Available online at www.sciencedirect.com
ScienceDirect
C. R. Mecanique 336 (2008) 512–517
COMPTES RENDUS MECANIQUE
http://france.elsevier.com/direct/CRAS2B/

Elastic modulus of a colloidal suspension of rigid spheres at rest

Laurentiu Pasol [a], Xavier Chateau [b,*]

[a] *Laboratoire physique thermique-ESPCI, 10, rue Vauquelin, 75231 Paris cedex 05, France*
[b] *Institut Navier, Laboratoire des matériaux et des structures du génie civil, 2, allée Kepler, 77420 Champs-sur-Marne, France*

Received 20 June 2007; accepted after revision 19 February 2008

Available online 14 April 2008

Presented by André Zaoui

Abstract

By modeling a colloidal suspension at rest as a solid, a new expression for the linear elastic modulus is obtained. This estimate is valid for a yield stress colloidal suspension submitted to a small strain. Interestingly, it is also possible to construct an hypothesis allowing one to recover the high-frequency modulus classically found by means of a classical 'fluid approach'. However, in most of the situations, the moduli obtained by the two approaches are different. ***To cite this article: L. Pasol, X. Chateau, C. R. Mecanique 336 (2008).***

Résumé

Module d'élasticité d'une suspension colloïdale de sphères dures au repos. En modélisant une suspension colloïdale au repos comme un solide, on obtient une nouvelle expression pour le module d'élasticité linéaire. Cette expression permet d'estimer le module d'une suspension colloïdale possédant un seuil d'écoulement soumise à une déformation infinitésimale. On montre également que sous certaines hypothèses, cette approche permet de retrouver l'expression du module élastique à grande fréquence obtenu par une approche classique de type fluide. ***Pour citer cet article : L. Pasol, X. Chateau, C. R. Mecanique 336 (2008).***

Keywords: Rheology; Colloidal suspension; Elastical modulus

Mots-clés : Rhéologie ; Suspension colloïdale ; Module d'élasticité

1. Introduction

The macroscopic rheological properties of a colloidal suspension are the counterpart at the macroscopic scale of phenomena occurring at the length scale of the particles. The forces applied to the particles originate from different phenomena: colloidal forces, hydrodynamic interactions, Brownian motions, etc. The intensity of these forces depends upon several parameters as the temperature, the size of the particles, the separation gap between particles, or the pH of the suspending fluid.

* Corresponding author.
E-mail addresses: laurentiu.pasol@espci.fr (L. Pasol), xavier.chateau@lcpc.fr (X. Chateau).

1631-0721/$ – see front matter
doi:10.1016/j.crme.2008.03.001

At the macroscopic scale, the elastic modulus is one of the parameters which characterize the suspension behavior. It has been recognized from a long time that its value depends in particular upon the interactions between particles. The problem of the transition from the microscale to the macroscale in view of the prediction of the macroscopic properties of the suspension has been the matter of intensive research for decades. The main underlying motivation for this work is to predict the overall behavior of the suspension from the description of the particles properties. Most of the results have been obtained in the framework of statistical physics. For example Zwanzig and Mountain computed the high frequency shear modulus of a simple monoatomic fluid where only binary interactions are likely to occur in the absence of Brownian motion and hydrodynamic forces [1]. Wagner generalized this result in order to account for Brownian motion and hydrodynamic interaction by means of a linear theory [2]. He showed that the Zwanzig and Mountain results are still valid when hydrodynamic interactions between particles are negligible. For concentrated suspensions Lionberger and Russel showed that long-range hydrodynamic interactions can be neglected, the main contribution coming from the lubrification forces [3]. Brady developed in [4] a theory accounting for specific interparticle force laws and their influence on the suspension rheology in the linear regime in the framework of a mechanical approach. Divergence of the viscosity at random close packing density was recovered and the value of the exponent is predicted as a function of the interparticles forces (Brownian hard spheres or particle interacting through strongly repulsive colloidal forces).

The difficulty encounted to experimentally measure colloidal forces also motivated interest in this field, mainly for elasticity. The idea is to use theoretical results obtained in the framework of change of scale methods in order to determine microscopic properties of the suspension from the measurement of macroscopic elastic modulus. Such a method was proposed in [5] to estimate the effective surface charge of particles of a concentrated suspension from the measurement of the high-frequency elastic modulus.

In most of these works, the suspension is modeled as a fluid. From a practical point a view, it is well known that concentrated colloidal suspensions often exhibit a yield stress: they flow and behave like a fluid only when submitted to a stress above the yield stress. Otherwise, they behave like a solid. In the solid state, a colloidal suspension can be seen as a disordered solid in which the particles form a connected network. As long as the applied forces are not big enough to trigger off finite displacement of the particles from their rest position, the overall mechanical properties of the suspension can be predicted in the framework of change of scale methods pertaining to heterogeneous solid materials.

In this Note, we show that it is possible to perform such approach in order to estimate elastic modulus for a colloidal suspension. For simplicity, we restrict ourselves to the situations where hydrodynamic interactions and Brownian motions are neglected. As a consequence, our results are valid only for naught-velocity loading in the solid regime (quasistatic elastic behavior) or high-frequency loading in the fluid regime.

The paper is organized as follows. We begin by recalling the relation linking the Cauchy stress tensor to the interaction force. Then, we compute the macroscopic strain–stress behavior law in the linear regime. Finally, a new estimate for the elastic shear modulus of the suspension is obtained before we conclude.

2. Cauchy tensor for a colloidal suspension at rest

We consider a monodiperse suspension of spherical particles with radius a distributed in an incompressible Newtonian fluid. Particles interact through colloidal interaction forces. The suspension is at rest both at the microscopic and the macroscopic scales, so that hydrodynamic interaction forces are negligible. It is assumed that no forces from outside are applied on the particles or on the fluid.

Consider a representative elementary volume (r.e.v.) of the suspension occupying the geometrical domain V and containing N particles ($N \gg 1$). The macroscopic Cauchy stress tensor $\boldsymbol{\sigma}$ can be computed from the knowledge of the microscopic quantities using the classical Batchelor equation [6,7]:

$$\boldsymbol{\sigma} = \frac{1}{V}\int_V \tilde{\boldsymbol{\sigma}}\,\mathrm{d}V = -\frac{1}{V}\int_{V_\mathrm{f}} p\boldsymbol{\delta}\,\mathrm{d}V + \frac{1}{V}\sum_{i=1}^{N} \boldsymbol{s}_i \tag{1}$$

where p denotes the fluid pressure, $\boldsymbol{\delta}$ the second order unit tensor, V_f the geometrical domain filled by the fluid and $\boldsymbol{s}_i$ the stresslet of the particle i, equal to

$$\boldsymbol{s}_i = \frac{1}{2}\int_{A_i} \left(\tilde{\boldsymbol{\sigma}}\cdot\underline{n}\otimes(\underline{x}-\underline{x}_i)+(\underline{x}-\underline{x}_i)\otimes\tilde{\boldsymbol{\sigma}}\cdot\underline{n}\right)\mathrm{d}S = \int_{A_i}(\underline{x}-\underline{x}_i)\otimes\tilde{\boldsymbol{\sigma}}\cdot\underline{n}\,\mathrm{d}S \tag{2}$$

with $\tilde{\boldsymbol{\sigma}}$, the Cauchy stress tensor field in the particles, $\underline{x}_i$ the center of particle i and A_i the boundary of the domain occupied by the particle i. In Eq. (2), $\underline{n}$ denotes the outer unit normal to the domain A_i and $\underline{x}$ the position vector in the studied configuration.

We consider only stable colloidal dispersions where interaction forces dominate Brownian effects. Then the particles form a disordered network. The only contribution of particle i to the stress tensor is the stresslet $\boldsymbol{s}_i$. Thanks to the assumption that no external forces apply on the particles, the strain tensor $\tilde{\boldsymbol{\sigma}}$ is symmetric and so is the macroscopic Cauchy stress tensor. Furthermore, the fluid pressure is uniform over the domain occupied by the fluid in the representative elementary volume. As it is classical, it is assumed that interparticle forces derive from a potential [8]. Then, $\underline{F}_{j\to i}$, the force applied by particle j to particle i reads $\underline{F}_{j\to i} = -\frac{\partial\psi}{\partial\underline{x}_i}(\underline{x}_{ij})$ where $\underline{x}_{ij} = \underline{x}_j - \underline{x}_i$ denotes the vector connecting the center of particle i to the center of particle j. It is advisable to note here that when the interparticle forces are described by force vectors, the Batchelor's equation (1) is no more valid. Putting the equilibrium equation for both the whole r.e.v. and each particle in Eq. (1) allows one to compute the macroscopic Cauchy stress tensor as a function of the interparticle forces and the fluid pressure [7–9]

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} - \frac{1}{V}\sum_{i<j}^{N}\underline{F}_{i\to j}\otimes\underline{x}_{ij} \tag{3}$$

This relation can also be obtained in the framework of a micromechanical approach to the behavior of a heterogeneous material [10]. It is recalled that mechanical homogenization techniques aim at finding the overall behavior of a system in a form of relationship between macroscopic stress and strain tensors from the response of the r.e.v. to a mechanical loading in which one of the two macroscopic tensors acts like a loading parameter. As the mechanical behavior of the suspension does not depend on the value of the fluid pressure, it is assumed that p is naught in the following.

Of course, one has to consider an arbitrary realization of the material system to compute Eq. (3). In order to obtain results which do not depend on the particular selected realization, it is necessary to average Eq. (3) over all the possible realizations of the system. Let $\mathcal{C}_N = \{\underline{x}_1, \underline{x}_2, \ldots, \underline{x}_N\}$ denotes a particular realization for the centers of the N particles embedded in the r.e.v. and let $P_N(\underline{x}_1, \underline{x}_2, \ldots, \underline{x}_N)$ denotes the probability of finding simultaneously the particle centers in $\underline{x}_1, \underline{x}_2, \ldots, \underline{x}_N$. As the particles are indistinguishable the probability to find simultaneously the center of one particle in $\underline{x}_1$ and the center of another particle in $\underline{x}_2$ reads

$$p_2(\underline{x}_1, \underline{x}_2) = \frac{1}{(N-2)!}\int_{V^{N-2}} P_N(\mathcal{C}_N)\,\mathrm{d}\underline{x}_3\cdots\mathrm{d}\underline{x}_N = n^2 g(\underline{r}) \tag{4}$$

where $\underline{r} = \underline{x}_1 - \underline{x}_2$ and $n = N/V$ denotes the number density of particles in the representative elementary volume. The second equality of Eq. (4) is only valid for statistically homogeneous suspensions. It is assumed that this condition is fulfilled in the following. g is the radial distribution function [11]. Averaging the stress tensor, Eq. (3), with the probability $p_2(\underline{x}_1, \underline{x}_2)$ defined by (4) yields

$$\langle\boldsymbol{\sigma}\rangle = -\frac{n^2}{2}\int_V \underline{r}\otimes\underline{F}(\underline{r})\,g(\underline{r})\,\mathrm{d}V(\underline{r}) \tag{5}$$

where the convention $\underline{F}(\underline{r}) = \underline{F}_{2\to1}(\underline{r})$ has be used to simplify the notations.

3. Elastic modulus

In order to identify the tangent moduli of the suspension, a macroscopic linearized strain $\boldsymbol{\varepsilon}$ is applied to the representative elementary volume occupying the geometrical domain V_0 in the undeformed configuration. A particle located at $\underline{X}_i$ in the reference configuration moves to the position $\underline{x}_i$ in the deformed configuration. Such a macroscopic loading can be defined by the so-called Hashin boundary condition according to which the displacement of

particles located on the boundary of the r.e.v. is prescribed, equal to $\boldsymbol{\varepsilon}\cdot\underline{X}_i$. As the particles are rigid, the macroscopic loading must comply with the incompressibility condition $\boldsymbol{\delta}:\boldsymbol{\varepsilon}=0$. It is worth noting that for each realization of the suspension, local material heterogeneities are responsible for microscopic fluctuations of the displacement around the linear field $\boldsymbol{\varepsilon}\cdot\underline{X}$.

Up to the first order in $\boldsymbol{\varepsilon}$, the Cauchy stress tensor on the deformed configuration reads

$$\langle\boldsymbol{\sigma}\rangle=\langle\boldsymbol{\pi}^0\rangle-\frac{n^2}{2}\int_{V_0}\left(\underline{R}\otimes\underline{F}\left(\frac{\mathrm{d}g_0}{\mathrm{d}\underline{R}}\cdot\mathbb{A}:\boldsymbol{\varepsilon}\right)+\left(\mathbb{A}:\boldsymbol{\varepsilon}\otimes\underline{F}+\underline{R}\otimes\frac{\mathrm{d}\underline{F}}{\mathrm{d}\underline{R}}\cdot\mathbb{A}:\boldsymbol{\varepsilon}\right)g_0\right)\mathrm{d}V \tag{6}$$

with

$$\langle\boldsymbol{\pi}^0\rangle=-\frac{n^2}{2}\int_{V_0}\underline{R}\otimes\underline{F}(\underline{R})\,g_0(\underline{R})\,\mathrm{d}V \tag{7}$$

$\boldsymbol{\pi}^0$ denotes the Piola–Kirchhoff stress tensor on the underformed configuration [12,13]. $\langle\boldsymbol{\pi}^0\rangle$ is equal to the Cauchy stress tensor in the undeformed configuration. It is worth noting that quantities $\underline{F}$, g_0 and $\mathbb{A}$ are function of the position vector $\underline{R}$ (the dependence have been omitted for simplicity). The relative displacement concentration tensor defined by $\mathbb{A}(\underline{R})=\mathrm{d}\underline{R}/\mathrm{d}\boldsymbol{\varepsilon}$ allows one to compute the relative displacement $\underline{r}-\underline{R}=\underline{x}_2-\underline{x}_1-(\underline{X}_2-\underline{X}_1)$ of two particles induced by the loading $\boldsymbol{\varepsilon}$.

Explicitly knowing the third order tensor $\mathbb{A}(\underline{R})$ would allow one to compute the behavior law linking the Cauchy stress tensor to the linearized strain tensor $\boldsymbol{\varepsilon}$. It is assumed in the following that the behavior of the suspension is linear elastic at the macroscopic scale. Then, the macroscopic state law reads [13]

$$\boldsymbol{\sigma}=\boldsymbol{\pi}^0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\pi}^0+\boldsymbol{\pi}^0\cdot\boldsymbol{\varepsilon}+\mathbb{C}:\boldsymbol{\varepsilon}=\boldsymbol{\pi}^0+\mathbb{L}(\boldsymbol{\pi}^0):\boldsymbol{\varepsilon} \tag{8}$$

where $\mathbb{L}(\boldsymbol{\pi}^0)$ denotes the tangent tensor and $\mathbb{C}$ the elastic tensor. It is recalled that the tensor $\mathbb{L}(\boldsymbol{\pi}^0)$ is generally not equal to the elastic tensor $\mathbb{C}$ and does not satisfy the classical property of definite positivity [13]. Comparing Eq. (6) with the second equality (8) allows one to compute $\mathbb{L}$.

$$\mathbb{L}=-\frac{n^2}{2}\int_{V_0}\left(\underline{R}\otimes\underline{F}\otimes\frac{\mathrm{d}g_0}{\mathrm{d}\underline{R}}\cdot\mathbb{A}+g_0\left(\underline{R}\otimes\frac{\mathrm{d}\underline{F}}{\mathrm{d}\underline{R}}\cdot\mathbb{A}+\underline{F}\underset{1\leftrightarrow2}{\otimes}\mathbb{A}\right)\right)\mathrm{d}V \tag{9}$$

with $\underline{F}\otimes_{1\leftrightarrow2}\mathbb{A}=F_j\mathbb{A}_{ik\ell}\underline{e}_i\otimes\underline{e}_j\otimes\underline{e}_k\otimes\underline{e}_\ell$. The elastic tensor $\mathbb{C}$ can be easily computed by combining Eqs. (8) and (9).

In the following, it is assumed that the suspension is isotropic in the undeformed configuration. Then the radial distribution function reads $g_0(\underline{R})=g_0(|\underline{R}|)=g_0(R)$. Moreover, it is also assumed that the interparticle forces are central, which writes $\psi(\underline{R})=\psi(R)$. The interparticle forces read

$$\underline{F}=-\frac{1}{R}\frac{\mathrm{d}\psi}{\mathrm{d}R}\underline{R} \tag{10}$$

Putting Eq. (10) into expression (5) yields the value of the stress tensor in the undeformed configuration

$$\langle\boldsymbol{\pi}^0\rangle=\frac{2\pi}{3}n^2\int_{R=2a}^{\infty}R^3\frac{\mathrm{d}\psi(R)}{\mathrm{d}R}g_0(R)\,\mathrm{d}R\,\boldsymbol{\delta} \tag{11}$$

In Eq. (11), it was assumed that R is unbounded whereas one would expect that the r.e.v. is of finite extent. Insofar as the r.e.v. must be large enough to be of typical composition and that its overall properties do not depend ont its size, the macroscopic behavior of the suspension can be defined only if the decay of the interparticle forces for large R is strong enough that the contribution of long range forces is negligible. When these conditions are fulfilled, it is possible to simplify the computation of quantities defined as an average over the r.e.v. by assuming that the r.e.v. is unbounded. The same truncature process is used in the sequel of the paper. As the stress tensor in the reference configuration is isotropic, the internal force is characterized by a pressure, equal (up to the fluctuation term nk_BT) to the osmotic pressure of a colloidal system classically defined in the framework of statistical mechanics [8]. Thanks to the fact that the initial configuration is isotropic and the interparticle forces are central, we obtain

$$\frac{\mathrm{d}g_0}{\mathrm{d}\underline{R}}=\frac{1}{R}\frac{\mathrm{d}g_0}{\mathrm{d}R}\underline{R} \tag{12}$$

The tensor field $\mathbb{A}$ depends upon the morphological properties of the suspension in the undeformed configuration. As it is not possible to compute $\mathbb{A}$ from a practical point of view, we purpose to compute the overall properties of the suspension using the classical choice $\forall \underline{R}$, $\mathbb{A}(\underline{R}) : \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon} \cdot \underline{R}$ leading to the popular "mean field theory". Using this particular localization field allows one to obtain only estimates of the overall properties of the suspension because this choice defines the solution of the problem under consideration only in particular situation (uniform radial distribution function, periodic lattice, ...).

Combining this estimate with the relations (6), (12) and the incompressibility condition $\boldsymbol{\varepsilon} : \boldsymbol{\delta} = 0$ yields the following behavior law of the suspension

$$\langle \boldsymbol{\tau} \rangle = 2G^s \boldsymbol{\varepsilon}, \quad \text{with } G^s = \frac{3\phi^2}{40\pi a^6} \int_{R=2a}^{\infty} \frac{\mathrm{d}}{\mathrm{d}R}\left(R^4 \frac{\mathrm{d}\psi}{\mathrm{d}R}(X) g_0(R) \right) \mathrm{d}R \tag{13}$$

where $\phi = n4\pi a^3/3$ denotes the volumic fraction and $\boldsymbol{\tau} = \boldsymbol{\sigma} - (\boldsymbol{\delta} : \boldsymbol{\sigma})/3\boldsymbol{\delta}$ the deviatoric part of the Cauchy stress tensor. It can be shown that the "solid modulus" (13) is no more than the classical Voigt estimate one can obtain using the uniform strain field as a trial field in a variational approach to the problem under consideration. Then, Eq. (13) defines an upper bound of the real solid shear modulus of the suspension.

It is reminded that classically, the actual configuration is taken as the reference configuration to compute the elastic moduli tensor [2]. This result can be recovered by performing exactly the same computations than above on the undeformed configuration. This approach yields the "liquid" elastic shear estimate

$$\langle \boldsymbol{\tau} \rangle = 2G^{\ell} \boldsymbol{\varepsilon}, \quad \text{with } G^{\ell} = \frac{3\phi^2}{40\pi a^6} \int_{R=2a}^{\infty} \frac{\mathrm{d}}{\mathrm{d}R}\left(R^4 \frac{\mathrm{d}\psi}{\mathrm{d}R}(R) \right) g_0(R)\, \mathrm{d}R \tag{14}$$

The difference between the two estimates comes from the fact that the radial distribution function is derived with respect to R in Eq. (13) and not in Eq. (14). It is possible to obtain the "liquid" estimate from the "solid" one by assuming the radial distribution function conservation in the course of deformation. Then, it is shown from Eq. (6) that, up to the first order of $\boldsymbol{\varepsilon}$, the Cauchy stress tensor reads

$$\langle \boldsymbol{\sigma} \rangle = \langle \boldsymbol{\pi}^0 \rangle - \frac{n^2}{2} \int_{V_0} \frac{\mathrm{d}[\underline{R} \otimes \underline{F}]}{\mathrm{d}\boldsymbol{\varepsilon}} : \boldsymbol{\varepsilon}\, g_0(\underline{R})\, \mathrm{d}V(\underline{R}) \tag{15}$$

(it is always assumed that the material is incompressible). Considering one more time that the suspension is isotropic in the reference configuration, one readily obtains from Eq. (15) the estimate (14) for the elastic shear modulus of the suspension in the framework of a mean field theory.

4. Conclusions

We have obtained a new expression for the elastic shear modulus of a colloidal suspension modeled as a solid. This expression allows one to estimate the elastic modulus of a yield stress suspension submitted to a load smaller than the yield stress. This result was obtained in the framework of an homogenization approach to the behavior of a colloidal suspension considered as a discrete solid medium. Even if this approach relies on assumptions rather different from those classically performed to obtain estimates for the overall properties of suspensions in the framework of statistical mechanics, it is worth noting that classical results can also be recovered. Thus, we have shown that our estimate coincides with the classical high-frequency modulus estimate when the actual configuration is taken as the reference. From our point of view, this result was recovered by modeling the suspension as a "liquid", i.e. a suspension without a yield stress. In this situation, it is not possible to define an "undeformed" configuration and the actual configuration is taken as the reference. In our opinion, this similarity is a strong indication that both approaches are consistent one to the other.

Furthermore, it has been recalled that the tangent modulus is not equal to the elastic modulus when the stress applied to the material in the reference configuration and the elastic modulus are of the same order of magnitude.

Acknowledgements

LMSGC de l'Institut Navier (Université Paris Est) is UMR 113 of the CNRS associated with the ENPC and the LCPC.

Support from the Agence Nationale de la Recherche (ANR) is acknowledged (grant ANR-05-JCJC-0214).

References

[1] R. Zwanzig, R.D. Mountain, High-frequency elastic moduli of simple fluids, J. Chem. Phys. 43 (1965) 4464–4471.
[2] N.J. Wagner, The high-frequency shear modulus of colloidal suspensions and the effects of hydrodynamic interactions, J. Colloid Interface Sci. 161 (1993) 169–181.
[3] R.A. Lionberger, W.B. Russel, High frequency modulus of hard sphere colloids, J. Rheology 38 (1994) 1885–1908.
[4] J. Brady, The rheological behavior of concentrated colloidal dispersions, J. Chem. Phys. 99 (1993) 567–581.
[5] J. Bergenholtz, N. Willenbacher, N.J. Wagner, M.J. Morrison van den Ende, Colloidal charge determination in concentrated liquid dispersions using torsional resonance oscillation, J. Colloid Interface Sci. 202 (1998) 430–440.
[6] G. Batchelor, The stress system in a suspension of force-free particles, J. Fluid Mech. 41 (1970) 545–570.
[7] G. Batchelor, The effect of Brownian motion on the bulk stress in a suspension of spherical particles, J. Fluid Mech. 83 (1977) 97–117.
[8] W.B. Russel, D.A. Saville, W.R. Schowalter, Colloidal Dispersions, Cambridge University Press, 1995.
[9] X. Chateau, P. Moucheront, O. Pitois, Micromechanics of unsaturated granular media, ASCE J. Eng. Mech. 128 (8) (2002) 856–863.
[10] A. Zaoui, Continuum micromechanics: Survey, ASCE J. Eng. Mech. 128 (8) (2002) 808–816.
[11] J.P. Hansen, I.R. McDonald, Theory of Simple Liquids, Academic Press, London, 1986.
[12] P. Germain, Cours de Mécanique des Milieux Continus, Masson, Paris, 1973.
[13] J. Salençon, Handbook of Continuum Mechanics. General Concepts, Thermoelasticity, Springer, Berlin, 2001.