ln \pi_\tau(p)$ as a function of p for different values of τ at $T=1.4>T_g$ and $\gamma=0.03$. Error bars are smaller than the symbols except on the tails; they are reported only for $\tau=7.5$ to avoid confusion. The line is a Gaussian fit to the data with $\tau>5$ for $p\in[0,2]$. Bottom: $\zeta_\tau(p)-\zeta_\tau(-p)$ as a function of $p\sigma_+$. The FR predicts the plot to be a straight line with slope 1 (full line) for large τ.

$\zeta(p)$ for $\tau \gtrsim \tau_\alpha$, τ_α being the relaxation time of the autocorrelation function of $\sigma(t)$.

In the upper panel of Fig. 2, we report the functions $\zeta_\tau(p)$ for $\gamma=0.03$ and $T=1.4>T_g$. The asymptotic function $\zeta(p)$ is obtained for $\tau \gtrsim 5$ and can be described by a simple Gaussian form, $\zeta(p)=-(p-1)^2/2\delta^2$, even if small non-Gaussian tails are observed. In the lower panel of Fig. 2, we report $\zeta_\tau(p)-\zeta_\tau(-p)$ as a function of $p\sigma_+$. The FR, Eq. (2), predicts the plot to be a straight line with slope 1 for large τ; this is indeed the case for $\tau \gtrsim 5$, consistently with what has been found in the literature [1,5].

In the upper panel of Fig. 3, we report the functions $\zeta_\tau(p)$ for $\gamma=0.03$ and $T=0.8<T_g$. In this case, the asymptotic regime is reached for $\tau \gtrsim 6$; this value is not so different from the one obtained in the previous case because the change in viscosity (and hence in relaxation time) going from $T=1.4$ to $T=0.8$ is very small at this value of γ (see Fig. 1). Also in this case the simple Gaussian form gives a good description of the data apart from the small non-Gaussian tails. In the lower panel of Fig. 3 we report $\zeta_\tau(p)-\zeta_\tau(-p)$ as a function of $p\sigma_+$. At variance to what happens for $T>T_g$, in this case the asymptotic slope reached for $\tau \gtrsim 6$ is smaller than 1; thus, the FR given by Eq. (2) has to be generalized according to Eq. (3). At this temperature, we get $X=0.83\pm 0.05$.

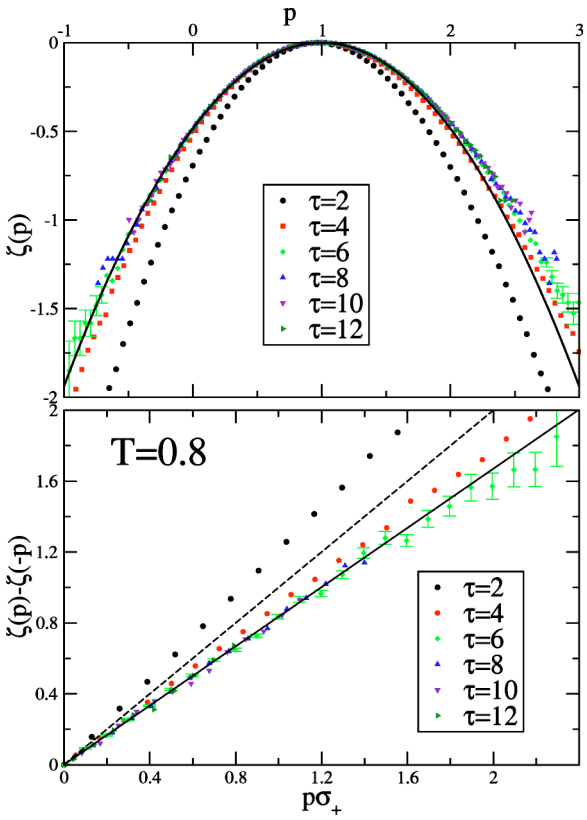

FIG. 3. (Color online) Same plots as in Fig. 2 for $\gamma=0.03$ and $T=0.8<T_g$. In the lower panel, the dashed line has slope 1 while the full line has slope $X=0.83$.

In Fig. 4, we report the behavior of the violation factor $X(T,\gamma=0.03)$ (full circles) as a function of the temperature T; note that X becomes smaller than unity exactly around $T_g\sim 1.1$, i.e., when the viscosity starts to diverge strongly (see Fig. 1). Below $T\sim 0.4$, σ_+ becomes so large that negative fluctuations of p are extremely rare and the violation factor is no longer measurable. We can conclude that below T_g, the FR does not hold, and our data are consistent with Eq.

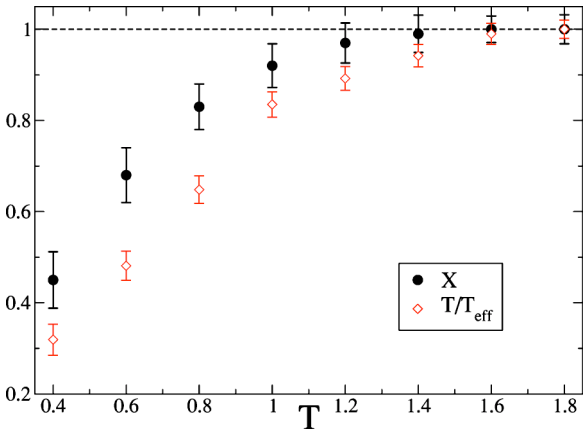

FIG. 4. (Color online) The violation factor $X=T/T_{FR}$ that enters Eq. (3) (full circles) and the ratio T/T_{eff} from the generalized FDR (open diamonds) as a function of the bath temperature T for $\gamma=0.03$.

(3), where the coefficient X is temperature dependent below T_g and equals 1 above T_g.

Having checked the validity of Eq. (3), following Ref. [12], we can define a nonequilibrium temperature as $T_{FR}=T/X$. Note that if we define $\sigma'(t)=W/T_{FR}=X\sigma(t)$, the variable p and the function $\zeta(p)$ are not affected by the rescaling while $\sigma'_+=X\sigma_+$. Thus, the FR for σ' is the usual one given by Eq. (2). If one assumes that the fluctuations of entropy production rate should satisfy Eq. (2), the entropy production rate should be given by $\sigma'(t)$ instead of $\sigma(t)$.

It is interesting to compare the temperature T_{FR} with the effective temperature T_{eff} that enters the generalized fluctuation-dissipation relation. The latter can be measured from the relation $T_{eff}=D/\mu$, where D is the diffusion constant and μ is the mobility of the particles in the considered steady state [9,19]. This relation generalizes the usual equilibrium FDR $D=\mu T$; to compute the diffusion constant and the mobility of type-A particles we followed the procedure discussed in Ref. [19]. In Fig. 4, together with $X=T/T_{FR}$, we report the ratio T/T_{eff} (open diamonds) as a function of the bath temperature T. The two effective temperatures have a similar qualitative behavior but do not coincide.

The origin of this discrepancy will be discussed in detail in [15]; roughly speaking, the point is that the modes at all frequencies contribute to the entropy production rate, while T_{eff} is the temperature of the slowest modes in the systems. At the values of γ we considered, the separation between a "fast" and a "slow" relaxation is not so sharp: hence, T_{FR} should be related to an average over all the frequencies of the frequency-dependent effective temperature. Note also that we are forced to use a very small system in order to observe large fluctuations of the entropy production rate, thus, size effects could affect the behavior of the investigated quantities. We believe, however, that the qualitative picture is correct even if size effects are not completely negligible. Future works will hopefully clarify this issue by exploring lower values of γ for which separation of time scales is more marked; however, for low values of γ, size effects are more relevant and the dynamics of the system is very slow; thus, very long simulations of bigger systems, requiring a large amount of CPU time, are mandatory.

An interesting microscopical derivation of Eq. (3) was proposed by Bonetto and Gallavotti [4], who related the factor X to the dimensionality of the attractive set of the system in its phase space. The latter can be measured by computing the Lyapunov spectrum, which in this kind of system is composed by pairs of conjugated exponents; the latter are constructed by pairing the largest exponent with the smallest one and so on [20]. The prediction of [4] is that $X=\mathcal{D}/\mathcal{N}$, where $\mathcal{D}$ is the number of pairs where one exponent is positive and the other is negative, and $\mathcal{N}$ is the total number of pairs. If the attractor is dense in phase space, $\mathcal{D}=\mathcal{N}$ and $X=1$. This relation is very interesting as—if true—it provides a link between the effective temperature and properties of the phase space of the system. The Lyapunov spectra have been measured by the mean of the standard algorithm of Benettin *et al.* [21] and are reported in Fig. 5 for $\gamma=0.03$, $T=1.2>T_g$, and $T=0.8<T_g$. Unfortunately, no qualitative change in the spectrum is observed on crossing T_g and in particular $\mathcal{D}/\mathcal{N}=1$ above and below T_g. Thus, it seems that the theory of [4]

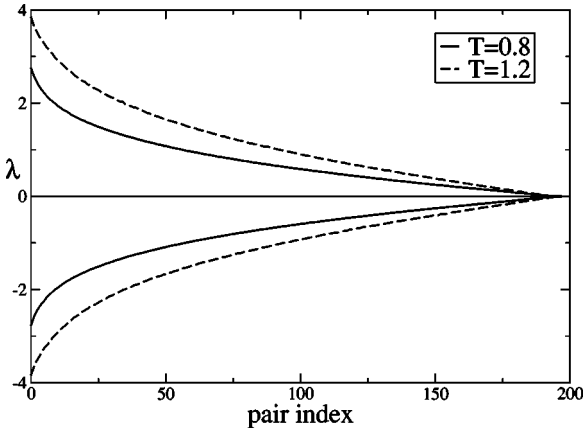

FIG. 5. Lyapunov exponents for $\gamma=0.03$ and $T=0.8,1.2$. For both temperatures each pair consists of one positive and one negative exponent, thus $\mathcal{D}/\mathcal{N}=1$.

does not apply to our model below T_g. Note, however, that this theory is developed under the assumption of a strong chaoticity of the system, while below T_g and for $\gamma\sim 0$ the dynamics of our system becomes slower and slower. Thus, our results should not be regarded as invalidating the conjecture of [4], but as indicating that the hypothesis of [4] (essentially, the requirement of strong chaoticity) are not satisfied by our model below T_g.

To resume, we studied the fluctuations of entropy production in a numerical simulation of a Lennard-Jones-like fluid above and below the glass transition temperature T_g. We showed that below T_g the fluctuation relation does not hold; in particular, our data are consistent with a modified form of the FR expressed by Eq. (3). We also showed that the behavior of the temperature derived from Eq. (3), $T_{FR}=T/X$, is qualitatively similar to that of the effective temperature T_{eff} that is usually defined from the generalized fluctuation-dissipation relation. A relation between T_{FR} and T_{eff} has been proposed in [13,14] and our results are consistent with a recent quantitative derivation of this relation in a simplified model [15]. Finally, we tested a conjecture that relates the factor X in Eq. (3) to properties of the phase space of the considered system; unfortunately, our data are not consistent with this conjecture; thus, we believe that the violation of the FR is, in our case, of different origin than that proposed in [4]. We hope that future work will clarify this important issue.

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