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Citation for published version (APA):

Zakhari, M. E. A., Hütter, M., & Anderson, P. D. (2018). Effect of particle-size dynamics on flow properties of dense spongy-particle systems. *Journal of Rheology*, 62(2), 543-557. <https://doi.org/10.1122/1.5004222>

DOI:

[10.1122/1.5004222](https://doi.org/10.1122/1.5004222)

Document status and date:

Published: 08/02/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Effect of particle-size dynamics on flow properties of dense spongy-particle systems

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(Dated: December 14, 2017)

Abstract

Suspensions of poroelastic particles are indispensable for applications where tailoring the overall properties is a necessity. The single-particle elastic network gives rise to their elastic behavior, while the flow of the viscous solvent through the particle structure gives rise to their rate-dependent behavior. In this work, we study the effect of the single-particle elastic modulus and permeability on the properties of the entire poroelastic-particle suspension subject to simple-shear deformation. For this purpose, the dynamic two-scale model developed by Hütter et al. [Faraday Discuss., **158**, 407-424 (2012)] is used. Upon deformation, both permeable- and impermeable-particle suspensions undergo a transition from a glassy state to a shear-induced ordered state. On the one hand, the particle permeability is found to affect the rate at which the ordered state is reached. At a fixed elastic modulus, increasing the particle permeability prolongs the time scale at which shear-induced ordering occurs. On the other hand, the long-time shear stress values are dominated by the elastic properties of the individual particle, through a sub-linear dependence. This is due to the fact that, the lower the particle elastic modulus, the larger are the occurring particle-volume changes, which in turn has ramifications for the dynamics and the mechanical behavior of the suspension.

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I. INTRODUCTION

Soft, open-porous, deformable particles are nowadays used in a wide variety of industrial applications such as paints [1], pharmaceuticals and cosmetics [2, 3], foods [4], and inks [5]. The fascinating macroscopic behavior of suspensions of such particles emerges from the peculiar properties of the individual particle. On the one hand, the elasticity of the supporting network of the particle provides the elastic behavior and, on the other hand, the flow of the viscous suspending fluid through the porous particle results in a viscous contribution. Particles of this nature are often envisaged as sponges, and will therefore be called spongy particles in this paper. These particles are sometimes also referred to as poroelastic particles due to their characteristic internal structure. The internal structure of spongy particles is characterized by the permeability and, hence, spongy particles will be referred to as permeable particles in the following sections.

Suspensions of spongy particles are especially useful for applications where tailored overall properties is a requirement. The tunability of the suspension properties is achieved through modifications of the individual particle properties [6, 7]. Unlike hard particles, soft particles can impinge in response to, for instance, steric effects [8, 9] or applied deformation [10–17]. The particle softness allows elastic particles, such as emulsion droplets, to impinge and change in shape by forming facets upon contact with other particles, approximately at a constant volume. The softness and the internal structure of poroelastic spongy particles, such as star polymers and microgels, allow not only for shape changes, but also for significant volume changes in response to applied stress or deformation, which can appreciably alter the overall rheological behavior.

In relation to the particle shape-change, particles in dense systems impinge, forming an elastic network that can resist deformation similar to a yielding solid [18]. The elasticity of the particle defines the extent of this shape change. If the applied deformation is sufficiently high, the particles can flow past each other, breaking the elastic network, which eventually leads to shear-thinning behavior [7, 14]. When the applied deformation is further increased, the particles rearrange into strings in the flow direction in order to minimize the interaction forces between them. These shear-induced structures have been reported in experiments for hard-particle systems [10, 19, 20] and for soft-particle systems [11–13, 15], see [16] for a detailed review. This anisotropic ordering is accompanied by a drop in stress as a function

of applied shear rate [11, 13]. Spongy particles, on the other hand, are endowed with a rate-dependent softness and the ability to change volume in addition to shape. The rate-dependent softness originates from the fact that permeable particles can take up or expel the viscous suspending solvent. The volume change depends on the internal structure of the particle, in particular the particle permeability. While the effect of the particle elasticity responsible for shape change is explored extensively in experiments of impermeable- and permeable-particle systems [7, 21–24] and in simulations of a wide variety of particles interacting through a soft interaction potential [25–27], the effect of rate-dependent volume change remains unclear. The limited results concerning the rate-dependent volume change is due to, on the one hand, the fact that the particle permeability is not easily varied independently from the particle elastic modulus. The permeability is commonly varied in experiments by changing either the particle size [28], the cross-link density [29], or the temperature [22, 26], which effectively vary the particle elasticity as well. On the other hand, the lack of models that take into account particle size and its dynamics typically limits simulations to studying the effect of the elastic softness only. Understanding the coupling of the microstructure degrees of freedom and their dynamics, and the rheological properties of spongy-particle systems motivates the work presented in this paper.

In order to study the effect of the internal degrees of freedom of spongy-particles, the dynamic two-scale model developed by Hütter et al. [30] is employed. This model rests on the principals of nonequilibrium thermodynamics, particularly, the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [31–33]. The particle size is treated as a separate degree of freedom in addition to the particle position, which allows the model to capture the size dynamics. The size dynamics naturally takes into account the particle internal structure, in particular the particle permeability, as well as the viscosity of the background solvent. The model can be casted into the form of stochastic differential equations which are suitable for Brownian dynamics (BD) simulations [30]. In this work, BD simulations are performed for systems of spongy particles with varying permeability values and particle moduli, in order to study the effect of the particle properties on the long-time response of the overall suspension as well as the transient behavior under applied shear flow. The properties of spongy-particle systems are compared with systems of impermeable particles and similar elastic properties.

This paper is organized as follows. Section II provides the basic elements of the dynamic

two-scale model in the case of applied deformation, in addition to the relevant dimensionless parameters and timescales involved in the problem. This is followed by the numerical setup in Sect. III. The shear-flow behavior of spongy-particles and the characteristic features of the stress response of dense-particle systems are described in Sect. IV. In Sect. V, the effect of the particle softness, elastic and rate-dependent, on the shear-flow response and particle dynamics are studied. In Sect. VI, the effect of the system density on the shear-flow properties is provided. Finally, the article is concluded with a discussion in Sect. VII.

II. EXTENDED BROWNIAN DYNAMICS MODEL

In this section, the basic elements of the dynamic two-scale model developed by Hütter et al. [30] are introduced and applied to systems subjected to constant shear-rate deformation. After presenting the general structure, the particle interaction potential is specified, based on which the driving forces for the dynamics of the system are derived. This is followed by the evolution equations of the particle degrees of freedom. The particle contributions to the stress are presented and, finally, the characteristic time scales and the relevant dimensionless numbers are introduced.

A. Fokker-Planck equation

The model considers a representative volume element at a macroscopic position $\mathbf{r}$ consisting of N spherical particles suspended in a Newtonian fluid with shear viscosity η . A $4N$ -dimension variable $\boldsymbol{\xi}$ denoting all microscopic dynamics degrees of freedom is defined as

$$\boldsymbol{\xi} = \{\mathbf{Q}_1, R_1, \dots, \mathbf{Q}_N, R_N\}, \quad (1)$$

where each particle is described by the position of its center $\mathbf{Q}_i$, measured with respect to $\mathbf{r}$, and its radius R_i . The evolution of the distribution function p of the microscopic states $\boldsymbol{\xi}$, normalized with the number density of the system n , is described by the Fokker-Planck equation [30]

$$\begin{aligned} \partial_t p = & -\mathbf{v} \cdot (\nabla_{\mathbf{r}} p) - \sum_i \nabla_{\mathbf{Q}_i} \cdot ((\nabla_{\mathbf{r}} \mathbf{v})^T \cdot \mathbf{Q}_i p) - \sum_i \partial_{R_i} (\alpha (\nabla_{\mathbf{r}} \cdot \mathbf{v}) R_i p) \\ & - \nabla_{\boldsymbol{\xi}} \cdot (\boldsymbol{\mu} \cdot [-(\nabla_{\boldsymbol{\xi}} \Phi) p - k_B T \nabla_{\boldsymbol{\xi}} p]), \end{aligned} \quad (2)$$

where $\mathbf{v}$ is the applied velocity field, k_B is the Boltzmann constant and T is the absolute temperature. The prefactor α indicates to what extent the particle size follows the velocity field. The mobility tensor $\boldsymbol{\mu}$ is a symmetric and non-negative $4N \times 4N$ tensor, while the driving force for $\boldsymbol{\xi}$ -dynamics is $-\nabla_{\boldsymbol{\xi}}\Phi$, where Φ is the potential energy of the system.

B. Particle interaction

Particles in dense systems are generally stabilized, and attractive forces are assumed to be negligible [23, 34, 35]. Hence, in this work, the interaction between the particles is assumed to be purely repulsive. Particles undergo elastic shape-change upon contact with neighboring particles and, at the same time, a particle can elastically change in volume. The former is described by the Hertzian potential Φ_{ij}^{Hz} [36], while the latter is described by the stored elastic energy Φ_i^{vol} [37] that drives the particle towards its equilibrium size R_{eq} . The equilibrium size R_{eq} is the size of the particle without constraints of surrounding particles. The total potential energy is defined as the sum of these two contributions,

$$\Phi(\boldsymbol{\xi}) = \sum_i \Phi_i^{\text{vol}}(\boldsymbol{\xi}) + \sum_{i \neq j} \Phi_{ij}^{\text{Hz}}(\boldsymbol{\xi}) = ER_{\text{eq}}^3 \tilde{\Phi}(\boldsymbol{\xi}), \quad (3)$$

where E is the Young's modulus. The symbol $(\tilde{\cdot})$ denotes the nondimensionalized $(\cdot)$. The prefactor ER_{eq}^3 is the energy scale given by the elastic interaction energy of the particles. The ratio of this elastic energy and the thermal energy $k_B T$, naturally, defines a dimensionless group that describes the elastic softness of the particles [9], that is

$$S^* = \frac{k_B T}{ER_{\text{eq}}^3}. \quad (4)$$

The following examples give a physical intuition of values of S^* . For instance, the softness dimensionless number is estimated to be 10^{-7} for oil-in-water emulsions [17] and between $10^{-4} - 10^{-5}$ for polyacrylamide particles of radius $0.1 - 1\mu\text{m}$, such as PNIPAM [17, 23].

The dimensionless Hertzian interaction potential due to the contact between particle i and its neighbors j is

$$\tilde{\Phi}_{ij}^{\text{Hz}}(\boldsymbol{\xi}) = \begin{cases} \frac{1}{2(1-\nu^2)} \left(C \tilde{h}_{ij}^m \tilde{R}_c^{3-m} + \tilde{k} \right) & \text{if } \tilde{h}_{ij} > 0, \\ 0 & \text{otherwise,} \end{cases} \quad (5)$$

where ν is the Poisson's ratio. The contact size is $\tilde{R}_c = \left(\frac{1}{\tilde{R}_i} + \frac{1}{\tilde{R}_j} \right)^{-1}$ where $\tilde{R}_i$ and $\tilde{R}_j$ are the current particle radii of particles i and j scaled with R_{eq} , respectively. The overlap

between particles is defined as $\tilde{h}_{ij} = \tilde{R}_i + \tilde{R}_j - |\tilde{\mathbf{Q}}_i - \tilde{\mathbf{Q}}_j|$ where all length scales are scaled with R_{eq} . Depending on the value of $\tilde{h}_{ij}$, the dimensionless constants C , m and $\tilde{k}$ in Eq. (5) are given by

$$\begin{aligned} \frac{\tilde{h}_{ij}}{\tilde{R}_i + \tilde{R}_j} < 0.1 : \quad C &= \frac{8}{15}, \quad m = \frac{5}{2}, \quad \tilde{k} = 0, \\ 0.1 \leq \frac{\tilde{h}_{ij}}{\tilde{R}_i + \tilde{R}_j} < 0.2 : \quad C &= \frac{5}{6} \sqrt{\frac{5}{2}}, \quad m = 4, \quad \tilde{k} = \frac{\sqrt{10}}{1250}, \\ 0.2 \leq \frac{\tilde{h}_{ij}}{\tilde{R}_i + \tilde{R}_j} < 0.6 : \quad C &= \frac{125}{144} \sqrt{\frac{5}{2}}, \quad m = 6, \quad \tilde{k} = \frac{89\sqrt{10}}{11250}, \end{aligned} \quad (6)$$

which ensure the continuity of energy and force, following the procedure described in detail in Appendix A of [9].

The dimensionless elastic energy due to volume change is [37]

$$\tilde{\Phi}_i^{\text{vol}} = \frac{2\pi}{9(1-2\nu)} \left(\tilde{R}_i^3 - 1 \right)^2, \quad (7)$$

where $\tilde{R}_i^3 - 1$ is the volumetric strain compared to the equilibrium size.

It is to be noted that the additive form of the potential Eq. (3) ensures that, in the dilute limit where $\tilde{\Phi}^{\text{Hz}} \approx 0$, a particle i strives towards the equilibrium size based on the minimization of $\tilde{\Phi}_i = \tilde{\Phi}_i^{\text{vol}}$.

C. Stochastic differential equations

The macroscopic velocity field $\mathbf{v}$, the driving forces due to the particle interactions, and the thermal fluctuations affect the position and size of the particles. In this paper, the imposed flow field is

$$\mathbf{v} = \dot{\gamma} y \mathbf{e}_x, \quad (8)$$

with a shear rate $\dot{\gamma}$, and $\mathbf{e}_x$ the unit vector in the x -direction.

The position- and size-dynamics are described by the stochastic differential equations corresponding to Eq. (2), using the Itô-interpretation [38]. In this paper, the hydrodynamic interaction with the background solvent considered is the single-particle Stokes' drag, while many-particle hydrodynamic interactions are neglected. The reason for neglecting the latter is that otherwise the computational cost would be prohibitive, in particular since the main goal of this paper is to conduct an extensive study of the effect of the single-particle elasticity

and permeability. In addition, the dynamic cross-coupling between position and size are neglected (see [30]), i.e. the irreversible change in particle position (size) is only driven by the derivative of the potential energy with respect to the particle position (size). It is also assumed that the size-dynamics of different particles are not hydrodynamically coupled. For more detail, the reader is referred to our previous work [9]. Based on the dimensionless potential energy and using the flow field described by Eq. (8), the position and size dynamics, respectively, are given by

$$d\tilde{\mathbf{Q}}_i = \dot{\gamma}\tilde{Q}_{i,y}\mathbf{e}_x dt + \zeta_{Q_i}^{-1}ER_{\text{eq}}\left(-\nabla_{\tilde{\mathbf{Q}}_i}\tilde{\Phi}\right)dt + \sqrt{2k_B T\zeta_{Q_i}^{-1}R_{\text{eq}}^{-2}}[d\mathbf{W}_t]_{\mathbf{Q}_i}, \quad (9a)$$

$$d\tilde{R}_i = \zeta_{R_i}^{-1}ER_{\text{eq}}\left(-\partial_{\tilde{R}_i}\tilde{\Phi}\right)dt + k_B T R_{\text{eq}}^{-2}(\partial_{\tilde{R}_i}\zeta_{R_i}^{-1})dt + \sqrt{2k_B T\zeta_{R_i}^{-1}R_{\text{eq}}^{-2}}[dW_t]_{R_i}, \quad (9b)$$

scaling all length scales by R_{eq} . In Eq. (9), $\tilde{Q}_{i,y}$ is the y -component of $\tilde{\mathbf{Q}}_i$, while $-\nabla_{\tilde{\mathbf{Q}}_i}\tilde{\Phi}$ and $-\partial_{\tilde{R}_i}\tilde{\Phi}$ are the driving forces for position change and size change, respectively. The full non-dimensional form of Eq. (9) is given later in Sect. II E. The mobility for position change is given as the inverse of the single-particle friction coefficient $\zeta_{Q_i}^{-1} = 1/(6\pi\eta R_i)$. On the other hand, the size mobility is $\zeta_{R_i}^{-1} = R_{\text{eq}}^3\chi/(12\pi\eta R_i^4)$ where, based on the theory of poroelasticity [39], the dimensionless χ -parameter depends on the permeability of the particle κ and the initial particle radius R_0 as $\chi = \pi^2\kappa/R_0^2$. The fluctuating Brownian contributions are given by the terms involving the Wiener-process increments $[d\mathbf{W}_t]_{\mathbf{Q}_i}$ and $[dW_t]_{R_i}$, in the position and size equations, respectively. The Wiener-process increment has an average of $\langle d\mathbf{W}_t \rangle = 0$ and a variance of $\langle d\mathbf{W}_t d\mathbf{W}_{t'} \rangle = \delta_{t,t'} dt \mathbf{I}$, where $\mathbf{I}$ is the unity tensor. The ratio of mobilities in the size and position dynamics gives rise to the second dimensionless number used to characterize the particle internal structure, of a certain particle system,

$$\zeta^* = \left. \frac{\zeta_{R_i}^{-1}}{\zeta_{Q_i}^{-1}} \right|_{R_i=R_{\text{eq}}} = \frac{\chi}{2}. \quad (10)$$

For sub-micron sized polyacrylamide particles, for example, the permeability given in [40] leads to a value of $\zeta^* \geq 10^{-3}$.

D. Constitutive relation for the stress

Changes in particle size and position, described in Sect. II C, lead to stresses $\boldsymbol{\sigma}$ on the macroscopic level which describe the overall behavior of the permeable-particle system. The constitutive relation governing the behavior of permeable-particle systems is given by the

relation derived in [30]. In this work, we focus on the particle contribution to the stress. The particle contribution originates, on the one hand, from the interaction forces between particles due to their relative position with respect to other neighboring particles. On the other hand, a particle size that is different from the equilibrium size R_{eq} results in an isotropic contribution to the stress tensor. An additional isotropic particle contribution arises when the interaction between particles depends on the system density [30]. This is, however, not the case in this work (see Eq. (5) and Eq. (7)). The dimensionless stress tensor due to the particle contribution, scaling the length scales involved by R_{eq} and using the dimensionless interaction potential, is

$$\tilde{\boldsymbol{\sigma}} = \frac{\boldsymbol{\sigma}}{E} = nR_{\text{eq}}^3 \left[\left\langle \sum_i (\nabla_{\tilde{\mathbf{Q}}_i} \tilde{\Phi}) \tilde{\mathbf{Q}}_i \right\rangle + \alpha \left\langle (\partial_{\tilde{R}_i} \tilde{\Phi}) \tilde{R}_i \right\rangle \mathbf{I} \right]. \quad (11)$$

In general, α is a function of the bulk modulus of the particle K^{part} and the surrounding solvent K^{sol} and defined as

$$\alpha = \frac{K^{\text{sol}}}{3K^{\text{part}}}. \quad (12)$$

The bulk modulus of incompressible particles is infinitely large, that is $K^{\text{part}} \rightarrow \infty$, which leads to $\alpha = 0$. On the other hand, if the particle is highly permeable, one can assume that it is mostly consisting of the solvent and their bulk moduli thus are comparable $K^{\text{part}} \approx K^{\text{sol}}$. In turn, this implies that the particle deforms affinely and one finds $\alpha = 1/3$. In general, $0 \leq \alpha \leq 1/3$. It is to be noted that, in this paper, we are interested in the shear stress component σ_{xy} that is directly affected by the applied deformation Eq. (8). In this case, the isotropic stresses play no role, i.e., the second term on the right-hand side of Eq. (11) does not contribute to the stress component of interest.

E. Characteristic time scales

The macroscopic-microscopic coupling is given by the particle dynamics, Eq. (9), described in Sect. IIC and by the constitutive relation for the stress, Eq. (11), described in Sect. IID. In this section, several characteristic time scales are defined based on the particle dynamics.

The interaction energy is dissipated through viscous damping over a certain time scale,

which is for position change

$$\tau_{Q_i} = \frac{\zeta_{Q_i}}{ER_{\text{eq}}}, \quad (13)$$

and for volume change

$$\tau_{R_i} = \frac{\zeta_{R_i}}{ER_{\text{eq}}}. \quad (14)$$

On the other hand, the time at which a particle diffuses its radius due to thermal fluctuations is known as the Brownian time scale

$$\tau_{Q_i}^{\text{Br}} = \frac{\zeta_{Q_i} R_{\text{eq}}^2}{k_B T}. \quad (15)$$

Similarly, one can define a Brownian time scale with respect to size,

$$\tau_{R_i}^{\text{Br}} = \frac{\zeta_{R_i} R_{\text{eq}}^2}{k_B T}. \quad (16)$$

Moreover, an additional time scale is related to the shear rate,

$$\tau_{\dot{\gamma}} = \dot{\gamma}^{-1}. \quad (17)$$

The above defined time scales can be used to express the dimensionless parameter S^* and ζ^* described earlier. The softness dimensionless parameter S^* can be expressed as the ratio between viscous damping and thermal time scales for either the position- or the size-dynamics,

$$S^* = \frac{\tau_{Q_i}}{\tau_{Q_i}^{\text{Br}}} = \frac{\tau_{R_i}}{\tau_{R_i}^{\text{Br}}}. \quad (18)$$

The second dimensionless number, the one describing the permeability of the particles ζ^* , can be expressed as the ratio of the thermal or the viscous damping time scales of position- and size-dynamics,

$$\zeta^* = \frac{\tau_{Q_i}^{\text{Br}}}{\tau_{R_i}^{\text{Br}}} \bigg|_{R_i=R_{\text{eq}}} = \frac{\tau_{Q_i}}{\tau_{R_i}} \bigg|_{R_i=R_{\text{eq}}}. \quad (19)$$

Moreover, one can compare the Brownian time scale for position and characteristic shear time, which is known as the Péclet number [41]

$$\text{Pe} = \frac{\tau_{Q_i}^{\text{Br}}}{\tau_{\dot{\gamma}}} = \dot{\gamma} \tau_{Q_i}^{\text{Br}}. \quad (20)$$

Péclet numbers smaller than unity indicate that the applied deformation is not strong enough to drive the system away significantly from thermal equilibrium, while for Péclet numbers

larger than unity, the thermal fluctuations have no significant effect on the properties of the system, and the system is far from equilibrium. The transition from $\text{Pe} < 1$ to $\text{Pe} > 1$ shows the deviation of the material response from linear to nonlinear, for instance, to shear thinning [42, 43]. In order to capture this nonlinear behavior, throughout this paper we model systems with Pe larger than unity.

In summary, a simulation of a system of number density n is fully described by the previously defined dimensionless numbers, that is $(S^*, \zeta^*, \text{Pe})$. Equation (9) can be expressed as

$$d\tilde{\mathbf{Q}}_i = \text{Pe} \tilde{Q}_{i,y} \mathbf{e}_x d\tilde{t} + \frac{1}{S^*} \left(-\nabla_{\tilde{\mathbf{Q}}_i} \tilde{\Phi} \right) d\tilde{t} + \sqrt{2} \left[d\tilde{\mathbf{W}}_t \right]_{\mathbf{Q}_i}, \quad (21a)$$

$$d\tilde{R}_i = \frac{\zeta^*}{S^*} \left(-\partial_{\tilde{R}_i} \tilde{\Phi} \right) d\tilde{t} + \zeta^* \left(\partial_{\tilde{R}_i} \ln \zeta_{R_i}^{-1} \right) d\tilde{t} + \sqrt{2\zeta^*} \left[d\tilde{W}_t \right]_{R_i}, \quad (21b)$$

where $\tilde{t} = t/\tau_{Q_i}^{\text{Br}}$ and, from the properties of $d\mathbf{W}$ given in Sect. II C, $d\tilde{\mathbf{W}} = d\mathbf{W}/\sqrt{\tau_{Q_i}^{\text{Br}}}$.

III. NUMERICAL SIMULATIONS, PARAMETER SPECIFICATION

The systems modeled consist of N particles suspended in a fluid with a shear viscosity η . The initial size R_0 of the particles is set to be equal to the equilibrium size R_{eq} . Particles are initially placed on a simple cubic (SC) lattice in a cubic box. At high-volume fractions, this is a high-energy state. However, this high-energy state of the initial configuration relaxes to a glassy state on time scales considerably shorter than the Brownian time scale, that is $\tilde{t} < 1$. The glassy state, in contrast, lasts considerably longer than the Brownian time scale (see Sect. IV A). Therefore, no additional equilibration is required in our simulations, and the results obtained after imposing shear deformation from $\tilde{t} = 0$ onwards will not depend on the initial state. The simulation box is subjected to Lees-Edwards periodic boundary conditions [44]. Equation (21) is solved numerically using a forward-Euler integration scheme [45]. To capture the fast dynamics, the time step used for the integration scheme, Δt , is set to be two orders of magnitude smaller than the smallest time scale. As the shear rate is variable, the time step should also follow $\Delta t \leq 10^{-2} \tau_{\dot{\gamma}}$. The total simulation time is kept constant, $\tilde{\tau}_{\text{sim}} \approx 385$, in all simulations performed which has consequences that are discussed in the following sections. The system density is changed by modifying the initial size of the simulation box for the same number of particles. The volume of the simulation box then remains constant over the simulation time.

The particles modeled in this paper are permeable particles with properties that mimic biological systems such as polyacrylamide gels used as substrates for neural cell growth [46], $S^* \sim 10^{-3}$. In addition, the behavior of systems build up of highly-soft particles, $S^* \sim 10^{-2}$, with different permeability values $\zeta^* = \{0.005, 0.05\}$ is examined in order to show the effect of the size change. The behavior of permeable-particle systems is also compared to impermeable-particle systems, $\zeta^* = 0$, of the same elastic properties. In the absence of flow, particle-size changes due to steric effects are found to be significant at volume fractions higher than 0.8 [8, 9]. To highlight the effect of the particle-size changes, systems of volume fractions ranging from $\{0.739 - 0.916\}$ are, hence, considered in this work. Table I lists the physical values for the systems studied throughout this paper. Table II gives the parameters needed in the actual numerical simulations, based on the parameters given in Table I.

TABLE I. Physical parameters.

Parameter	Symbol	Physical value
Equilibrium particle radius	R_{eq}	$2.5 \times 10^{-7} \text{ m}$
Solvent shear viscosity	η	10^{-3} Pa s
Poisson's ratio	ν	0.4
Young's modulus	E	$\{3, 10, 30, 100\} \text{ Pa}$
Permeability	κ	$6.3 \times \{0, 10^{-17}, 10^{-16}\} \text{ m}^2$
Temperature	T	293 K

TABLE II. Model parameters.

Parameter	Symbol	Physical value
Number of particles	N	12^3
Volume fraction	φ_{free} (based on Eq. (22))	$\{0.739 - 0.916\}$
Brownian time scale	$\tau_Q^{\text{Br}} \Big _{R_i=R_{\text{eq}}}$	$7.28 \times 10^{-2} \text{ s}$
Softness, dimensionless	S^*	$\{86, 26, 8.6, 2.6\} \times 10^{-3}$
Permeability, dimensionless	ζ^*	$\{0, 0.5, 5\} \times 10^{-2}$
Péclet number	Pe	$\text{Pe} \geq 1$

IV. PROPERTIES OF SPONGY-PARTICLE SUSPENSIONS IN SHEAR FLOW

A. Stress evolution and characterization of the transient behavior

A dense system of permeable particles with a number density of $n = 1.3 \times 10^{19} \text{ m}^{-3}$ is used to demonstrate the characteristic features of the stress evolution over time. This number density corresponds to a volume fraction,

$$\varphi_{\text{free}} = \frac{4}{3}\pi R_{\text{eq}}^3 n, \quad (22)$$

based on the equilibrium size R_{eq} , of $\varphi_{\text{free}} = 0.850$. The system is subjected to a Péclet number well above unity. The dimensionless numbers describing this example are $(S^*, \zeta^*, \text{Pe}) = (8.6 \times 10^{-3}, 0.05, 20.0)$.

Figure 1 shows the evolution of the shear stress of this system. The evolution of the shear stress shows a transition over time between two plateau values of stress in response to the applied shear deformation. The initial SC structure rapidly relaxes into the high-stress plateau at $\tilde{t} < 1$. The transition between the different plateau values occurs at the transition time $\tilde{\tau}_t$. From Fig. 1, $\tilde{\tau}_t$ is significantly longer than the Brownian time scale, $\tilde{\tau}_t \simeq 40$. This transition is associated with particles forming ordered structures, driven by the applied deformation. The long transition time suggests that the high-stress state is a disordered, long-lived glassy state which is driven by shear deformation to an ordered state, the latter consisting of strings of particles in the flow direction. The evolution of the microstructure over time and the structure formed at the end of the simulation corresponding to Fig. 1 are given in Fig. 2 (Multimedia view). The string structure can be clearly seen in the xy -projection, while the yz -projection of the structure shows a hexagonal arrangement. This type of string structures are found in several systems at high shear rates, for instance, in experiments on suspensions with hard particles [10], elastic particles [47] and permeable particles [13, 15], and in simulations with hard particles [48], and elastic particles [49].

Based on our previous work [9], the transition is found to depend on the collective motion of particles which, in turn, depends on the system history. By system history, we denote the initial state of the particles as well as the pathway followed by the particles over time. Both can be modified through changing the initial configuration and the realization of the noise, respectively. To this end, throughout this paper we base our results on the average output of simulations performed with five different realizations of the noise while the initial

FIG. 1. Evolution of the shear stress $\tilde{\sigma}_{xy}$ for a system with $(S^*, \zeta^*, \text{Pe}) = (8.6 \times 10^{-3}, 0.05, 20.0)$. The density of the system is $\varphi_{\text{free}} = 0.850$ ($n = 1.3 \times 10^{19} \text{ m}^{-3}$). The unit of dimensionless quantities, such as $\tilde{\sigma}_{xy}$ and $\tilde{t}$, are denoted by $[-]$. This holds also for the rest of the paper.

FIG. 2. Particle arrangement for a system with $(S^*, \zeta^*, \text{Pe}) = (8.6 \times 10^{-3}, 0.05, 20.0)$ at $\tilde{t} = 384.6$. The density of the system is $\varphi_{\text{free}} = 0.850$ ($n = 1.3 \times 10^{19} \text{ m}^{-3}$). The evolution of the microstructure over time up to $\tilde{t} = 96.15$, is given in the animation (Multimedia view).

configuration is fixed to the simple cubic structure. The transition time and long-time stress, $\tilde{\tau}_t$ and $\tilde{\sigma}_{xy}$, respectively, are used to characterize the shear-flow changes in the sequel. These

quantities are obtained from fitting the shear stress-time with a hyperbolic tangent function.

B. Flow curves

In this section, the shear-flow properties of permeable-particle suspensions are studied and compared to suspensions of impermeable particles. The permeable-particle suspensions, at high shear-rates, undergo a transition over time to ordered structures. Their behavior can be expressed in terms of the long-time plateau values for the shear stress $\tilde{\sigma}_{xy}$ and the transition time $\tilde{\tau}_t$, as described in Sect. IV A. The system density of the two suspensions examined in this section is $\varphi_{\text{free}} = 0.850$ ($n = 1.3 \times 10^{19} \text{ m}^{-3}$) in order to show the behavior in the dense regime. The effect of the system density on the overall behavior is studied in detail in Section VI. Both systems have the same softness dimensionless parameter $S^* = 8.6 \times 10^{-3}$ and the Péclet number is varied between $0 < \text{Pe} < 28$. The permeable-particle systems is described by $\zeta^* = 0.05$, while $\zeta^* = 0$ for the impermeable-particle systems.

Figure 3 shows the shear-stress values for the suspensions described above as a function of Péclet number for both permeable- and impermeable-particle systems. Initially, the shear stress increases with Pe with a slope that is equivalent to the viscosity of the overall system. At intermediate Pe , this slope decreases as the shear rate increases, which confirms that these suspensions show shear-thinning behavior. This is in accordance with experimental observations of elastic impermeable particle systems [13] and permeable-particle systems such as PNIPAM particles [14, 15]. Upon further increasing the applied shear rate, both systems show a drop in stress. The stress drop has been reported in the work of Chen et al. [13], where they performed creep and constant shear-rate experiments on suspensions of polystyrene latex particles. They observed a stress drop in both experimental procedures. For our study, it is to be noted that, keeping the simulation time fixed, both the high-stress disordered state and the low-stress ordered phase were observed for permeable-particle systems around $\text{Pe} \approx 20$, depending on the specific realization of thermal noise. These points are marked with red squares in Fig 3. It is important to realize that, at Pe where both states are observed, if the simulation time, $\tilde{t}_{\text{sim}}$, is increased sufficiently, all these systems would eventually evolve towards the ordered state. Based on Fig. 1 and since the oriented structures are promoted by the imposed deformation, if $\tilde{t}_{\text{sim}} < \tilde{\tau}_t$, e.g. $\tilde{t}_{\text{sim}} = 10$, only the high-stress state is observed. If $\tilde{t}_{\text{sim}} > \tilde{\tau}_t$, e.g. $\tilde{t}_{\text{sim}} = 100$, the simulation

time is long enough for the transition to the shear-induced ordered state to occur and the low-stress state is reached. Therefore, the simulation time affects the Péclet number at which the transition occurs, particularly it shifts to lower (higher) values upon increasing (decreasing) the simulation time. The shape of the curve remains nonetheless qualitatively unchanged. Hence, the data reported in Fig. 3 (and similar figures) depend in this sense on the observation time-span, i.e. the total simulation time.

Moreover, it can be seen in Fig. 3 that, while both systems show the stress drop, this transition occurs at lower Pe for impermeable particles than for permeable particles. This is due to the fact that forces between impermeable particles are higher than those between permeable particles, since the latter can change their size to relax the forces between them [9]. As a result, permeable-particle systems are more compliant than impermeable-particle systems and can sustain stronger forcing prior to forming ordered structures.

To investigate the stability of the low-stress ordered phase, the final structure obtained at a $Pe = 21.84$ is used as the initial configuration, i.e. positions and sizes of the particles, for simulations performed at $Pe < 21.84$. The result is shown by the dashed lines in Fig. 3. Both systems, with permeable and impermeable particles respectively, show a transition back to the high-stress state, however, upon further investigation, we find that the cause of this reversion to the high-stress state is remarkably different. Impermeable-particle systems, on the one hand, show a reversion to the high-stress state depending on the starting configuration. Particularly, we find that the impermeable-particle system forms two different types of string phases at the end of the high shear-rate ($Pe = 21.84$) simulation: the straight string-phase (SS) and the tilted string-phase (TS), see Fig. 4. The SS-phase is similar to the configuration shown in Fig. 2, while for the TS-phase the hexagonal structures are tilted with respect to the y -axis and the layers in the (x, y) -plane are thus not developed. We observe in our simulations that the TS-phase has a higher energy and stress than the SS-phase. When exposing such structures to low shear-rates ($Pe < 21.84$), impermeable-particle systems show a transition to the high-stress state only for simulations where the TS-phase has been developed at high shear-rates. The SS-phase is more stable and does not revert back to the high-stress state.

Permeable-particle systems, on the other hand, develop only the SS-phase, but despite of this they show a transition to the high-stress state at low Pe . We hypothesize that the competition between size and position dynamics drives this transition. Initially, the

particle size is driven by the high shear rate away from the equilibrium value R_{eq} (see Sect. VB). When subjected to lower shear-rates, the reduced size cannot be sustained anymore and the particles relax as they strive to reach the equilibrium size. The particle relaxation time scale $\tilde{\tau}_R = 0.173$ is compared to the shear rate where the reversion to the high-stress state occurs, this is approximately $\text{Pe} \approx 5.8$. One finds $\tilde{\tau}_R \text{Pe} \leq 1$, i.e., the shear deformation is slow enough that the particle size continuously relaxes towards equilibrium, despite the applied deformation. Consequently, one concludes that the shear-induced transition to ordered state is reversible for the case of permeable particles. This conclusion is in accordance with experimental observations. Chen, Zukoski, and coworkers [11–13] have reported that systems of latex polystyrene particles undergo a transition from a crystalline state at equilibrium to a layered structure upon application of constant shear rate. They have found that this transition is reversible upon increasing and decreasing of the shear rates in constant shear-rate experiments. This reversible transition has also been reported for polystyrene/polyisoprene core-shell particles in constant shear-rate experiments [50, 51]. To the best of our knowledge, the reversibility of the shear-induced string-structure formation in permeable-particle systems has not been reported in simulations before, as the particle-size dynamics were not accounted for explicitly.

V. EFFECT OF PARTICLE SOFTNESS

In this section, the effect of the elastic properties of the particles as well as the particle permeability on the overall response are studied in detail. The elastic properties of the particles can be changed by varying the softness dimensionless number S^* . Three different particle systems, with different permeability given by $\zeta^* = (0, 0.005, 0.05)$, are modeled. Each of these systems is modeled for four different values of particle elastic modulus, that is $S^* = \{2.6, 8.6, 26, 86\} \times 10^{-3}$. The effect of S^* on the flow properties as well as the particle dynamics is studied for systems at different Péclet numbers.

A. Shear-flow properties

The effect of S^* and ζ^* on the shear-flow properties, in particular the long-time shear stress and transition time, is investigated here. Figure 5 shows the shear-stress of systems

FIG. 3. Shear stress $\tilde{\sigma}_{xy}$ for permeable- and impermeable-particle systems with $(S^*, \zeta^*, Pe) = (8.6 \times 10^{-3}, 0.05, 0 < Pe < 28)$ and $(S^*, \zeta^*, Pe) = (8.6 \times 10^{-3}, 0, 0 < Pe < 28)$, respectively. The average data points are obtained from five simulations performed with different realizations of the noise. The density of these systems is $\varphi_{\text{free}} = 0.850$. The error bars are based on the standard error obtained from the response of simulations performed with different realizations of the noise. The red square symbols denote simulation conditions where both high- and low- stress states were observed. The black solid lines connect the response of the systems where simulations are performed with SC as the initial configuration subjected to different Pe . The green dashed lines show the response of the system with final structure of simulation performed at $Pe = 21.84$ when subjected to $Pe < 21.84$.

with different permeability, ζ^* , where the Young's modulus of the particles is varied as indicated by the different values of S^* .

First, we study the effect of the permeability ζ^* at a fixed S^* . Considering any of the four panels given in Fig. 5, it can be seen that, for given Pe , the stress response of impermeable-particle systems is higher than that of permeable-particle systems similar to the effect seen in Sect. IV B. The higher the permeability the lower the shear stress as particles are effectively softer and are able to reduce the contact between particles by changing their size more easily. Comparing systems of different softness S^* , Figure 5 also shows that, for given Pe , the differences between permeable and impermeable particles in shear-stress become

FIG. 4. Configurations at $\tilde{t} = 384.6$ for impermeable-particle systems corresponding to Fig. 3 subjected to $Pe = 21.84$ at two different realizations of the noise. Straight string-phase (left) and tilted string-phase (right).

more noticeable as the elastic modulus of the particle decreases, i.e. increasing S^* (see for instance $Pe = 20$). The elastically-softer permeable particles undergo more size change to accommodate the applied deformations which increases the deviation in dimensionless shear-stress $\tilde{\sigma}_{xy}$ from that of impermeable-particle system of the same S^* , at a given shear rate. This effect is explained more thoroughly in Sect. VB where the size change is presented.

The effect of the particle elastic modulus given by S^* is studied by comparing the different panels of Fig. 5. By scaling the shear stresses in Fig. 5 with the corresponding Young's modulus, the explicit effect on the modulus is canceled out. The explicit contribution of the Young's modulus originates from the dependence of the interaction potential and the driving force on the particle modulus. Based on Eq. (3) and Eq. (11), one finds that the stress scales linearly with the Young's modulus, $\sigma_{xy}^{\text{exp}} \propto E$. This implies that the stresses calculated for a given configuration of particles with different Young's moduli scales with their corresponding modulus. However, in a full dynamic system there is an additional implicit contribution of the particle elastic modulus which affects the particle dynamics. Particularly, the distribution of states sampled in a dynamic simulation depends on the particle modulus, which brings about an additional, implicit, dependence of the average stress on the particle modulus. Having said that, Figure 5 pinpoints the effect of the implicit dependence of the shear stress on E which appears to be an inverse dependence with a sub-linear nature, $\tilde{\sigma}_{xy} \propto E^{-a}$, where $0 < a < 1$. This follows directly from the fact that particles

FIG. 5. Shear stress $\tilde{\sigma}_{xy}$ for impermeable- and permeable-particle systems with $\zeta^* = \{0, 0.005, 0.05\}$ and $S^* = 2.6 \times 10^{-3}$ (upper-left), $S^* = 8.6 \times 10^{-3}$ (upper-right), $S^* = 2.6 \times 10^{-2}$ (lower-left), and $S^* = 8.6 \times 10^{-2}$ (lower-right). The density of these systems is $\varphi_{\text{free}} = 0.850$. The error bars are based on the standard error obtained from the response of simulations performed with different realizations of the noise. The red square symbols denote simulation conditions where both high- and low- stress states were observed.

with higher modulus avoid coming in contact with other particles more than particles with lower modulus, as this is not energetically favored (see Sect. V B). Therefore, it is concluded that the overall dependence of the shear stress on the particle elastic modulus is a sub-linear one, $\sigma_{xy} \propto E^{1-a}$.

Finally, we study the deformation-induced transition in terms of the transition Pe denoted by Pe_t and the transition time $\tilde{\tau}_t$. The transition to the low-stress ordered phase is observed for the systems shown in Fig. 5 with the exception of the lowest modulus (lower-left plot) and the permeable particles in the lower-right plot. The effect of ζ^* can be investigated by

comparing the shear-stress response at a given S^* (a given panel in Fig. 5). The transition Péclet number Pe_t is higher for permeable particles as they are more compliant compared to their impermeable counterparts as explained in Sect. IV B. One can compare the difference in Pe_t between permeable- and impermeable-particle systems as the particle softness increases by considering the different panels in Fig. 5. We can see that the Pe_t of permeable and impermeable particles become distinctively separate as the particle modulus is reduced, while the effect of the (non-zero) value of the permeability is insignificant.

Figure 6 shows the transition time corresponding to the systems shown in Fig. 5. The first data point in the panels of Fig. 6 corresponds to the transition time at Pe_t . It is to be noted that Pe_t depends on the total simulation time $\tilde{\tau}_{\text{sim}}$. In other words, for $Pe < Pe_t$, the transition to the low-stress state might occur at times longer than the simulation time. The effect of the permeability is studied by considering one of the four panels in Fig. 6. Consider for instance the upper right panel in Fig. 6, permeable particles require more time to nucleate the low-stress phase than impermeable particles, at a given Pe . The states available for impermeable particles are only a subset of those available for permeable particles, as permeable particles have more degrees of freedom. This restriction on impermeable particles drives them towards forming ordered structures on shorter time scales than permeable particles. In addition, the transition time is found to strongly decay with increasing the Péclet number for both systems. The effect of the particle modulus S^* is explored by comparing the previously described behavior of the different panels of Fig. 6. At a given Pe , one clearly sees that as the particle softness S^* increases, the difference in $\tilde{\tau}_t$ between permeable- and impermeable-particle systems increases (see for instance $Pe = 20$ in the upper row plots in Fig. 6).

In view of the results shown in this section, it is clear that the single particle properties, the particle elastic modulus contained in S^* and the particle permeability given by ζ^* , have a significant influence on the flow properties of these systems. However, there is only a minor effect of permeability when comparing systems with different but finite ζ^* , i.e., when comparing different permeable systems.

FIG. 6. Transition time $\tilde{\tau}_t$ for impermeable- and permeable-particle systems with $\zeta^* = \{0, 0.005, 0.05\}$ and $S^* = 2.6 \times 10^{-3}$ (upper-left), $S^* = 8.6 \times 10^{-3}$ (upper-right), and $S^* = 2.6 \times 10^{-2}$ (lower-left). The density of these systems is $\varphi_{\text{free}} = 0.850$. The error bars are based on the standard error obtained from the response of simulations performed with different realizations of the noise. The red square symbols denote simulations where both high- and low- stress states were observed.

B. Particle dynamics

In this section, quantities characterizing changes in particle position and particle size are identified for the purpose of relating them to changes in the rheological response. The particle dynamics are characterized in terms of the diffusion coefficient and the average particle-size.

The position dynamics can be characterized by the mean square displacement (MSD) of the particles, which, in turn, can be used to calculate the diffusion tensor. A single-particle in a dilute system experiences Brownian forces that drive it to diffuse in the solvent with a diffusion tensor that is diagonal. The diagonal components, in this case, are $D_{xx} = D_{yy} =$

$D_{zz} = D_0$, where D_0 is the single particle diffusion coefficient given by

$$D_0 = \frac{k_B T}{6\pi\eta R_{\text{eq}}}. \quad (23)$$

For the particles used in this study, $D_0 = 8.58 \times 10^{-13} \text{ m}^2/\text{s}$. In a single particle system, the MSD is a linear function of time and the slope of the MSD- t curve is $2D_0$ in each direction. This relation becomes nonlinear over time as more particles are added to the system. Over time, the motion of a particle is hindered by other neighboring particles in the system and their diffusion is therefore lowered. For a many-particle system, the dimensionless diffusion tensor is defined as

$$\tilde{\mathbf{D}}(\tilde{t}) = \frac{1}{2} \frac{\partial}{\partial \tilde{t}} \langle \delta \tilde{\mathbf{q}}_i(\tilde{t}) \otimes \delta \tilde{\mathbf{q}}_i(\tilde{t}) \rangle_{N, N^{\text{sample}}}, \quad (24)$$

where $\langle \cdot \rangle$ denotes the average performed over the number of particles N and the number of samples N^{sample} , where samples are extracted from the same simulation. The displacement vector is $\delta \tilde{\mathbf{q}}_i(\tilde{t}) = \tilde{\mathbf{q}}_i(\tilde{t}) - \tilde{\mathbf{q}}_i(\tilde{t}_0^{\text{sample}})$, where $\tilde{\mathbf{q}}_i$ is the (dimensionless) displacement vector of particle i relative to the flow-field and $\tilde{t}_0^{\text{sample}}$ is the initial time of the sample. The MSD is defined as

$$\text{MSD} = \text{tr} \left(\langle \delta \tilde{\mathbf{q}}_i(\tilde{t}) \otimes \delta \tilde{\mathbf{q}}_i(\tilde{t}) \rangle_{N, N^{\text{sample}}} \right), \quad (25)$$

see Appendix A for an exemplary MSD- $\tilde{t}$ plot. The short-time diffusion tensor is calculated from Eq. (24) at short times. At longer times, Eq. (24) gives the long-time diffusion tensor denoted by $\tilde{\mathbf{D}}^{\text{L}}$. A sample is defined to run long enough to capture the long-time diffusion regime. In an equilibrium simulation, we find that the transition from short-time diffusion to long-time diffusion occurs at around $\tilde{t} = 10^{-2}$ for the permeable systems $\zeta^* = 0.05$ and $\varphi_{\text{free}} = 0.850$. Consequently, we use samples that run over a period of $\tilde{t}_{\text{sample}} = 0.1$ in this analysis. In general, the long-time diffusion coefficient is smaller than the short-time diffusion coefficient. In the sequel, we focus on the long-time diffusion coefficient in the flow direction, i.e. the x -direction, that is component $\tilde{D}_{xx}^{\text{L}}$.

Figure 7 shows the long-time diffusion coefficient in the x -direction, that is the $\tilde{D}_{xx}^{\text{L}}$ component of the diffusion tensor, for permeable- and impermeable- particle systems at different values of S^* . The general properties of the long-time diffusion coefficient can be seen by focusing on systems for given S^* and ζ^* in one of the four panels in Fig. 7. For a system with given S^* and ζ^* , the long-time diffusion coefficient increases with increasing Pe

up to the transition Pe_t , followed by a drop at Pe_t . This drop is attributed to the disorder-order transition. Particles in the ordered state form larger assemblies which move as one entity. The collective motion of particles in the ordered state leads to a lower long-time diffusion coefficient.

The effect of permeability, given by ζ^* , is studied by comparing the data within one panel of Fig. 7. The long-time diffusion appears to be insensitive to the particle permeability, within the accuracy of our simulations.

To study the effect of the elastic softness S^* , we compare the four panels in Fig. 7. The long-time diffusion coefficient, at a given $Pe < Pe_t$, shows no significant dependence on the particle elasticity. However, in the ordered state $Pe > Pe_t$, elastically-softer particles diffuse more in response to a given Pe (compare for instance the plots in the upper row in Fig. 7 at $Pe = 22$). Particle-encounters in soft-particle systems reduce the diffusion less as compared to systems with harder particles.

The other measure of particle dynamics investigated is the particle size. The particle size, initially equal to the equilibrium size R_{eq} , varies over time as the flow field is applied. The average particle size $\langle \tilde{R} \rangle_{N, \Delta \tilde{t}=96}$ is computed as the average over all particles and over a period of $\Delta \tilde{t} = 96$ at the end of the simulation. In the remainder, the notation $\langle \tilde{R} \rangle_{N, \Delta \tilde{t}=96}$ for the average particle size is reduced to $\langle \tilde{R} \rangle$ for convenience. Figure 8 shows the average particle size $\langle \tilde{R} \rangle$ for permeable- and impermeable-particle systems for different values of S^* and ζ^* as a function of Pe . The effect of permeability, i.e. ζ^* , is explored by comparing systems of a given S^* in one of the panels in Fig. 8. Impermeable particles inherently retain their initial size, that is $\tilde{R} = 1$. The average size of permeable particles decreases with increasing the shear rate applied, so that the particles can more easily accommodate the contact forces. It is important to note that, while the difference in particle size between permeable and impermeable particles is significant, the effect of the (non-vanishing) permeability value is almost unnoticeable. Conversely, the effect of the particle softness, S^* , is significant. Comparing the four panels in Fig. 8, permeable particles with lower elastic modulus, i.e. higher S^* , are found to experience larger volume changes than particles with a higher particle modulus (lower S^*), at a given Pe .

The presented results concerning the particle size lead to the following conclusion. The particle permeability affects how fast a particle will change in size in order to minimize the interaction forces. The final size reached, however, is determined by the energetics of the

FIG. 7. Long-time diffusion coefficient in the flow direction $\tilde{D}_{xx}^L$ for impermeable- and permeable-particle systems with $\zeta^* = \{0, 0.005, 0.05\}$ and $S^* = 2.6 \times 10^{-3}$ (upper-left), $S^* = 8.6 \times 10^{-3}$ (upper-right), $S^* = 2.6 \times 10^{-2}$ (lower-left), and $S^* = 8.6 \times 10^{-2}$ (lower-right). The density of these systems is $\varphi_{\text{free}} = 0.850$. The error bars are based on the standard error obtained from the response of simulations performed with different realizations of the noise. The red square symbols denote simulation conditions where both high- and low-stress states were observed.

system, and that is directly related to the elastic properties of the particle.

VI. EFFECT OF SYSTEM DENSITY

In this section, we study the effect of the system density on the shear-flow properties of permeable-particle systems in comparison to impermeable-particle systems. To that end, two systems are investigated in this section, both systems have the same $S^* = 2.6 \times 10^{-3}$, while the permeability is $\zeta^* = 0$ for the impermeable-particle system and $\zeta^* = 0.005$ for the

FIG. 8. Average particle size, $\langle \tilde{R} \rangle$, for impermeable- and permeable-particle systems with $\zeta^* = \{0, 0.005, 0.05\}$ and $S^* = 2.6 \times 10^{-3}$ (upper-left), $S^* = 8.6 \times 10^{-3}$ (upper-right), $S^* = 2.6 \times 10^{-2}$ (lower-left), and $S^* = 8.6 \times 10^{-2}$ (lower-right). The density of these systems is $\varphi_{\text{free}} = 0.850$. The error bars are based on the standard error obtained from the response of simulations performed with different realizations of the noise. The red square symbols denote simulation conditions where both high- and low-stress states were observed. The data for the two permeable-particle systems, i.e. $\zeta^* = 0.005$ and $\zeta^* = 0.05$, are indistinguishable within symbol size.

permeable-particle system. The volume fractions used in this study are $\varphi_{\text{free}} = \{0.739 - 0.916\}$, in order to emphasize the effect of the particle-size changes as explained in Sec. III. The system density is changed by modifying the size of the simulation box for the same number of particles.

Figure 9 shows the shear stress $\tilde{\sigma}_{xy}$ as a function of Pe for permeable-particle systems with different particle volume fractions φ_{free} . The stress response is found to increase as the density of the system increases, even in the low-stress string phase. These systems also show

a decrease in Pe_t as the system density increases, which can be rationalized as follows. As the density increases, the interactions between particles become stronger and the system is driven more readily into the string phase in order to minimize the contact forces between them.

FIG. 9. Shear stress values $\tilde{\sigma}_{xy}$ for permeable-particle systems with $(S^*, \zeta^*, Pe) = (2.6 \times 10^{-3}, 0.005, 0 < Pe < 12)$ at different system densities for one realization of the thermal noise. The density of these systems is varied between $\varphi_{free} = \{0.739 - 0.916\}$ ($n = \{1.13 - 1.4\} \times 10^{19} \text{ m}^{-3}$).

The trends described above with respect to the effect of density are also observed for impermeable-particle systems at different system densities. Figure 10 compares the shear stresses of spongy- and impermeable-particle systems at different Péclet numbers and volume fractions. Fig. 10 shows the ratio of the stresses of permeable (“P”) versus impermeable (“IP”) particles. It shows that the deviation of the stress of the permeable-particle system from the stresses of impermeable particles increases as the system density increases. This is because the nature of the permeable particles allows the system to attain states with lower energy and stress as compared to the impermeable-particle systems, because of the additional degree of freedom. In Fig. 10, the data at different Pe collapse implying that the Péclet number has an only minor influence on the ratio between the shear-stress response of permeable- and impermeable-particle systems.

FIG. 10. Ratio in shear-stress response of impermeable- and permeable-particle systems with $\zeta^* = \{0, 0.005\}$, respectively, with $S^* = 2.6 \times 10^{-3}$ subjected to $\text{Pe} = \{1.456, 2.184, 3.640\}$. The density of these systems is varied between $\phi_{\text{free}} = \{0.739 - 0.916\}$ ($n = \{1.13 - 1.4\} \times 10^{19} \text{ m}^{-3}$).

VII. CONCLUSIONS

In this paper, the shear-flow properties of suspensions of permeable, spongy particles are studied in detail. Spongy particles, in addition to their ability to deform by Hertzian contacts with neighboring particles, can swell (deswell) by taking up (expelling) the viscous suspending solvent. This work aims at investigating the dependence of the overall shear-flow behavior of these suspensions on the properties of the individual particles. Of particular interest is the distinction between the elastic softness and the rate-dependent softness of the particles. To that end, the dynamic two-scale model developed by Hütter et al. [30] is applied to suspensions of spongy particles subject to simple shear deformation. In order to capture the rate-dependent size change, the model treats the size of the particle as an independent degree of freedom. The driving forces for the dynamics of particle positions and sizes originate from an energy expression that includes a repulsive contribution to account for the elastic shape-change in Hertzian inter-particle contacts, and an additional contribution that allows the particle to strive towards its equilibrium shape even in the absence of other interacting particles. In terms of rate-dependence, it is mentioned that the particle permeability plays a key role in the size dynamics.

The main results presented in this paper are summarized as follows. Both suspensions of permeable and impermeable particles show shear-thinning behavior at $Pe > 1$. As the Péclet number is further increased, most of the suspensions examined in this paper undergo a transition to a low-stress string state, within time scale of observation. The transition times, i.e. the time scales at which the string phase develops, are considerably longer than the Brownian time scale for position change, specifically for low and intermediate values of the softness parameter S^* examined in this study. The systems that did not show this transition might do so if the simulations were run substantially longer. Therefore, the identification of a certain Péclet number, called Pe_t , beyond which an ordered low-stress state is observed, inherently depends on the total simulation time. Consequently, we emphasize the importance of the observation window based on which the measurements are performed. With respect to the dependence of the transition Péclet number Pe_t on physical parameters, we find that comparing systems with the same elastic properties, spongy particles form ordered structures at higher shear rates, i.e. they have a higher Pe_t , than what is observed for impermeable particles. Moreover, at the same shear rate where both systems form ordered structures, spongy particles take more time to nucleate the low-stress ordered phase. We also find that, as the particle elastic-softness increases, the transition Péclet number and the transition time for a given Pe increases. Furthermore, we find that, while there is a clear strong difference in long-time properties between permeable- and impermeable-particle systems, the differences are rather minor when comparing two permeable-particle systems. In other words, the value of the non-vanishing permeability has a minor influence on the long-time properties of the permeable-particle system. It has also been shown that Pe_t decreases as the system density increases. Furthermore, we identify in this work the main differences in the hysteresis process between impermeable- and permeable-particle systems. For permeable particles, it occurs when the particle size is allowed to continuously equilibrate despite the applied flow, i.e., the imposed rate of deformation is smaller than the single-particle size relaxation, $\dot{\gamma}\tau_R < 1$.

The presented approach and simulation results capture qualitatively various fundamental features of the experimentally observed behavior of dense permeable-particle systems. Shear thinning for instance has been observed for systems of PNIPAM particles [14, 15]. Shear-induced ordering has been experimentally studied for various types of particles, such as hard particles [10], elastic particles [47], and permeable particles [13, 15]. Finally, the hysteresis behavior of permeable particles has been reported in literature in experimental work (e.g.,

[12, 13]); however, to the best of our knowledge, this phenomenon has not been observed in simulations, yet.

In view of these results, we recall the leading attraction of industrial applications to using permeable particles, that is the versatility in modifying the overall properties of the system through tailoring the individual particle properties. This work accentuates the effect of the single particle permeability and elastic properties, in view of the rate-dependent size-dynamics, on the overall behavior of suspensions of these particles. In a nutshell, we have demonstrated that the particle permeability affects the rate at which the final state is reached, hence the dynamics of the system, while the shear-stress response of the final state itself is dominated by the elastic properties of the individual particle. In addition, the volume fraction of spongy-particle systems is an important parameter that dictates the state of the system, however it is often ambiguously defined [23]. We show in this work that the volume fraction of spongy-particle systems, although evolves in time, is independent of the (non-vanishing) permeability and primarily dependent on the elastic properties of the individual particle at long times. Furthermore, we speculate that these results are particularly interesting in the particle-synthesis stage. For instance, PNIPAM particles are synthesized by cross-linking the polymer network which in turn affects both the permeability of the particle as well as its elasticity [52, 53]. One can then adjust the amount of cross-linker depending on whether the particles dynamics or the long-time properties are more important in a certain the application. However, ultimately it would be desirable to have synthesis protocols that allow for tuning the particle permeability and elasticity separately.

In future work, the stress relaxation of spongy-particle suspensions will be investigated. The slow dynamics of such systems suggest that their properties evolve continuously over time, akin to the phenomenon of physical aging in polymers [18]. We have shown in this paper and our previous work, where we studied the equilibrium behavior of spongy-particle suspensions [9], that the size dynamics play a significant role in the overall behavior of these suspensions. In addition to particles changing in size, the next natural step would be to even account for shape change.

VIII. SUPPLEMENTARY MATERIAL

See supplementary material for the multimedia file (video) associated with Fig. 2, and the corresponding first frame (picture).

ACKNOWLEDGMENTS

This work forms part of the research programme of the Dutch Polymer Institute (DPI), project #738.

Appendix A: Mean square displacement

The mean square displacement, MSD, of permeable particles with $\zeta^* = 0.05$ and $S^* = 8.6 \times 10^{-3}$ is presented as a function of time $\tilde{t}$, in order to show the deviation from the simple diffusive behavior. The MSD is given by Eq. (25). To do so, two systems with the same realization of the thermal noise are considered, one at $Pe = 7.28$ and the other at $Pe = 24.02$. The latter undergoes a transition to a shear-induced ordered state and the former does not (see shear-stress response in Fig. 5).

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FIG. 11. Double logarithmic plot of the mean square displacement (MSD) as a function of time of permeable-particle systems with $\zeta^* = 0.05$ and $S^* = 8.6 \times 10^{-3}$ subjected to $Pe = \{7.28, 24.02\}$. The dashed line indicates the mean square displacement for a diffusive process with slope of unity.

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