Velocity autocorrelation function of a Brownian particle

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Abstract. In this article, we present molecular dynamics study of the velocity autocorrelation function (VACF) of a Brownian particle. We compare the results of the simulation with the exact analytic predictions for a compressible fluid from [6] and an approximate result combining the predictions from hydrodynamics at short and long times. The physical quantities which determine the decay were determined from separate bulk simulations of the Lennard-Jones fluid at the same thermodynamic state point. We observe that the long-time regime of the VACF compares well the predictions from the macroscopic hydrodynamics, but the intermediate decay is sensitive to the viscoelastic nature of the solvent.

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1 Introduction

Brownian motion is the random motion of a particle, which is large compared to the solvent molecules, but is not of macroscopic size. It has become a paradigm in various branches of science and remains an active area of research among theoreticians and experimentalists. It is not only a preferred tool of theoretical modeling, but is also extensively used to probe microscopic environments in experiments[23,20,10]. A considerable effort is also spend in investigating transport properties of colloidal suspensions and complex fluids, primarily due to the relevance of such systems in industry, using molecular simulations of Brownian motion [22,13,18,14,8]. Such simulations always invariably involve using discrete particles to explain continuum predictions of theory, and therefore, requires a clear understanding of the molecular and continuum regimes.

In this article, using molecular dynamics simulation, we investigate the velocity autocorrelation function (VACF) of a Brownian particle. We choose a large system size so that the effect of finite-size of the simulation box is small. The internal degrees of freedom of the nanoparticle is also resolved in the simulation, such that stick boundary conditions apply on the surface of the particle[15]. The erratic motion of a Brownian particle exhibits a far more rich behavior than predicted by the simple Langevin picture. In the continuum description, a fluid is well described by the Stokes equation, with the particle dynamics coupled to the solvent through the imposed boundary conditions. The inadequacy of the Langevin picture in describing such erratic motion can be immediately seen from the VACF of the Brownian particle. While a simple exponential decay is predicted at all times in the Langevin model, in reality the decay exhibits distinct features of both continuum, as well as discrete nature of the solvent. Accordingly, we classify the decay in three separate regimes, a short-time regime - where molecular nature of the solvent plays a crucial role, an intermediate regime - governed by the interplay between sound propagation, vorticity diffusion and the viscoelasticity of the solvent, and a long-time regime where the VACF decays as a power law $t^{-d/2}$ ($d$ is the dimension of space) due to the development of the slow viscous patterns in the solvent [1,2,12,6,5]. We compare the results from the simulations with the exact predictions from hydrodynamics, and observe, that, while the decay of the VACF at long times compares well with the predictions from hydrodynamics, the intermediate decay is sensitive to the viscoelastic nature of the fluid and can not be explained by only considering the compressible nature of the fluid.

Using a molecular dynamics simulation to investigate short and long-time dynamics of isothermal Brownian motion is a non-trivial task. The key points in such simulations, are the identification of relevant length and time scales. The two important length scales in the system are the simulation box size $L$ and the radius of the particle $R$. In a typical molecular dynamics simulation periodic boundary conditions are imposed, implying that the dynamics of the particle is effected by the periodic images of the particle. The strength of such finite size effect is determined by the ratio of the two length scales, $R/L$, we have the choice of a small $R$ or large $L$. Both of these choices are unfortunately restricted. While the choice of $L$ is solely determined by the computational resources at hand, the choice of $R$ is determined by a number of factors. Ideally,
one would prefer a clear separation of the time scales in
the simulation, in particular, the sonic time \( \tau_s = R/c \)
and the vorticity diffusion time \( \tau_\nu = R^2/\nu \), both of which
determine the decay of the VACF. A small choice of \( R \) does
not resolve these time scales properly.

The lower bound for \( R \) is determined by the Knudsen
number, defined as the ratio of the mean free path to
the characteristic length scale of the flow – typically, the
diameter of the particle. The Knudsen number decides
whether a continuum or a statistical mechanics description
of the system is appropriate. Besides the length scales, the
time scales involved in a Brownian motion range from the
order of \( 10^{-15} \) s to seconds. The simulation must also be
able to resolve the various time scales in the problem, the
smallest of which is the collision time of solvent molecules
and the largest time scale is the colloid diffusion time, over
which the colloid diffuses over its own radius.

The remainder of the article is organized as follows. In
Section 2 we explain our molecular dynamics simulation
in brief. The transcription of the simulation results with
the exact prediction from the theory is done in Section 3
and an approximate result is presented in Section 4 on page 5.

2 Molecular Dynamics Simulation

In this section, we provide the details of our molecular
dynamics simulation. To begin with, the natural choice of
units is the Lennard–Jones reduced units, where length,
time and energy in units of \( \sigma, \tau = \sqrt{m\sigma^2/\epsilon} \) and \( \epsilon \). Throughout
the article, the numerical values of the physical quantities
are given in reduced units, unless otherwise explicitly
stated.

Our model system is made of a simple Brownian par-
ticle, with internal degrees of freedom resolved, immersed
in a Lennard–Jones solvent. The particles in the system
interact via the Lennard–Jones interaction,

\[
U(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^12.
\]

Additionally, the nearest-neighbor interaction of the atoms
in the spherical cluster of the nanoparticle is the FENE
interaction,

\[
U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \log \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right],
\]

where \( k = 30\epsilon/\sigma^2 \) is the spring constant and \( R_0 = 1.5\sigma \).
In order to keep the finite-size effects from the image particles
to a reasonable value, we choose a large system size with
a total of 256000 particles. The initial configuration of the
system was chosen to be a perfect FCC lattice with velocities
drawn from a Boltzmann distribution. The nanopar-
ticle was obtained from a spherical cut of the FCC lattice.
For the smallest size of the nanoparticle \( (R = 3) \) there
were 177 atoms in the cluster while for largest size of the
nanoparticle \( (R = 5) \) we have 767 atoms in the cluster.

The ratio \( L/R \), which quantifies the finite-size in the
system are 22.5795 and 13.5409 for the \( R = 3 \) and \( R = 5 \),
respectively.

The system was first equilibrated under NPT ensemble,
with the system coupled to a thermostat and barostat,
at a thermodynamic pressure of \( P_0 = 0.01 \) and temperature
\( T_0 = 0.75 \). For the implementation of the NPT en-
semble we chose the \( \alpha \)-Nose–Hoover equations of motion as modified by Melchionna[16].

\[
\dot{\mathbf{r}}_i = \mathbf{v}_i + \alpha (\mathbf{r}_i - \mathbf{R}_0), \quad \dot{\mathbf{v}}_i = \mathbf{F}_i - \left( \alpha + \gamma \right) (\mathbf{r}_i - \mathbf{R}_0) \quad \dot{\gamma} = \nu^2 \left( \frac{T(t)}{T_0} - 1 \right), \quad \dot{\alpha} = \nu^2 \frac{\alpha}{Nk_BT_0} V(p(t) - p), \quad \dot{V} = 3\nu \alpha.
\]

The barostating variable \( \alpha \) can be eliminated between
the last two equations in Eq. (3), and the resulting equa-
tions are then numerically integrated using Leap-Frog in-
tegration scheme[21].

The molecular dynamics simulations were implemented
on Graphics Processing Units (GPU) and is similar to
those of Anderson et. al. [3] and Colberg [7], more closely
resembling the later in the construction of the Verlet list.
We briefly describe our implementation in the following
lines.

We use the atom decomposition method in the simu-
lation, for efficient parallel implementation of our MD code.
Every particle in the simulation is assigned a thread, which
is responsible for updating the coordinates and momenta
of the particle. A GPU optimized cell list algorithm is used
for construction of the Verlet list. For this purpose, the
simulation domain is divided into cubes of size \( r_c \), where
\( r_c \) is the cutoff length scale for the Lennard-Jones poten-
tial (\( r_c = 2.5\sigma \) in the present application). The particles
were first sorted into their respective cells using the paral-
lel radixsort algorithm [7]. To construct of the Verlet list,
the entries of 26+1 cells are copied to the shared memory.
Every cell has an upper limit for the maximum number of
entries, determined by the size of the shared memory on
the GPU. This limitation also prevented us from simulta-
nously copying the particle coordinates to the shared memory.
For a given particle in a cell, an iterative search is
made of the neighboring cells and the particle coordinates
are read from a texture array. The stability and numerical
accuracy of our molecular dynamics code was verified by
outputting the total energy and total momentum of the
system. With an integration time-step \( \delta t = 0.001 \), trajec-
tories of \( 2 \times 10^6 \) steps (corresponding to a physical duration
of 20 ns) were simulated for the data points.

3 Velocity Autocorrelation Function

The long time tails in the VACF can be explained by the
generalized Langevin equation,

\[
\dot{P} = -\frac{1}{M} \int_0^t \zeta(t-t')P(t') + \xi(t)
\]

\( \zeta(t-t') \) is the correlation function of the friction
force, \( \xi(t) \) is a Gaussian white noise with zero mean and
variance \( \sigma^2 \). The parameter \( \zeta(t-t') \) is given by

\[
\zeta(t-t') = \frac{\nu^2}{m} \left( \frac{T(t)}{T_0} - 1 \right) \delta(t-t'),
\]

where \( \nu^2 \) is the viscous shear modulus and \( T(t) \)
is the temperature at time \( t \). The function \( \zeta(t-t') \) is
a memory function that describes the interaction between
the particle and the surrounding medium. The function
\( \zeta(t-t') \) is a delta function, which indicates that
the interaction between the particle and the surrounding
medium is instantaneous. The function \( \xi(t) \) is a Gaussian
white noise, which describes the random fluctuations
in the surrounding medium. The function \( \xi(t) \) is zero
mean, which indicates that the fluctuations in the
surrounding medium are random. The function \( \xi(t) \)
is Gaussian, which indicates that the fluctuations in the
surrounding medium are normally distributed.

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the particle and the surrounding medium is instantaneous.

The zero-frequency limit of Eq.(6) produces the Stokes-Einstein relation 

$$D = k_B T \zeta_0, \quad \text{Transforming back to real time, the normalized VACF of the Brownian particle is given by}$$

$$\tilde{C}(t) = \frac{1}{M} \int_0^t \zeta(t-t') C(t') \, dt', \quad (5)$$

which, in the frequency space is written as,

$$\tilde{C}(\omega) = C(0) \left(-i\omega + \tilde{\zeta}(\omega) \right)^{-1} \equiv C(0) Y(\omega). \quad (6)$$

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$$\frac{C(t)}{C(0)} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} R e[Y(\omega)] \cos(\omega t) \quad (7)$$

For an incompressible fluid, the frequency dependent friction coefficient is given by [12,24]:

$$\tilde{\zeta}(\omega) = 6\pi \eta_0 R (1 + R(-i\omega/\nu)^{1/2} - (i\omega R^2/9\nu)), \quad (8)$$

where, \(\eta_0\) and \(\nu\) are the steady-state dynamic and kinematic viscosities of the solvent, respectively. The square-root singularity in Eq.(8) gives rise to the power law decay of the VACF at long times. Because of the incompressibility condition, the equal-time value of the VACF suffers a discontinuity from the equipartition value of \(k_B T/M\) to \(k_B T/M^*\), with the effective mass \(M^*\) given by \(M^* = M + M_f/2\). \(M_f\) is the mass of the displaced fluid.

In simulations, however, the discontinuity is not observed due to the finite compressibility of the fluid [21,16]. In a compressible solvent, the sound propagation occurs with a finite speed, and the solvent surrounding the colloid is not instantly set in motion. A fraction of the energy of the Brownian particle is thus spent in creating these sound waves. To account for the compressibility effect of the solvent, we need to consider the Boussinesq force for unsteady motion in a compressible solvent [21,16]. For this purpose, we consider the frequency dependent friction coefficient presented in the works of Chow et. al. [6]. For simplicity, we follow the notations in [6]. In terms of the vorticity diffusion time \(\tau_v = R^2/\nu\) and the sonic time \(\tau_c = R/c\), \(\tilde{\zeta}(\omega)\) is written as

$$x = i\sqrt{i\omega \tau_c}, \quad y = i\omega \tau_c \left[1 - \frac{i\omega \tau_c^2 (\mu + (4/3)\eta)}{\tau_v \eta} \right]^{1/2} \tilde{\zeta}(\omega) = -\frac{4}{3} \pi \eta R x^2 [(1 - y)Q + 2(x - 1)P], \quad (9)$$

where \(P\) and \(Q\) are functions of the dimensionless variables \(x\) and \(y\). We refer the readers to [6], for an explicit expression of these functions. Substituting Eq. (9) in Eq. (5), and subsequently using Eq. (7), we obtain the normalized VACF in real time.

The physical parameters which enter Eq. (9) were determined from separate molecular dynamics simulations of the bulk Lennard-Jones fluid at the same thermodynamic state point. The shear viscosity \(\eta\) and the bulk viscosity \(\mu\) were estimated from the off-diagonal and diagonal components of the stress tensor and using the Green-Kubo formula,

$$\eta(t) = \frac{V}{k_B T} \int_0^t \langle \sigma_{xy}(t') \sigma_{xy}(0) \rangle \, dt' \quad (10)$$

$$\mu(t) = \frac{V}{k_B T} \int_0^t \langle \delta p(t') \delta p(0) \rangle \, dt' \quad (11)$$

The infinitesimal limit of Eq. (10) and Eq. (11) provided the steady state values of the shear and bulk viscosity, \(\eta_0\) and \(\mu_0\), respectively. The adiabatic sound speed in the solvent was estimated from the relation

$$c^2 = \frac{\gamma}{\rho m c^2 T}, \quad (12)$$

where \(\gamma\) is the ratio of the specific heats \(C_P/C_V\), \(\rho\) is the density of the solvent, \(m\) is the mass of the solvent particles and \(c^2\) is the isothermal thermal compressibility.

Before we compare the results of the molecular dynamics simulations with the predictions from hydrodynamics, the assumptions of the macroscopic theory needs to validated. The crucial assumption which enters the theory is the boundary condition on the surface of the particle. While Eq. (9) assumes a stick boundary condition on the particle surface, such an assumption may break down in a microscopic scale. To validate this we measured the friction coefficient for different radius of a rough Brownian particle. In figure [1] we show this dependence of the friction coefficient on the radius of the Brownian particle and compare it with predictions from Stokes law with stick and slip boundary condition. The reasonable agreement of the steady-state friction coefficient with the Stokes law \(\zeta_0 = 6\pi \eta_0 R\) indicates that hydrodynamic boundary conditions applicable on the surface of the sphere are those of stick boundary conditions. Additionally, the Knudsen number (Kn) for the system was determined by measuring the mean-free path of the solvent from the ballistic regime of the solvent mean-square displacement. The Knudsen number determines whether a statistical mechanics or a continuum description is more appropriate for the system and for large values of Kn (typically Kn > 0.1), deviations from the continuum description become relevant. The measured values of Kn were Kn = 0.02261 and Kn = 0.01366, for R = 3 and R = 5, respectively, which indicates that the assumptions in the macroscopic hydrodynamics remains valid in the present scenario.

3 When the radius of the Brownian particle is comparable to the size of the solvent particles, the Stokes-Einstein relation with standard stick or slip boundary conditions can break down and a non-standard boundary condition may be required [15]. However, for the particle sizes for which the velocity autocorrelation function has been investigated in the present article, stick boundary conditions are valid as depicted in Figure [1].
Moreover, due to the periodic boundary condition imposed in the simulations, the data suffers from finite-size effects from the long-ranged flow field of the image particles. We chose a sufficiently large simulation box, so that the artifact of the image particles is small. To substantiate this, we performed simulations with two different box lengths, \( L = 68 \) and \( L = 87 \), the result of which is depicted in the Figure 2. The measured velocity autocorrelation functions does not exhibit pronounced finite-size effects, particular in the intermediate regime of interest.

To compare the results from the simulation with the theoretical predictions for the VACF, the numerical evaluation of Eq. (7) was first carried out with the steady state values of the shear viscosity. However, we observed that the intermediate decay of the VACF can not be accurately described by only treating the solvent as compressible and it was essential to consider the viscoelastic nature of the solvent [24]. As already pointed out in [11], the interaction of a colloid in a viscoelastic solvent can be visualized by considering the colloid connected to the fluid by a dashpot and spring in series. At times larger than \( \tau_r \), the viscous dissipation is represented by the dashpot, while at shorter times the colloid interacts with the fluid via elastic forces. This caging effect is more pronounced when the ratio of the mass of the Brownian particle to the solvent particles is small [17]. To this end, we model the Lennard-Jones solvent as Maxwell fluid with the frequency dependent viscosity given by

\[
\tilde{\eta}(\omega) = \eta_0/(1 - i\omega\tau),
\]  

where \( \eta_0 \) is the steady-state shear viscosity of the solvent (\( \omega = 0 \) component). The relaxation time \( \tau \) is related to the infinite frequency shear modulus \( G_\infty \) as \( \tau = \eta_0/G_\infty \).

For a Lennard-Jones solvent, the single exponential relaxation in Eq. (13) ignores the algebraic decay of the stress autocorrelation at long times. This is also evident from the time dependent viscosity obtained from the simulation using Eq. (10). To illustrate this more clearly, we plot the variation of the quantity \( 1 - \eta(t)/\eta_0 \) with time in Fig. 3. The two distinct decays shown in Fig. 3 can be modelled as simple exponential with decay times \( \tau_1 \) and \( \tau_2 \). To determine the VACF in the intermediate regime using Eq. (7) and Eq. (9), we use \( \tau_2 \) as the relaxation time for the model fluid. Since the colloid is made of discrete number of particles, the radius of the sphere \( R \) was determined from the radius of gyration using the relation

\[
\langle R^2_g \rangle = \frac{1}{N} \sum_r (\mathbf{r}_r - \mathbf{R}_{CM})^2 = \frac{3}{5} R^2.
\]
Decay of the velocity autocorrelation function of a Brownian particle for two particle radius $R = 5$ (□) and $R = 3$ (○). The solid-line is numerical evaluation of the normalized VACF using Eq. (7) and Eq. (8) together with a frequency dependent viscosity (Eq. (13)). The decay in the intermediate regime is sensitive to the viscoelastic nature of the solvent, and can not be accurately described using only the assumption of compressible fluid (see inset). The dashed line in the inset is the numerical evaluation with a constant viscosity.

| Physical quantities | From bulk simulation | Value used in numerical evaluation |
|---------------------|----------------------|----------------------------------|
| $\eta$              | $2.79961 \pm 0.12963$| $2.79961$                        |
| $\mu$               | $0.78556 \pm 0.07442$| $0.78561$                        |
| $c$                 | $5.18256 \pm 0.05225$| $5.15444$                        |

Table 1. Comparison of the numerical values of the physical quantities $\eta$, $\mu$ and $c$, obtained from the bulk simulations of Lennard–Jones fluid and from best fit of the simulated VACF using Eq. (7). We note, that the values of these parameters agree within statistical error bars.

In the numerical evaluation of the VACF, we observed that the radius of the particle which gives a more accurate fit to the data was close to $R + \sigma / 2$, where $\sigma$ is the diameter of the Lennard–Jones fluid particles. The values of $R$ used were 5.35 and 3.33 compared to the value of $R + \sigma / 2 = 5.37$ and $R + \sigma / 2 = 3.42$, respectively. In Table 1 we compare the numerical values of the physical quantities $\eta$, $\mu$ and $c$ for a bulk Lennard–Jones fluid and those which provided the best fit to the simulated velocity autocorrelation function using Eq. (7). Additionally, the mass of the colloidal particle was always taken as the reduced mass of the system.

**4 Approximate Result for the VACF**

The inverse transformation of Eq. (7) is only possible numerically and an exact closed form analytical expression for the VACF is difficult. However, an approximate result can be formulated using the argument of time-scale separation between $\tau_c$ and $\tau_v$. The sound waves created in the solvent always precedes the development of slow viscous patterns, with $\tau_c$ usually an order of magnitude larger compared to $\tau_v$. Assuming this time scale separation, the complete decay of the VACF can be constructed by a simple addition of the VACF at short and long-time regime.

In the long-time regime, following [12][19], the normalized VACF of a Brownian particle can be written as:

$$M(V(t)V(0))/k_BT = \frac{2\rho_c}{3\rho_f} \frac{1}{3\pi} \int_0^\infty dx \frac{e^{-xt/\tau_c}x^{1/2}}{1 + \sigma_1 x + \sigma_2 x^2}$$

(15)

with $\sigma_1 = (1/9)(\pi - 4\rho_c/\rho_f)$ and $\sigma_2 = (1/3)(1 + 2\rho_c/\rho_f)^2$. In Eq. (15), $\rho_c$ is the density of the colloid and $\rho_f$ is the density of the fluid. At $t = 0$, the integral gives the value $\pi(1 - \sqrt{\sigma_1^2 - 4\sigma_2})/\sqrt{2(\sigma_1 - \sqrt{\sigma_1^2 - 4\sigma_2})}$, and the right-hand side of Eq. (15), after simplification, becomes $(2\rho_c/\rho_f)(1 + 2\rho_c/\rho_f)$, producing the well known discontinuity. The discontinuity is quite easily removed when we take into account the finite compressibility of the fluid. To this end, we consider the general expression of Zwanzig [25],

$$M(V(t)V(0))/k_BT = e^{-\alpha_1 t/\tau_c} \left[ \frac{\alpha_2 t}{\tau_c} \right] \frac{\cos \left( \frac{\alpha_2 t}{\tau_c} \right)}{\sin \left( \frac{\alpha_2 t}{\tau_c} \right)}$$

(16)

with $\alpha_1 = (1 + \rho_f/2\rho_c)$ and $\alpha_2 = (1 - \rho_c^2/4\rho_f^2)^{1/2}$. For a neutrally buoyant particle ($\rho_c = \rho_f$) the two contribution takes the form

$$\langle V(t)V(0) \rangle = \frac{2k_BT}{3M} \frac{1}{3\pi} \int_0^\infty dx \frac{e^{-xt/\tau_c}x^{1/2}}{1 + x^3 + x^2/9}$$

(17)
and

$$\langle V(t)V(0) \rangle = \frac{K_B T}{3M} e^{-\langle 3/2 \rangle(t/t_c)} \left[ \cos \left( \frac{\sqrt{3}t}{2\tau_c} \right) - \sqrt{3} \sin \left( \frac{\sqrt{3}t}{2\tau_c} \right) \right]$$

(18)

To a first order, the complete VACF of a colloidal particle can be described by a simple addition of Eq.(17) and Eq.(18):

$$\langle V(t)V(0) \rangle = \frac{2k_BT}{3M} \frac{1}{3\pi} \int_{0}^{\infty} dx \frac{e^{-xt/t_c} x^{1/2}}{1 + x^3 + x^2/9}$$

$$+ \frac{K_B T}{3M} e^{-\langle 3/2 \rangle(t/t_c)} \left[ \cos \left( \frac{\sqrt{3}t}{2\tau_c} \right) - \sqrt{3} \sin \left( \frac{\sqrt{3}t}{2\tau_c} \right) \right]$$

(19)

In Fig.6, we compare the normalized VACF of the Brownian particle with the theoretical predictions obtained by addition of Eq.(15) and Eq.(16).

Finally, we compare the VACF of a Brownian particle in the intermediate regime in Fig.6. The intermediate decay, between the molecular collision time and the sonic time, is clearly sensitive to the viscoelastic nature of the fluid.

In conclusion, using molecular dynamics simulations, we have investigated the decay of the velocity autocorrelation function (VACF) of a colloid in a Lennard-Jones solvent. The numerical values of the shear and kinematic viscosities and the speed of sound, which determine the decay, were obtained from separate simulations of the bulk Lennard-Jones fluid at the same thermodynamic state point. These values were used to determine VACF from the exact analytical prediction. Accordingly, we divide the complete decay in three regimes, a short-time regime where the discrete nature of the fluid plays an important role, an intermediate regime - governed by the interplay between sound propagation, vorticity diffusion and viscoelasticity of the fluid and a long-time regime of algebraic decay due to vorticity diffusion. We observe that the decay in the intermediate regime can not be accurately described by only considering the compressibility of the fluid, but the viscoelastic nature of the solvent should also be taken into account.

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