Author manuscript, published in "Physical Review E 74 (2006) 011202"

Long time behaviour of the velocity autocorrelation function at low density and near critical point of simple fluids

R.F.A Dib and F. Ould-Kaddour

Laboratoire de Physique Théorique, Faculté des Sciences,
Université de Tlemcen BP 119, Tlemcen 13000 Algerie

D. Levesque

Laboratoire de Physique Théorique, Université Paris-Sud,
Bâtiment 210, 91405 Orsay, France[*]

Abstract

Numerous theoretical and numerical works have been devoted to the study of the algebraic decrease at large times of the velocity autocorrelation function of simple fluid particles. The derivation of this behaviour, so-called the long-time tail, generally based on linearized hydrodynamic makes no reference to any specific characteristic of the particle interactions. However, in the literature, doubts have been expressed on the possibility that by numerical simulations the long-time tail can be observed in all the fluid phase domain of systems where the particles interact by soft-core and attractive pair potentials. In this work, extensive and accurate molecular dynamics simulations establish that the predicted long-time tail of the velocity autocorrelation function exists in low density fluid of particles interacting by a soft-repulsive potential and near the liquid-gas critical point of a Lennard-Jones system. These results contribute to confirm that the algebraic decay of the velocity autocorrelation function is universal in the fluid systems.

PACS numbers: 05.10.-a, 61.25.-f

---

[*] Author to whom correspondance should be addressed. Electronic address: dominique.levesque@th.u-psud.fr.

I. INTRODUCTION

The long time tail of the velocity autocorrelation function (VAF), discovered first by the pioneering work of Alder and Wainwright [1] using molecular dynamic (MD) simulation of elastically colliding hard disks and spheres, came as a complete surprise. This result was in contradiction with the prediction of an exponential decay of the VAF supported by the explicit solutions of almost all known solvable models, such as the linearized Boltzmann equation [2] and the Fokker-Planck equation [3].

Alder and Wainwright found that the VAF long-time tail was well fitted by the analytic form $\alpha t^{-3/2}$. They explained this unexpected behaviour by a simple hydrodynamic model, describing the motion of a hard disk or sphere by that of a circular or spherical particle in a continuum fluid formed by the other disks or spheres. The forward motion of the particle gives rise in the fluid to a vortex of size approximately equal to three particle diameter. This vortex mode predominates at long times leading to the long-time tail $\alpha t^{-3/2}$ of the VAF.

For fluid systems and without reference to the details of the particle interactions, Ernst et al. [4, 5] were able to derive the VAF asymptotic time behaviour by assuming the existence of a local equilibrium and using the linearized Navier-Stokes equation. For a system of hard disks and hard spheres, Dorfman and Cohen [6] derived the long-time tail of the VAF from kinetic theory. They showed that a sequence of correlated binary collisions, *ring collisions*, is the main process responsible for the vortex formation leading to the VAF slow decay.

Light scattering experiments [7, 8] or diffusive wave spectroscopy [9, 10] indicate the presence of the long-time tail in the VAF of colloidal particles. These experimental results agree with the theoretical description of the Brownian particle motion [11, 12]. Neutron scattering experiments [13, 14] also indicate that, in atomic liquids, the VAF decreases algebraically at large times. However, present experimental evidences of the VAF long-time tail are restricted to a few type of liquids (colloids, alkaline liquids and liquid argon) and few thermodynamic states.

Furthermore in MD simulations, doubts remain about the possibility of observing the long-time tail in a low density fluid of soft-repulsive particles [15] and in Lennard-Jones (LJ) fluid in thermodynamic states close to the liquid-vapour critical point [16]. According to the simulation results [15] it seems that the nonexponential decrease of the VAF with time is easily observed only for systems at moderate densities, since, in this work, the $\alpha t^{-3/2}$ tail is not found at low densities. The simulations [16] indicate that, for a LJ system, the VAF decays at long times in agreement with the theoretical exponent $-3/2$ only at high densities, and that, along an isochore close to the critical density, the VAF decreases with an exponent equal to -3.

Motivated by these apparent disagreements between these simulation results and the theoretical derivation of the VAF asymptotic time behaviour, it is shown in this paper, by means of accurate and extensive MD simulations, that the VAF exhibits the $\alpha t^{-3/2}$ power law decay for a fluid of soft-repulsive particles at low density and for a LJ fluid close to the critical point, confirming the theoretical claim of a universal power law tail of the VAF in all the thermodynamic states of simple fluids [5], independently on the particle interactions.

We give in Sec. II a theoretical overview, and in Sec. III the MD simulation details. Sec. IV presents and discusses the simulation results for the VAF. The paper ends by a conclusion.

II. THEORETICAL OVERVIEW

The expression of the velocity autocorrelation function for a three dimensional fluid, at large times, is given by [4] :

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{2k_BT}{\rho_N m}\frac{1}{[(4\pi(D+\nu)t]^{3/2}} = \alpha t^{-3/2} \qquad (1)$$

where $\mathbf{v}$ is the particle velocity vector at time t, k_B the Boltzmann's constant, T the temperature, m the mass of the particles, ρ_N the particle density, D the self-diffusion coefficient, and ν the kinematic viscosity of the fluid. The angular brackets indicate an equilibrium ensemble average.

The derivation of Eq. (1) is made under the general assumption that the approach of non-equilibrium distribution to local equilibrium distribution evolves at long times according to the laws of hydrodynamic [4]. The following arguments, which summarize this derivation, are taken from [17, 18]. We consider a d-dimensional system of N particles in equilibrium, containing a tagged particle with an initial velocity $\mathbf{v}(0) = \mathbf{v}_0$. From this initial non-equilibrium state, the evolution of the system towards equilibrium is supposed to be described by means of linearized hydrodynamic equations :

$$\frac{\partial P(r,t)}{\partial t} = D\nabla^2 P(r,t), \qquad (2)$$

$$\frac{\partial \mathbf{u}_\perp(r,t)}{\partial t} = -\nu\nabla \times (\nabla \times \mathbf{u}_\perp(r,t)). \tag{3}$$

where $P(r,t)$ is the probability density for the tagged particle to be at position r at time t and $\mathbf{u}_\perp(r,t)$ is the transverse part of the velocity density field. The longitudinal part of the velocity density field does not appear in the equations because its contribution to the velocity autocorrelation decays exponentially [18].

From the Fourier transforms of Eqs. (2) and (3), it is shown that :

$$\widetilde{P}\,(k,t) = e^{-Dk^2t}, \tag{4}$$

$$\widetilde{\mathbf{u}}_\perp\,(k,t) = [\mathbf{v}_0 - \frac{(\mathbf{v}_0\cdot\mathbf{k})\mathbf{k}}{k^2}]e^{-\nu k^2 t}. \tag{5}$$

With the assumption that, at long times, the tagged particle has the same average velocity as its neighbouring particles, we have :

$$\mathbf{v}(t) = \int d^d r P(r,t)\frac{1}{\rho_N}\mathbf{u}_\perp(r,t) = \frac{1}{\rho_N}\frac{1}{(2\pi)^d}\int d^d k\ \widetilde{P}\,(k,t)\ \widetilde{\mathbf{u}}_\perp\,(-k,t). \tag{6}$$

The insertion of Eqs. (4) and (5) into Eq. (6) gives :

$$\begin{aligned}\mathbf{v}(t) &= \frac{1}{\rho_N}\frac{1}{(2\pi)^d}\int d^d k[\mathbf{v}_0 - \frac{(\mathbf{v}_0\cdot\mathbf{k})\mathbf{k}}{k^2}]e^{-(\nu+D)k^2t} \\ &= \frac{1}{\rho_N}\frac{d-1}{d}\frac{1}{[(4\pi(D+\nu)t]^{d/2}}\mathbf{v}_0.\end{aligned} \tag{7}$$

where the $(d-1)/d$ coefficient comes from the fact that only the transverse part of the velocity field contributes at large times.

Averaging over $\mathbf{v}_0$ with respect to the Maxwell-Boltzmann velocity distribution :

$$\begin{aligned}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle &= \frac{1}{\rho_N}\frac{d-1}{d}\frac{1}{[(4\pi(D+\nu)t]^{d/2}} \\ &\quad \int d^d v_0 \left(\frac{m}{2\pi k_B T}\right)^{d/2} v_0^2 e^{-mv_0^2/2k_BT}\end{aligned} \tag{8}$$

leads to the expression of the VAF given by Eq. (1) :

$$\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{(d-1)\,k_BT}{m\rho_N}\frac{1}{[(4\pi(D+\nu)t]^{d/2}}\ . \tag{9}$$

The derivation of Eq. (1) from kinetic theory, valid for particle systems with short range repulsive potentials as the hard disk or sphere systems, is more sophisticated [6, 19, 20]. As it is mentionned above, the vortex mode responsible of the long-time tail of the VAF finds its origin in the so-called ring-collisions, a sequence of correlated binary collisions where the initial momentum of the tagged particle is transferred to the surrounding particles in a ring-like motion. It can even be found from more complex derivations [19] that the $t^{-3/2}$ long-time behaviour of the VAF is the first term in an infinite series of general order t^{-l}, where $l = 1/2^n - 2$ with n integer ≥ 1 and $-2 \leq l \leq -3/2$.

In the expression of the VAF derived by kinetic theory appears the so-called "bare" transport coefficients D_0 and ν_0 [6] corresponding to a "bare" value α_0 of the long-time tail amplitude α. The values of D_0 and ν_0 are close, but not identical to those of D and ν of the hydrodynamical approach. The numerical simulations compute a long time tail with a "bare" amplitude for times between 10 and 50 mean collision times, it is only for longer times that the hydrodynamic amplitude α is obtained [18].

In summary, the asymptotic behaviour of the VAF has been determined either by means of hydrodynamical assumptions, independently of the details of the particle interactions, or by kinetic theory for hard-core particles. The two approaches lead to predict the $\alpha t^{-3/2}$ long-time tail of the VAF.

III. MOLECULAR DYNAMICS SIMULATIONS

To determine the long-time behaviour of the VAF by MD simulation we have to be sure that there is no influence of the periodic boundary conditions of the simulation cell on the VAF computation [20, 21]. To achieve this goal, we choose a maximum correlation time t_{max} smaller than the time needed by a sound wave to cross the entire periodic cell, i.e.

$$t_{max} \leq (N/\rho_N c_s^3)^{1/3}, \tag{10}$$

where c_s is the speed of sound in the fluid. It is expected that, at times greater than t_{max}, the VAF becomes strongly influenced by the sound modes [21]. Thus, before to compute the VAF for any system of arbitrary but reasonably large number of particles ($N > 500$), it is necessary first to estimate the velocity of sound c_s at the phase point we want to study from the formula [22]:

$$c_s = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T}{\rho^2 \left(\frac{\partial E}{\partial T}\right)_V} \left(\frac{\partial P}{\partial T}\right)_V^2} \ , \tag{11}$$

where P is the pressure, E the total energy and V the volume. Once the value of c_s obtained, the maximum correlation time t_{max} is estimated through Eq. (10).

To test the theoretical prediction $\alpha t^{-3/2}$ of the behaviour of the VAF at long times against the simulation results, we have to make an estimate of α which depends on the diffusion coefficient and kinematic viscosity. We use the Green-Kubo integral formula [23] to calculate the self-diffusion coefficient :

$$D = \frac{1}{3N}\sum_{i=1}^{N}\int_0^\infty \langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle dt = \frac{3k_BT}{m}\int_0^\infty dt \quad \mathrm{vaf}(t) \tag{12}$$

where the average over all the particles is used to reduce the statistical uncertainty on the normalized velocity autocorrelation function vaf(t). The kinematic viscosity ν is obtained through the shear viscosity η given by [23] :

$$\eta = \lim_{t_u\to\infty}\eta(t_u) = \frac{1}{k_BTV}\int_0^{t_u}\langle\sigma^{xz}(t)\sigma^{xz}(0)\rangle dt, \tag{13}$$

where σ^{xz} is an off-diagonal element of the stress tensor

$$\sigma^{xz} = \sum_{i=1}^{N}\Big(mv_{ix}v_{iz} + \frac{1}{2}\sum_{j\neq i}^{N}x_{ij}F_{ij}^z\Big), \tag{14}$$

with F_{ij}^z the z-component of the force between particles i and j and x_{ij} the x-component of the vector joining particles i and j.

In this paper, we use the reduced quantities: $T^* = k_BT/\epsilon$, $\rho^* = \rho\sigma^3$, $t^* = t\sqrt{\epsilon/m\sigma^2}$, and $r^* = r/\sigma$, where ϵ and σ are the energy and length parameters of the LJ potentials $v_{LJ}(r)$. The unit of time is thus $\tau_0 = \sqrt{m\sigma^2/\epsilon}$.

We have considered two systems : a low density system, at $\rho^* = 0.2$ and $T^* = 2.07$, of 32000 particles interacting via a soft-repulsive potential

$$v(r) \;=\; v_{LJ}(r) + \epsilon = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] + \epsilon \quad \text{for} \quad r \le 2^{\frac{1}{6}}\sigma \tag{15}$$

$$\;=\; 0 \quad \text{for} \quad r > 2^{\frac{1}{6}}\sigma\,, \tag{16}$$

and a LJ system near the liquid-vapour critical point at $\rho* = 0.3$ and $T^* = 1.35$ of 10976 particles interacting by a LJ potential truncated at a cutoff distance equal to r^* =6.5. This value of the cutoff is the same as that used in the work of Meier *et al* [16] in which a t^{-3} behaviour of the VAF was reported near the critical point.

The simulations were realized at constant energy using the standard Verlet algorithm with a time step $\Delta t^* = 0.003$ for the low density fluid and $\Delta t^* = 0.001$ at the critical point to insure the stability of the total energy value to within 0.01%. The simulations were carried out for 100 000 equilibration time steps followed by 10 10^6 time steps during which the VAF or the stress correlation function, were computed over blocks of $2000\Delta t^*$ to allow an evaluation of the statistical errors.

For the soft-repulsive particle system at $\rho^* = 0.2$ and $T^* = 2.07$, the computed thermodynamic properties are : $P^* = 0.632$, $E^*_{total} = 3.242$ and $c_s = 2.682\sigma/\tau_0$ and, near the LJ critical point at $\rho* = 0.3$ and $T^* = 1.35$: $P^* = 0.153$, $E^*_{total} = -0.15$ and $c_s = 2.09\sigma/\tau_0$. From Eq. (10), we find the maximun correlation time t^*_{max} equal to 20.2 in the first case and 15.8 near the LJ critical point. The derivatives on P and E in Eq. (11) were computed from canonical ensemble MD simulations performed at densities and temperatures close to those of the considred thermodynamiques states.

IV. VELOCITY AUTOCORRELATION RESULTS

We give in Fig. 1 the normalized VAF multiplied by $t^{*3/2}$ for the studied systems. The maximum correlation times are those fixed previously from the computation of c_s. The statistical error on the normalized VAF is estimated to be $\pm 2.\,10^{-5}$ which gives a relative error of 10% on the asymptotic part of the VAF. The data clearly indicates the existence of $t^{-3/2}$ behaviour in both cases.

For the soft particle system, the asymptotic tail appears above t^* =10. This explains why, in the similar work of McDonough *et al* [15], it was not possible to observe the long time tail at a density ρ^* =0.25 because it occurs at larger time than the maximum correlation time considered in this work equal to ∼5. Noticing that the system size being equal to 4000 particles, it was not possible to consider correlation times higher than 7 due to the coupling between diffusion and sound modes [21].

Fig. 2 shows a log-log plot of the VAF versus reduced time for the soft-repulsive fluid. A linear fit of the data in the range $11 < t^* < 18$ gives : $\log \mathrm{vaf}(t) = (-4.05 \pm 0.08) - (1.50 \pm 0.03) \log t^*$, leading to a value of $\alpha_{fit} = 0.0174 \pm 0.0015$. In order to test the theoretical value of α, we have computed the diffusion coefficient from the integral of the VAF (cf. Eq. (12)) up to $t^* = 11$ in agreement with the remark quoted above [18]. The value found was $D^* = 0.294 \pm 0.001$. A similar computation was for the kinematic viscosity. Fig. 3 shows the stress correlation function Eq. (14) computed up to a correlation time equal to 5, beyond which the stress correlation function is zero within the statistical error. It is important to remark that the statistical error on the vaf(t) due the average on the particles is smaller than that on the stress correlation function by almost two orders of magnitude. In addition, since the integral is truncated at $t^* = 5$, a contribution to $\eta(t)$ is missing which is due to the long time part of the stress correlation function. This contribution can account to about 15-20% of the η value as it was shown [24]. In Fig. 3, the plot of the integral $\eta(t_u)$ over the stress tensor correlation is also included. The plateau gives the value of η and that of the kinematic viscosity equal to $\nu^* = 1.71 \pm 0.08$ to which we should add a systematic error of $\sim$0.3. The corresponding calculated value for the amplitude $\alpha_{cal} = 0.026 \pm 0.006$ including the systematic error on ν^*. Then, the agreement between the fitted and theoretical values of α is correct. The difference of 20-30% between the α estimates, reported in the literature [15, 25], seems probably due to the uncertainty on ν^*.

Fig. 4 gives a log-log plot of the VAF versus reduced time for the LJ fluid near critical point. A linear fit of the data in the range $9 < t^* < 15$ gives : $\log \mathrm{vaf}(t) = (-3.66 \pm 0.05) - (1.53 \pm 0.02) \log t^*$, leading to a value of $\alpha_{fit} = 0.0258 \pm 0.0015$. Similarly to the previous system, the computation of the diffusion coefficient and kinematic viscosity gives the values: $D^* = 0.620 \pm 0.007$ and $\nu* = 1.20 \pm 0.06$. The stress tensor correlation function versus reduced time is given in Fig. 5 together with its integral. Thus incorporating these values of D^* and $\nu*$ into Eq. (1) leads to a value of $\alpha_{cal} = 0.02$. The difference between the fitted and calculated values amounts in this case to 13% which stays within the statistical and systematic errors on ν^* following the discussion made above. This result confirms the universality of the $t^{-3/2}$ behaviour at long times of the VAF also in the temperature and density domain close to the liquid-vapour critical point.

V. CONCLUSION

The velocity autocorrelation function has been computed by constant energy MD simulations for a fluid of soft-repulsive particles at low density and for a LJ system near the critical point. By using larger systems, and by correlating over a longer time than those used of the literature [15, 16], we show that the velocity autocorrelation function presents the universal asymptotic behaviour $\alpha t^{-3/2}$ as predicted by the theory. The uncertainty between the computed and fitted values of the amplitute α of the asymptotic part of the VAF is mainly due to the uncertainty in the computation of the kinematic viscosity.

These results remove all the ambiguities related to the existence of the long time tail in almost all domain of the fluid phase. However, close to triple point, the onset of long-lived damped oscillations in the VAF due to the backscattering of particle by their next neighbours [23], precludes the computation of the long time tail. Therefore the observation of the VAF asymptotic behaviour in these thermodynamic states stays a challenge.

[1] B. J. Alder and T. E. Wainwright, Phys. Rev. A **1**, 18 (1970).

[2] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases, 3rd ed.*, (Cambridge University Press, Cambridge, 1970).

[3] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[4] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. **25**, 1254 (1970); J. Stat. Phys. **15**, 7 (1970); J. Stat. Phys. **15**, 23 (1970); Phys. Rev. A **4**, 2055 (1971).

[5] M. H. Ernst, arXiv:cond-mat/0501638 (2005).

[6] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A **6**, 776 (1972); Phys. Rev. A **12**, 292 (1975).

[7] J. P. Boon and A. Bouiller, Phys. Lett. **55A**, 391 (1976).

[8] G. L. Paul and P. N. Pusey, J. Phys. A **14**, 3301 (1981).

[9] J. X. Zhu, D. J. Durian, J. Muller, D. A. Weitz, and D.J. Pine, Phys. Rev. Lett. **68**, 2559 (1992).

[10] M. H. Kao, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **70**, 242 (1993).

[11] A. Widom, Phys. Rev. A **3**, 1394 (1971).

[12] R. Zwanzig and M. Bixon, Phys. Rev. A **2**, 2005 (1970); J. Fluid Mech. **69**, 21 (1975).

[13] J. Bose, W. Götze, and M. Lucke, Phys. Rev. A **20**, 1603 (1979).

[14] C. Morkel, C. Gronemeyer, W. Glaser, and J. Bosse, Phys. Rev. Lett. **58**, 1873 (1987).

[15] A. McDonough, S.P. Russo, and I.K. Snook, Phys. Rev. E **63**, 026109 (2001).

[16] K. Meier, A. Laesecke, and S. Kabelac, J. Chem. Phys. **12**, 9526 (2004).

[17] H. van Beijeren, Rev. Mod. Phys. **54**, 195 (1982).

[18] F. den Hollander, Long time tails in physics and mathematics, in Proceedings of the 1993 NATO Advanced Study Institute (1993).

[19] Y. Pomeau, Phys. Rev. A **5**, 2569 (1972); Phys. Rev. A **7**, 1134 (1973).

[20] Y. Pomeau and R. Resibois, Phys. Rep. **19**, 64 (1975).

[21] J.J . Erpenbeck and W. W. Wood, Phys. Rev. A **26**, 1648 (1982).

[22] K. Huang, *Statistical Mechanics*, (Wiley, New York, 1987).

[23] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, (Academic Press, London, 2006).

[24] F. Ould-Kaddour and D. Levesque, Phys. Rev. E **63**, 011205 (2001).

[25] D. Levesque, and W. T. Ashurst, Phys. Rev. Lett, **33**, 277(1974).

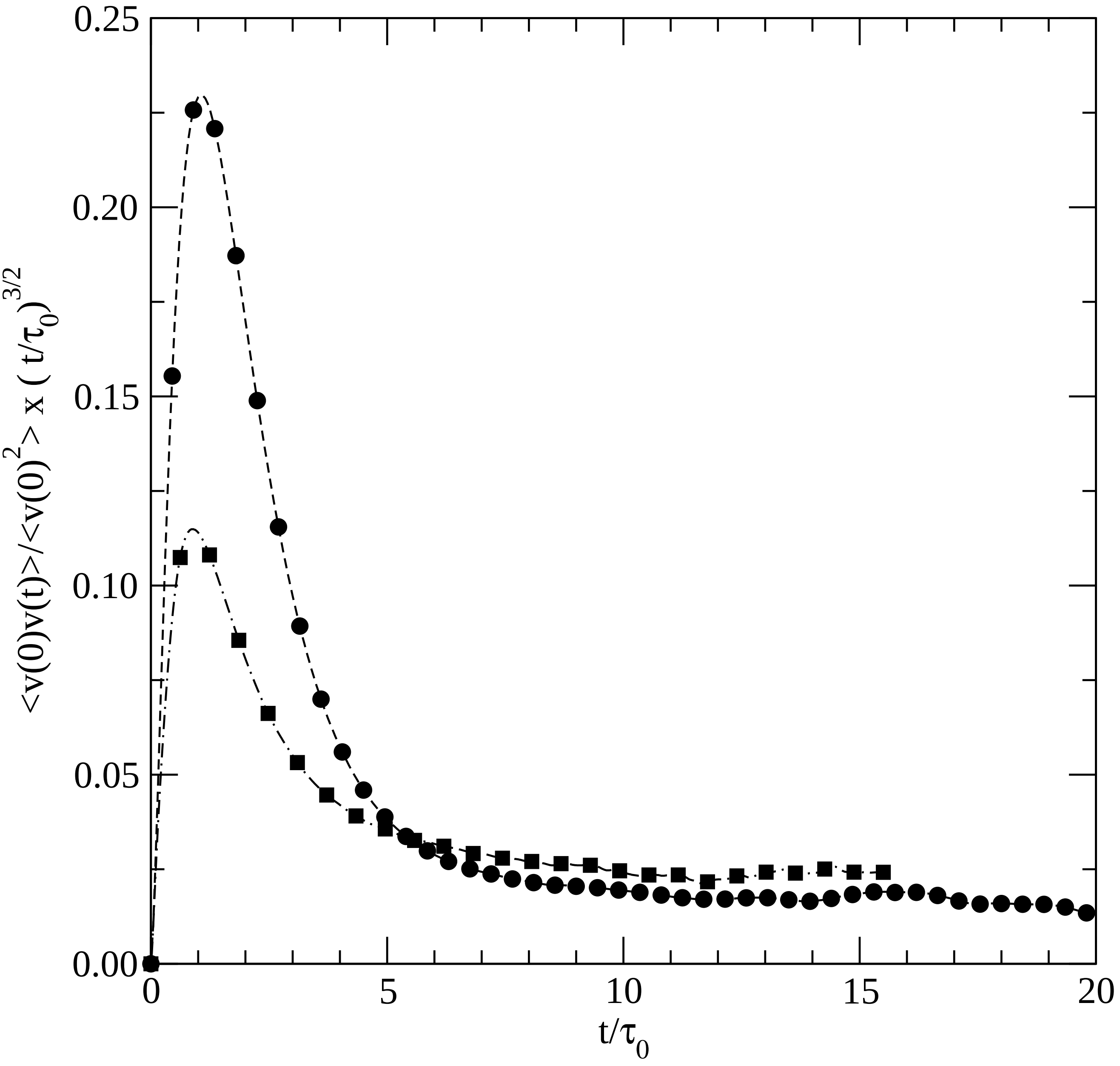

FIG. 1: Plots of the normalized VAF multiplied by $(t/\tau_0)^{3/2}$. Dashed-dotted line and black square : system of soft-repulsive particles at $\rho^* = 0.2$ and $T^* = 2.07$, dashed line and black circle : LJ system at $\rho^* = 0.3$ and $T^* = 1.35$.

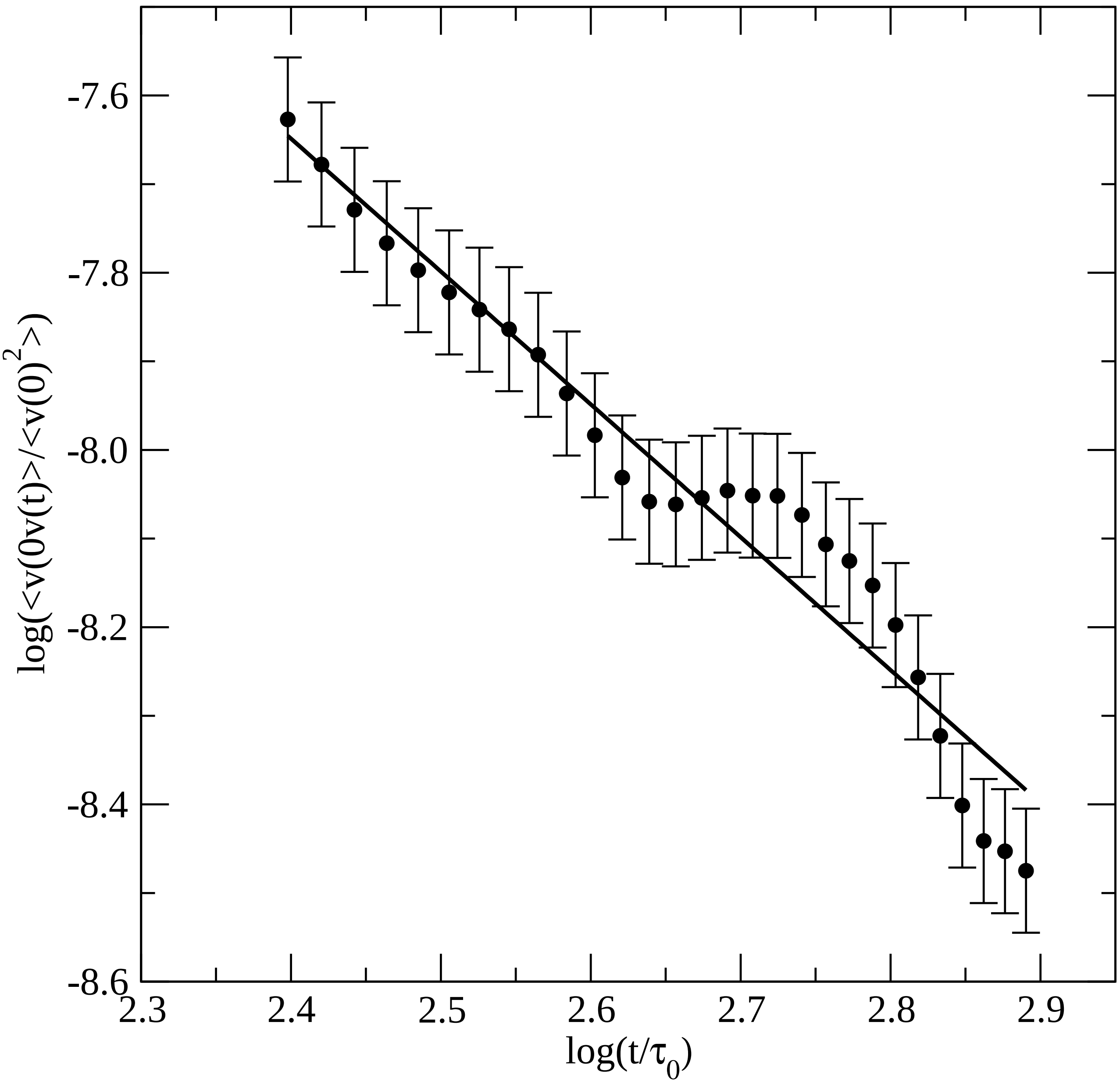

FIG. 2: Log-log plot of the normalized VAF of the soft-repulsive particle system at $\rho^* = 0.2$ and $T^* = 2.07$: black circle and error bars. Thick line : linear fit.

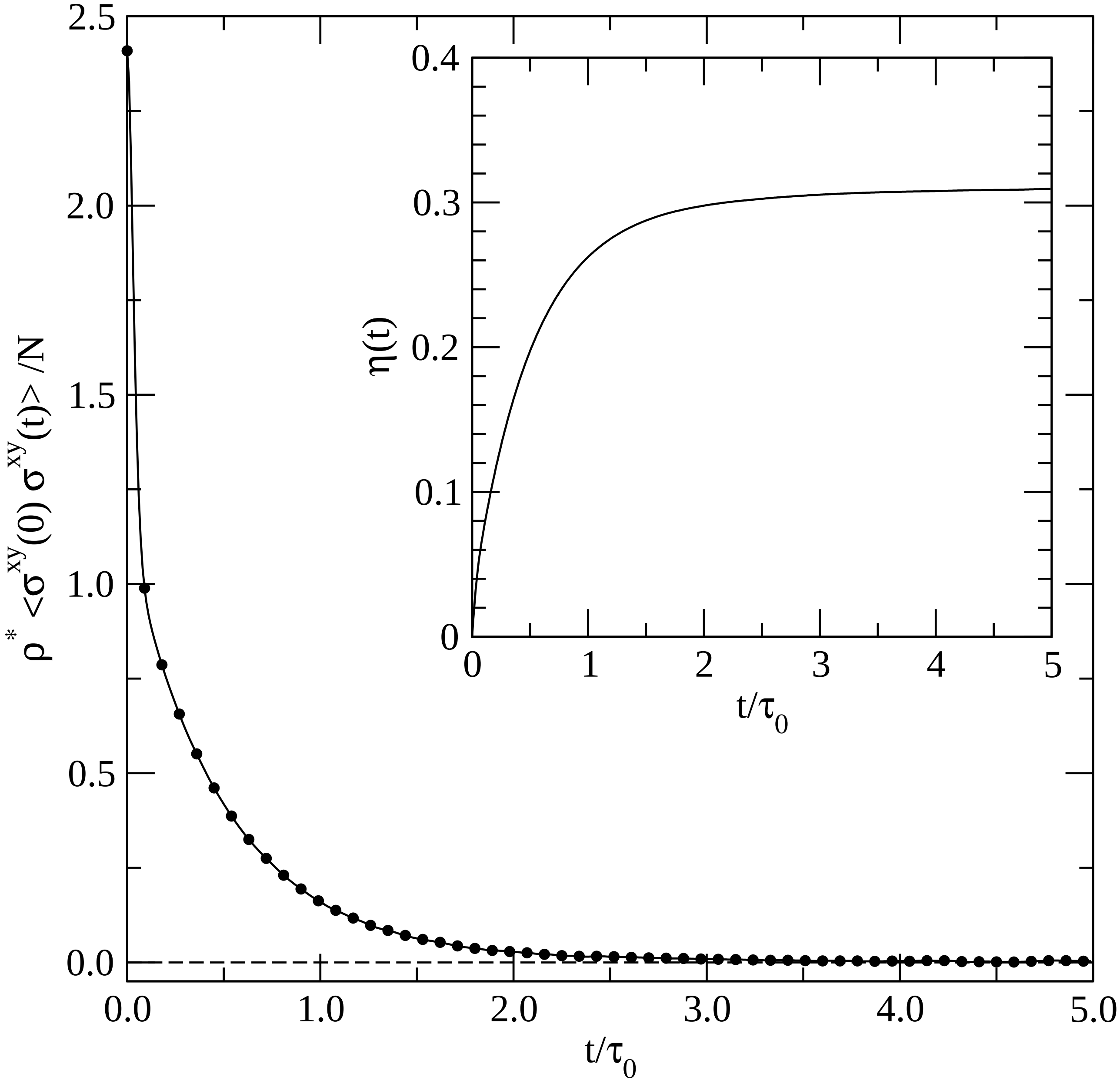

FIG. 3: Stress tensor correlation function versus time for soft-repulsive particle system at $\rho^* = 0.2$ and $T^* = 2.07$: dot and solid line. Inset integral $\eta(t)$.

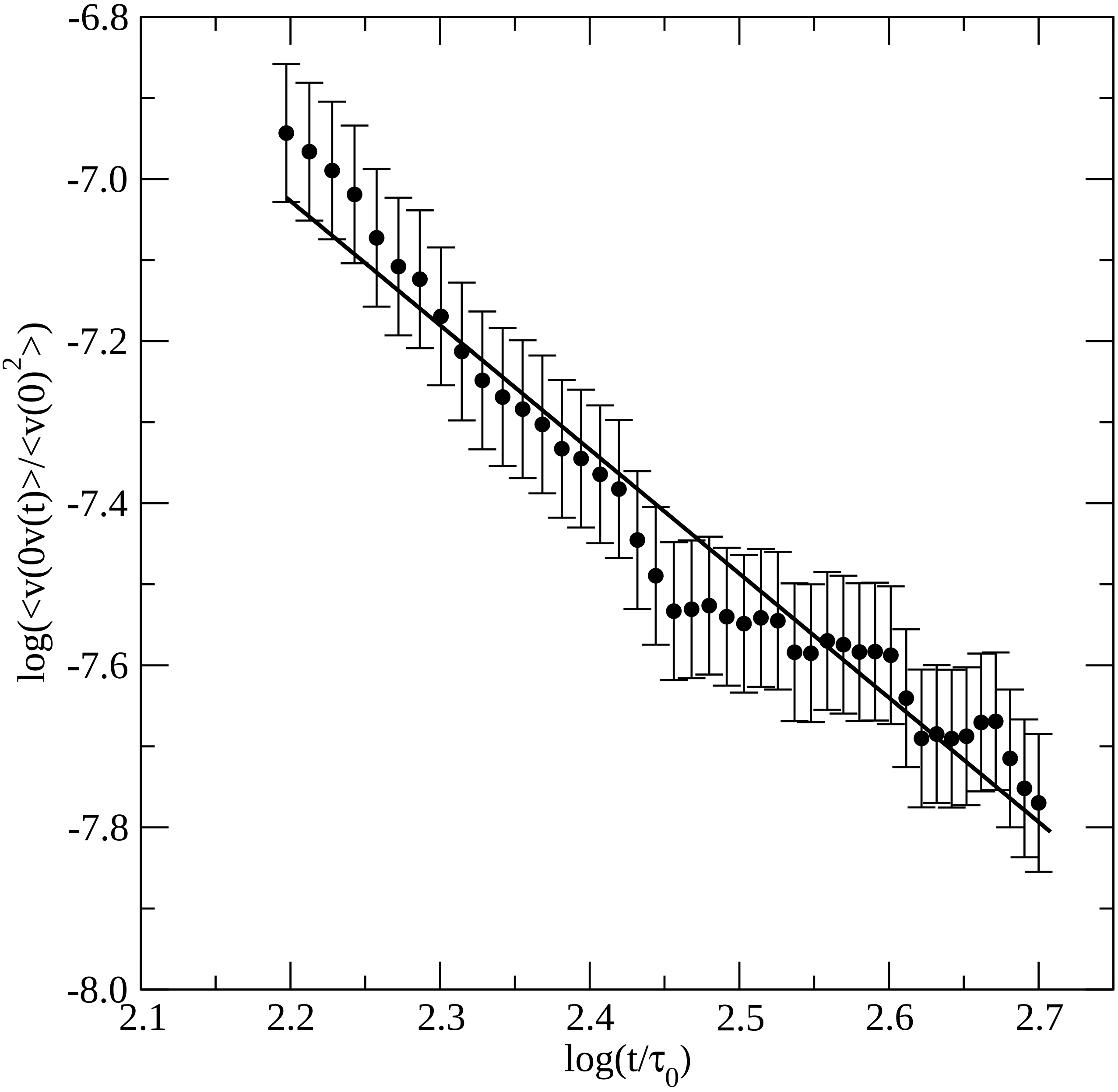

FIG. 4: Log-log plot of the normalized VAF of the LJ system at $\rho^* = 0.3$ and $T^* = 1.35$: black circle and error bars. Thick line : linear fit.

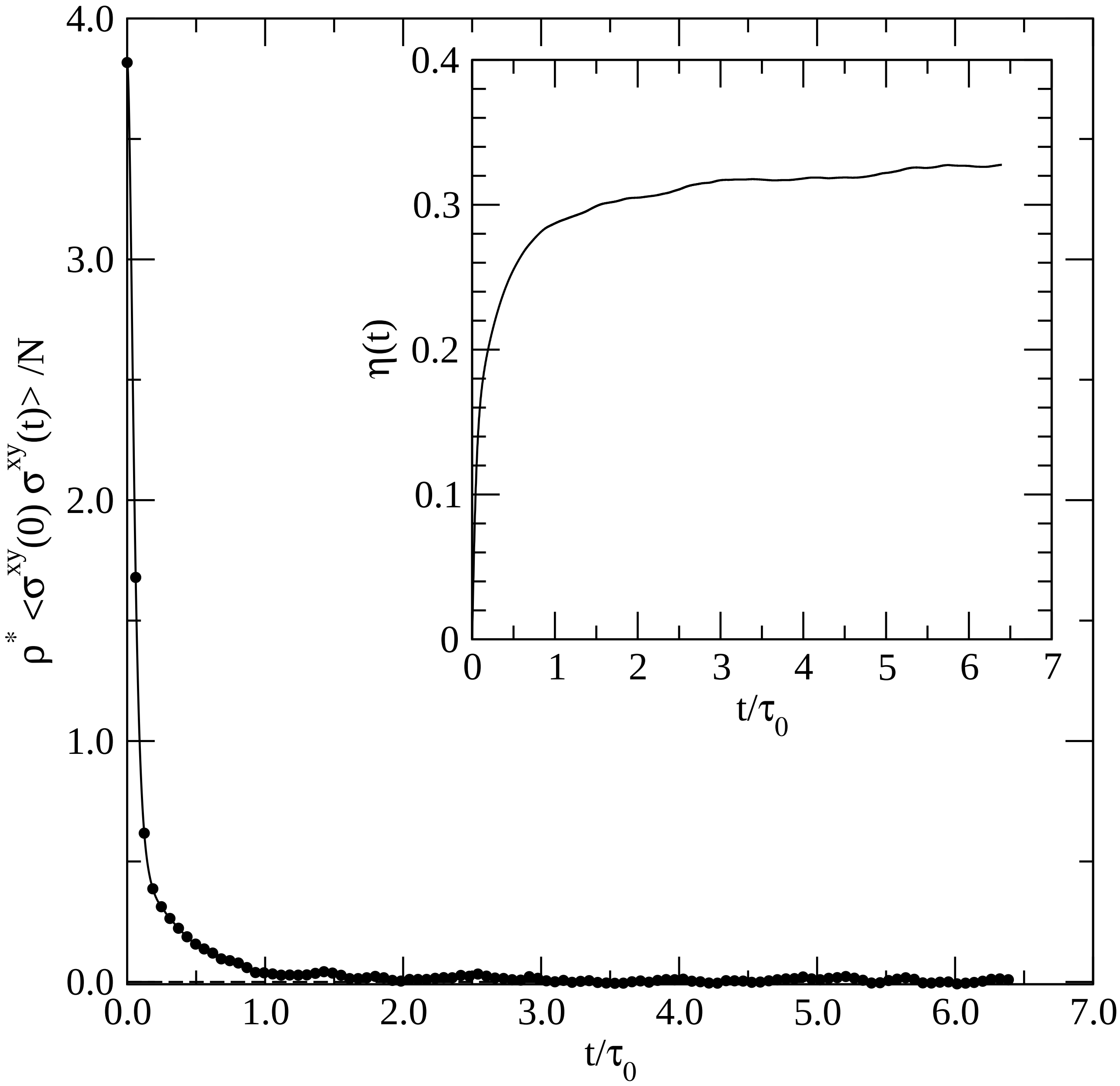

FIG. 5: Stress tensor correlation function versus time for LJ system at $\rho^* = 0.3$ and $T^* = 1.35$: dot and solid line. Inset integral $\eta(t)$.