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Abstract. – The equilibrium statistics of quantities computed by means of DPD (dissipative particle dynamics) are usually very sensitive to the time step used in the simulation. In this letter we show how to eliminate this sensitivity by considering the irreversible dynamics in DPD as the limiting case of a thermostat that leaves Maxwell-Boltzmann distribution invariant even for finite time steps. The remaining dependency on time step is solely due to the discretization of the conservative part of the dynamics and is independent of the thermostat.

Introduction. – Dissipation particle dynamics (DPD) is a particle-based simulation technique. It was originally proposed to simulate fluids on a mesoscopic scale [1]. A DPD particle models a blob of atoms that have effective, soft interactions. By means of dissipative and fluctuating pair-forces, the equilibrium state of the system is made to satisfy the Boltzmann distribution. Alternatively, one can view upon DPD as a thermostatic scheme in a molecular dynamics (MD) code. In this case, the (conservative) interactions need not be soft.

Because DPD is particle-based, it does not have problems associated with the use of a grid such as, *e.g.*, lattice Boltzmann simulations. It is Galilean invariant and momentum is conserved. This is different from Brownian dynamics, Stokesian dynamics and the Andersen thermostat. Different from to the Nosé-Hoover thermostat, the DPD thermostating occurs locally in space through pair interactions. Therefore, the dynamics is expected to be more realistic.

A drawback of DPD is that the results of the simulation depend on the chosen time step. None of the DPD schemes proposed up to now give the exact Boltzmann distribution when a finite time step is used. Lowe [2] has introduced a scheme that is similar to the Andersen thermostat, but considers relative velocities of nearby pairs instead of the velocity of individual particles. This scheme gives the Boltzmann distribution, even for finite time steps. It has similar characteristics as DPD, but is not equivalent. In this paper we show how to generalise the ideas of Lowe. The resulting scheme always gives correct equilibrium statistics and reduces to the DPD equations in the limit of zero time step.

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In DPD the equations of motion for particle i have the form [1,3]

$$\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \frac{\boldsymbol{p}_i}{m_i},$$

$$\mathrm{d}\boldsymbol{p}_i = \left[\boldsymbol{f}_i^{\mathrm{C}} - \sum_j \gamma\boldsymbol{\omega}(\boldsymbol{r}_{ij}) \cdot \boldsymbol{v}_{ij}\right]\mathrm{d}t + \sum_j \sqrt{2kT\,\gamma\,\boldsymbol{\omega}(\boldsymbol{r}_{ij})} \cdot \mathrm{d}\boldsymbol{W}_{ij}, \tag{1}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and $\boldsymbol{v}_{ij} = \boldsymbol{v}_i - \boldsymbol{v}_j$.

A dissipative, or frictional, force acts between pairs of particles and is proportional to the relative velocity. It depends on the connecting vector by means of the tensor $\boldsymbol{\omega}(\boldsymbol{r}_{ij})$. In this paper we consider the commonly used form

$$\boldsymbol{\omega}(\boldsymbol{r}_{ij}) = \omega(r_{ij})\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}, \qquad \text{with} \qquad \omega(r) = \max(1 - r/r_{\mathrm{c}}, 0)^2, \tag{2}$$

where r_{ij} is the length of the connecting vector, $\hat{\boldsymbol{r}}_{ij}$ is the unit vector pointing in its direction and r_{c} is the characteristic interaction length.

The last term in eq. (1) is the fluctuating, or Brownian, force. Here $\mathrm{d}\boldsymbol{W}_{ij}$ is a time differential of a Wiener process. For one pair $\mathrm{d}\boldsymbol{W}_{ij} = -\mathrm{d}\boldsymbol{W}_{ji}$. An increment of the Wiener process, $\Delta\boldsymbol{W}_{ij}$, is a normally distributed random variable with variance $\langle\Delta\boldsymbol{W}_{ij}\Delta\boldsymbol{W}_{ij}\rangle = \boldsymbol{I}\Delta t$ and zero mean. For different pairs the Wiener processes are statistically independent. Time increments over non-overlapping time intervals are also statistically independent.

The dissipative and the fluctuating term are related via a fluctuating-dissipation relation. As a result, the DPD equations in the differential sample the canonical ensemble. In practice, a finite time step discretization of the equations of motion is used. One usually finds a (large) dependency of equilibrium properties on the chosen time step [4].

The generalised Lowe thermostat. – To eliminate this time step dependence, we will introduce a new approach for deriving the DPD equations, starting from the Lowe thermostat [2]. In the Lowe thermostat, one considers two particles i and j and re-equilibrates their relative momentum using the Maxwell-velocity distribution. The thermostat leaves the total momentum of the two-particle system unchanged. Another way of stating this is that the centre-of-mass velocity of the two-particle system remains unchanged.

By splitting off the centre-of-mass velocity explicitly, one can rewrite the velocity of particles i and j as

$$\boldsymbol{v}_i = \boldsymbol{v}_{\mathrm{cm},ij} + \frac{\mu_{ij}}{m_i}\mathrm{v}_{ij}, \qquad \boldsymbol{v}_j = \boldsymbol{v}_{\mathrm{cm},ij} - \frac{\mu_{ij}}{m_j}\mathrm{v}_{ij}, \quad \text{where} \quad \frac{1}{\mu_{ij}} = \frac{1}{m_i} + \frac{1}{m_j}, \tag{3}$$

$\boldsymbol{v}_{\mathrm{cm},ij}$ is the centre-of-mass velocity of the two particles and μ_{ij} the reduced mass. In his paper Lowe considers pairs that have the same mass, but we have generalised this a little bit by allowing for different masses.

Since the thermostat leaves the centre-of-mass velocity unchanged, it is useful to rewrite the two-particle Maxwell-Boltzmann distribution by using eq. (3) as

$$\exp\left[-\frac{m_i v_i^2 + m_j v_j^2}{2kT}\right] = \exp\left[-\frac{(m_i + m_j)\boldsymbol{v}_{\mathrm{cm},ij}}{2kT}\right]\exp\left[-\frac{\mu_{ij}\boldsymbol{v}_{ij}^2}{2kT}\right]. \tag{4}$$

This shows that distribution of the centre-of-mass velocity and of the relative velocity are statistically independent.

From eq. (4) combined with eq. (3), one can deduce a recipe to fully re-equilibrate the relative velocity, but leaving the total momentum of the two-particle system unchanged. The

recipe is to first compute the centre-of-mass of the two-particle system and next draw the relative velocity from a normal distribution with variance $kT/\mu_{ij}\boldsymbol{I}$. The new velocities v_i and v_j can be constructed by means of eq. (3) by using the unchanged centre-of-mass velocity and the freshly drawn relative velocity. If one wants the scheme to conserve angular momentum only the relative velocity component in the direction of the connecting, $\hat{\boldsymbol{r}}_{ij}$, vector should be re-equilibrated. In this case, the scheme (in terms of momenta instead of velocities) is

$$\tilde{\boldsymbol{p}}_i := \boldsymbol{p}_i + \mu_{ij}\big(-(\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}) + v_{ij}^{\mathrm{EQ}}\big)\hat{\boldsymbol{r}}_{ij}\,,$$
$$\tilde{\boldsymbol{p}}_j := \boldsymbol{p}_j - \mu_{ij}\big(-(\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}) + v_{ij}^{\mathrm{EQ}}\big)\hat{\boldsymbol{r}}_{ij}. \tag{5}$$

Here the tilde indicates the equilibrated values. The quantity v_{ij}^{EQ} is drawn from a normal distribution with variance kT/μ_{ij}.

The scheme eq. (5) is the core operation in the Lowe thermostat. The full procedure proposed by Lowe [2] is to find all pairs with $r_{ij} < r_{\mathrm{c}}$, where r_{c} is an interaction radius. For all these pairs one decides with probability $\Gamma\Delta t$ to perform eq. (5) or not.

Here we propose a new scheme that uses a generalisation of eq. (5) as its core operation. Instead of performing a full re-equilibration of the relative velocity, we perform a partial re-equilibration,

$$\tilde{\boldsymbol{p}}_i := \boldsymbol{p}_i + \mu_{ij}\big(-\alpha(\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}) + \sqrt{2\alpha-\alpha^2}\,v_{ij}^{\mathrm{EQ}}\big)\hat{\boldsymbol{r}}_{ij}\,,$$
$$\tilde{\boldsymbol{p}}_j := \boldsymbol{p}_j - \mu_{ij}\big(-\alpha(\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}) + \sqrt{2\alpha-\alpha^2}\,v_{ij}^{\mathrm{EQ}}\big)\hat{\boldsymbol{r}}_{ij}, \tag{6}$$

where $0 < \alpha < 1$. For $\alpha = 1$, one recovers the Lowe method.

Similarly to eq. (5), this scheme leaves the centre of mass of the two-particle system unchanged. Also the relative velocity in the two directions perpendicular to $\hat{\boldsymbol{r}}_{ij}$ remains unchanged. Only the relative velocity in the $\hat{\boldsymbol{r}}_{ij}$ is changed. In this direction one finds that

$$\tilde{v}_{ij} := (1-\alpha)v_{ij} + \sqrt{2\alpha-\alpha^2}\,v_{ij}^{\mathrm{EQ}}. \tag{7}$$

We claim that, when v_{ij} obeys the Maxwell-Boltzmann distribution, also the new relative velocity obeys this distribution. The sum of two independent Gaussian variables is also normally distributed. This means that we only have to consider the variance (and the mean which is zero) to proof the claim,

$$\langle\tilde{v}_{ij}^2\rangle := (1-2\alpha+\alpha^2)\langle v_{ij}^2\rangle + (2\alpha-\alpha^2)\frac{kT}{\mu_{ij}}\,. \tag{8}$$

When $\langle v_{ij}^2\rangle = kT/\mu_{ij}$, also $\langle\tilde{v}_{ij}^2\rangle = kT/\mu_{ij}$. Furthermore, when applying eq. (6) in an iterative manner starting from a non–Maxwell-Boltzmann distribution, the resulting distribution for the relative velocity will converge toward the Maxwell-Boltzmann distribution. Since it only acts on momenta, it does not change the spatial part of Boltzmann distribution and therefore the full Boltzmann distribution is invariant under the transformation.

The combination of the instantaneous partial re-equilibration using eq. (6) at discrete times and the exact solution of the equations of motion given by the Hamiltonian for the time intervals in between builds the full Boltzmann distribution. (An extra constraint on the final distribution is that the total momentum is an invariant.)

The advantage of this partial re-equilibration compared to the full re-equilibration of the Lowe scheme is that one can choose the variable α. This variable α replaces the re-equilibration

frequency Γ in the Lowe scheme. It is possible to make α depend on the distance between pairs of particles and on the time step, Δt, in a simulation. Due to this, one can easily choose α such that in the limit $\Delta t \to 0$ the DPD equations are recovered.

The new scheme and the Lowe scheme (with a position-dependent Γ) cannot be made equivalent. The reason is that in the Lowe scheme all moments of the velocity will converge toward the equilibrium value with a rate proportional to Γ. In DPD higher-order moments converge with a rate that is approximately $n\omega$, where n is the order of the moment. There is probably no pressing physical reason to prefer one scheme above the other. The practical reason to choose for the new method is the DPD limit.

The simulation algorithm. – Although the re-equilibration scheme leaves the Boltzmann distribution invariant, there are no discretization schemes for conservative motion that have this property for finite time steps. The simplest and most widely used integrator for reversible Hamiltonian dynamics is the Verlet scheme [5]. In our simulations every time step the reversible part of the motion will be solved using the velocity Verlet algorithm,

$$
\begin{aligned}
\boldsymbol{p}_i\left(t + \frac{1}{2}\Delta t\right) &= \boldsymbol{p}_i(t) + \frac{\Delta t}{2}\boldsymbol{f}_i^{\mathrm{C}}(t), \\
\boldsymbol{r}_i(t + \Delta t) &= \boldsymbol{r}_i(t) + \frac{\Delta t}{m_i}\boldsymbol{p}_i\left(t + \frac{1}{2}\Delta t\right), \\
\boldsymbol{p}_i(t + \Delta t) &= \boldsymbol{p}_i\left(t + \frac{1}{2}\Delta t\right) + \frac{\Delta t}{2}\boldsymbol{f}_i^{\mathrm{C}}(t + \Delta t).
\end{aligned}
\tag{9}
$$

Next, the momenta will be partly re-equilibrated using

$$
\begin{aligned}
\boldsymbol{p}_i &:= \boldsymbol{p}_i + \big(-a_{ij}(\boldsymbol{v}_{ij} \cdot \hat{\boldsymbol{r}}_{ij})\Delta t + b_{ij}\Delta W_{ij}\big)\hat{\boldsymbol{r}}_{ij}, \\
\boldsymbol{p}_j &:= \boldsymbol{p}_j - \big(-a_{ij}(\boldsymbol{v}_{ij} \cdot \hat{\boldsymbol{r}}_{ij})\Delta t + b_{ij}\Delta W_{ij}\big)\hat{\boldsymbol{r}}_{ij},
\end{aligned}
\tag{10}
$$

for all pairs i, j. To prevent biasing, we access the pairs i, j in a random sequence. The coefficients a_{ij} and b_{ij} are chosen such that eq. (10) is of the form of eq. (5). This requirement gives that

$$
b_{ij} = \sqrt{2kT\,a_{ij}\left(1 - \frac{a_{ij}\Delta t}{2\mu_{ij}}\right)}.
\tag{11}
$$

For $\Delta t = 0$, eq. (11) is identical to the relation between the dissipative and the fluctuating part in DPD.

The first main differences with the usual DPD simulation routines is this Δt correction factor in b_{ij}. The other difference is that the velocity is updated subsequent to every individual irreversible pair interaction (10). The recently proposed scheme by Shardlow [6] is similar in this last respect. The combination of these two subtle changes gives that the thermostating part of this new DPD discretization rigorously maintains the Maxwell-Boltzmann distribution. The only possible deviation of the equilibrium statistics is due to the discretization errors made by the Verlet algorithm, eq. (9).

In table I we give two possible choices for a_{ij} and b_{ij} that obey eq. (6) and give the DPD frictional and fluctuating forces for $\Delta t \to 0$. The first possibility is obtained by simply equating $a_{ij}\,\mathrm{d}t$ with the friction term in eq. (1) for pair i, j. The second possibility is obtained by only considering one pair i, j and integrate the DPD equation for a time step, Δt. The advantage of the second expression is that in this case the irreversible motion imposes no restriction on the choice of Δt.

TABLE I – *Two possible choices of a_{ij} and b_{ij} that in the limit $\Delta t \to 0$ reduce to the DPD expressions, but also for finite Δt do not give rise to deviations in the equilibrium statistics.*

Scheme	a_{ij}	b_{ij}^2
I	$\gamma\omega(r_{ij})$	$2kT\gamma\omega(r_{ij})\left(1 - \dfrac{\gamma\omega(r_{ij})\Delta t}{2\mu_{ij}}\right)$
II	$\dfrac{\mu_{ij}}{\Delta t}\left(1 - \exp\left[-\dfrac{\gamma\omega(r_{ij})\Delta t}{\mu_{ij}}\right]\right)$	$\dfrac{kT\mu_{ij}}{\Delta t}\left(1 - \exp\left[-2\dfrac{\gamma\omega(r_{ij})\Delta t}{\mu_{ij}}\right]\right)$

One can approximate increments ΔW_{ij} of the Wiener processes by non-Gaussian stochastic variables with zero mean and the same second-order moment. We did simulations with both normally and uniformly distributed increments and found virtually no differences in the results.

Simulations. – In our simulation we fixed the units by setting $kT = 1$, $m = 1$ and $r_c = 1$. We consider two model systems that were also used in earlier studies [4]. The first system is a model A. This is a, so-called, ideal DPD fluid with no conservative forces and with $\gamma = 4.5$ and $n = 4$. For model A, our method predicts all equilibrium properties without any time step dependence because there are no conservative forces. For most DPD schemes the pair correlation function $g(r)$ is one of the quantities that is most sensitive to finite time step effects.

For model A the theoretical pair correlation function has no r-dependence: $g(r) = 1$. The left graph of fig. 1 shows that the computed deviation from $g(r) = 1$ indeed obeys the expected behaviour. There is only a noticeable deviation from $g(r) = 1$ very near $r = 0$. This deviation is due to poor statistics in this region. In our simulations we computed the pair correlation function by constructing a histogram with bins of width $\Delta r = 10^{-2}$. The number of particles in a bin scales as $N \propto r^2 \Delta r$ and the relative error is proportional to $1/\sqrt{N} \propto 1/r$. Although there is no time step dependence of the equilibrium properties for model A, the dynamical quantities do show a dependence. The right graph of fig. 1 shows the time step dependence of the self-diffusion.

Model B is as model A, apart from the fact that a pairwise repulsive conservative force of the form is added:

$$\boldsymbol{f}^{C}(\boldsymbol{r}_{ij}) = a\sqrt{\omega(\boldsymbol{r}_{ij})}\hat{\boldsymbol{r}}_{ij}, \tag{12}$$

with $a = 25$. For model B there is a time step dependence of equilibrium properties. This
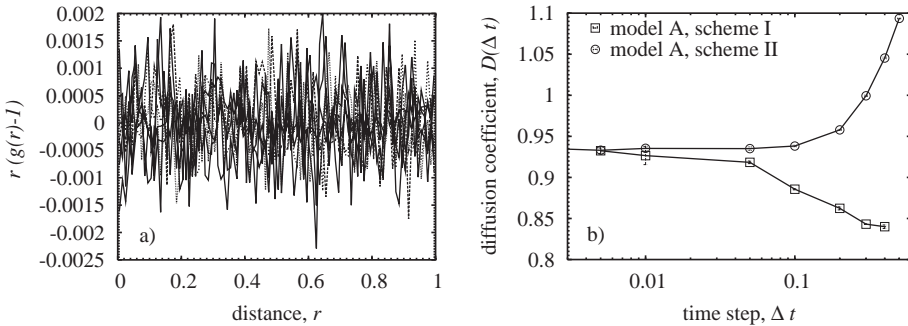

Fig. 1 – a) For model A, deviation from the theoretical pair correlation $g(r) = 1$ is purely of statistical origin. Three lines are shown for $\Delta t = 0.01$, 0.1 and 0.5. b) The time step dependence of the self-diffusion in model A when using the schemes I and II.
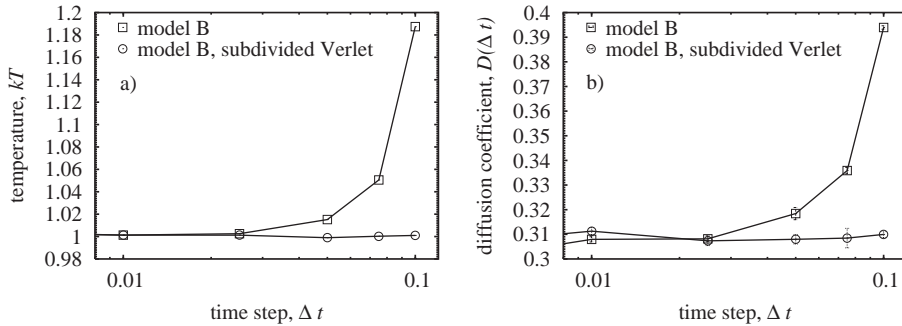
Fig. 2 – The time step dependence of a) the temperature and b) the self-diffusion in model B. When the Verlet step is subdivided into 10 smaller steps, the dependence almost disappears.

dependence is illustrated in the left graph of fig. 2 for the kinetic temperature. This dependence is caused by the discretization of the conservative dynamics. This is illustrated by subdividing the Verlet step into 10 sub-steps of size $\Delta t/10$. Subsequent to the 10 Verlet sub-steps, the partial equilibration step is performed once. The left graph of fig. 2 shows that the measured temperature becomes almost independent of Δt (for that range). Surprisingly, also dynamic quantities improved upon subdivision of the Verlet step. The right graph of fig. 2 illustrates this for the self-diffusion.

Discussion. – In a recent paper by Nikunen *et al.* [4], the authors present a comparative study of the efficiency of several "novel" DPD integration schemes. The study includes, among others, the Shardlow scheme [6] and also the Lowe scheme [2]. They concluded that the Lowe scheme performs best (but it is not a discretization of the DPD equations). The Shardlow scheme is next best and has the advantage that it does discretise the DPD equations. Our method is in a way a combination of the two methods that uses the best from both.

The core operation in our method is a generalised Lowe thermostating which strictly conserves the Maxwell-Boltzmann velocity distribution. Because we allow for the partial equilibration of the (central) relative velocities of pairs, we can use the scheme to discretise the DPD equations. Similarly to the Lowe scheme, the velocities of pair of particles are updated subsequent to each pair equilibration. Also the irreversible interactions and the conservative interactions are split and treated separately. The method has in common these two features with the Shardlow method [6]. This is different from the usual DPD discretizations where first the contributions of all pair interactions are added and subsequently the update of velocities and positions are computed. The main difference of our method to Shardlow's is a small but important Δt term in fluctuating term, eq. (11). Because of this term, our method exactly preserves the Maxwell-Boltzmann distribution and Shardlow method does not.

The main conclusion that can be drawn from the Nikunen *et al.* paper [4] is that different (advanced) DPD discretizations perform differently in predicting the equilibrium properties in model A (*e.g.*, constant $g(r)$ and a kinetic temperature of 1). With respect to time step dependence of the dynamic quantities, such as diffusion, in model A and both the equilibrium and dynamic properties of model B, all the discretizations they considered perform equally well (or bad). Our method ranks in this classification as the best because it exactly predicts the equilibrium properties of model A independent of time step and the deviations in the other categories are of the same magnitude as the other DPD discretization methods.

For model B, we showed that the major part of the deviations of both equilibrium quantities and dynamical ones (up to $\Delta t = 0.01$) are due to the inaccuracy of the Verlet algorithm. As

an alternative to dividing the Verlet step in smaller sub-steps (see fig. 2) we tested a fourth-order simplectic integrator. This did not improve the results. We conclude therefore that the measured deviations are due to the fact that for larger Δt the time step is too close to the boundary of the stability region of the Verlet (and also of the higher-order) scheme. The results might be improved by using a (simplectic?) integrator with a larger stability region.

Although the proposed scheme predicts equilibrium properties exactly (assuming that the conservative part is integrated exactly), dynamic quantities remain having a Δt-dependence. The smallest relevant time scale in the system is the momentum relaxation time,

$$\tau_m = m\gamma^{-1}n^{-1}r_c^{-3}, \tag{13}$$

since the rate of relaxation in eq. (1) is γ/m and a particle interacts with about $4/3\pi n r_c^3$ other particles ($n = \rho/m$ the particle number density). In any explicit integration method this time scale has to be resolved.

To make matters worse, some authors [2,7] have argued that DPD only is meaningful for simulation of liquids when the Schmidt number, Sc, has a value typical of liquids, $i.e.$, of the order 1000. The Schmidt number is the ratio of the kinematic viscosity and the self-diffusion. It is proportional to τ_m^{-1} [7]. Combined with the fact that $\Delta t < \tau_m$, one finds that the CPU time scales proportional to Sc. From a simulation point of view, one would therefore like to use Sc of order one.

One should realise that the self-diffusion in liquids is that of individual molecules and not of DPD blobs, so the particle-based Sc is ill-defined within a DPD simulation. The centre-of-mass motion of a collection of neighbouring DPD particles is not influenced much by self-diffusion of individual DPD particles, because the total momentum is locally conserved. For larger-scale motion D is irrelevant. An indication for this is that it does not appear in the Navier-Stokes equation. To avoid non-hydrodynamic modes at small length scales, one might prefer the use of $Sc > 1$. There is, however, no need to simulate "realistically" large $Sc \approx 1000$ and waste CPU time.

If one wants to perform accurate simulations with $\Delta t > \tau_m$, some kind of implicit scheme needs to be used. One might think of using a multiscale approach where at small length scales the force balance between dissipative, fluctuating and conservative forces is approximately solved. This is similar to, $e.g.$, Brownian dynamics. At larger length scales inertial effects should be taken into account. Inertial effects only become important at length scales where the Reynolds number associated with that scale becomes of order 1.

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