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Irreversible thermodynamics for the rheological properties of colloids

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Abstract—The viscoelastic and plastic properties of globular colloids are treated on the grounds of the strictly linear Onsager theory of irreversible processes. In the case of emulsions, the effect of interfacial tension is also taken into account. The intricate mechanical behaviour of colloids is reported by classical non-equilibrium thermodynamics using only three material constants.

INTRODUCTION

IN RECENT years the Onsager theory of non-equilibrium processes proved an excellent method for treating rheological phenomena. The versatility of the method is shown here for the example of globular colloids, which are very important as they are present almost everywhere in technology. We mention only some foodstuffs, such as milk, butter or various kinds of paste, paints, some lubricants, adhesives, etc. Their viscoelastic and plastic behaviour is very important and the easy description is considerable in engineering.

The model used here for colloidal systems is rather simplified, nevertheless, the final results can be generalized with ease. The body is supposed to be fluid and to have two phases. The continuous phase is a Newtonian fluid, while the dispersed phase consists of elastic spheres of uniform size, moreover, we will only be concerned with isochoric (i.e. steady volume) motions.

THERMODYNAMIC PRELIMINARIES

As a starting point of the thermodynamics treatment, the elastic energy of the colloid particles is assumed to be not dissipated. This means that the specific entropy can be calculated from the internal energy after reducing it with the elastic energy

$$s = s(u^*)$$
$$u^* = u - \phi\frac{\mu}{\rho}\underline{\varepsilon}:\underline{\varepsilon} \tag{1}$$

where s is the specific entropy, u the specific internal energy, ρ the average density, ϕ the volume fraction of the dispersed phase, and μ the shear modulus of the spheres. The strain tensor $\underline{\varepsilon}$ of the particles is symmetric and has zero trace, moreover, it equals zero in any equilibrium state. Making use of the balance equation of internal energy

$$\rho\dot{u} + \operatorname{div}\mathbf{J}_q = \underline{t}:\underline{\mathring{d}} \tag{2}$$

where $\underline{t}$ is the deviatoric part of Cauchy's stress and $\underline{\mathring{d}}$ is the symmetric part of the velocity gradient tensor, we obtain

$$T\sigma_s = \underline{t}:\underline{\mathring{d}} - 2\phi\mu\underline{\varepsilon}:\underline{\dot{\varepsilon}} - \frac{1}{T}\mathbf{J}_q\cdot\operatorname{grad}T. \tag{3}$$

Here T is the temperature, $\mathbf{J}_q$ the heat flux and σ_s the entropy production density. The details of the calculations are given in refs. [1–4].

We mention that equation (3) is valid in case of any frame of reference according to the Gibbs–Duhem equation. For this reason and keeping convenience in mind, the time derivative of the strain tensor is evaluated in a corotating frame and transformed to the actual one afterwards. This means that the so-called Jaumann derivatives of the tensors are used from now on. The third term on the right-hand side of equation (3) concerns the heat conduction, which does not interest us in this paper. So, dropping this term and using the objective time derivative, we obtain

$$T\sigma_s = \underline{t}:\underline{\mathring{d}} - 2\phi\mu\underline{\varepsilon}:\underline{\mathring{\varepsilon}}. \tag{4}$$

This is the very form of the entropy source strength that can be applied to obtain the constitutive equations [1–3]. Onsager's linear laws result in

$$\underline{t} = L_{11}\underline{\mathring{d}} - 2\phi\mu L_{12}\underline{\varepsilon}$$
$$\underline{\mathring{\varepsilon}} = -L_{12}\underline{\mathring{d}} - 2\phi\mu L_{22}\underline{\varepsilon}. \tag{5}$$

Since the entropy production is always positive, we have the inequalities

$$L_{11} > 0, \quad L_{22} > 0. \tag{6}$$

Sometimes the deformation of the particles is not of interest to us. In this case, it is worth eliminating it from equations (5) to give

$$\underline{t} + \tau_t\underline{\mathring{t}} = 2\eta(\underline{\mathring{d}} + \tau_d\underline{\mathring{d}}), \quad \tau_t > \tau_d > 0, \quad \eta > 0. \tag{7}$$

Here we have introduced the notations

NOMENCLATURE

$\underset{\circ}{d}$ symmetric part of the velocity gradient tensor
$d_{i,k}$ Cartesian components of the velocity gradient tensor ($i,k = 1,2,3$)
$\mathbf{J}_q$ heat flux density
L_{11}, L_{22}, L_{12} Onsager's coefficients
p complex frequency
s specific entropy
$\underline{t}$ deviatoric part of Cauchy's stress tensor
T temperature
u specific internal energy
u^* quantity defined in equation (1)
v_x, v_y, v_z Cartesian components of velocity.

Greek symbols
η^* average (complex) viscosity
η_0 viscosity of the continuous phase
η_K viscosity of the Kelvin body defined in equation (30)
κ rate of shear
μ shear modulus of the dispersed phase
μ^* average (complex) shear modulus
μ_0 (complex) shear modulus of the continuous phase
μ^K shear modulus of the Kelvin body defined in equation (30)
ρ average density
σ_s entropy source strength
$\sigma(\kappa)$ normal stress function
σ normal stress
τ_t, τ_d, η material constants defined in equation (8)
$\tau(\kappa)$ shear stress function
ϕ volume fraction of the dispersed phase
$\underline{\omega}$ angular velocity tensor (i.e. the skew symmetric part of the velocity gradient)
ω_{ik} Cartesian components of the angular velocity tensor ($i,k = 1,2,3$)
$\boldsymbol{\omega}$ angular velocity vector (i.e. the vector invariant of $\underline{\omega}$)
ω_i Cartesian components of the angular velocity vector ($i = 1,2,3$).

$$\tau_t = \frac{1}{2\phi\mu L_{22}}; \quad \tau_d = \frac{L_{11}}{2\phi\mu(L_{11}L_{22}+L_{12}^2)};$$

$$2\eta = L_{11} + \frac{L_{12}^2}{L_{22}}. \quad (8)$$

The constitutive equation (7) shows a close analogy to that of a Jeffery body and is identical to it if no rotation occurs. The difference lies only in its derivation but this slight deviation results in remarkable consequences.

SMALL OSCILLATIONS

In the case of small oscillations, the objective derivatives approximately equal the ordinary ones, then the constitutive equation (7) becomes

$$\underline{t} = 2\eta \frac{1+\tau_d\rho}{1+\tau_t\rho}\underset{\circ}{\underline{d}} \quad (9)$$

where ρ is the so-called complex frequency. The values of the phenomenological coefficients are determined by comparing the complex viscosity given above with the formula derived by Oldroyd for the same model of globular colloids [5]. The Oldroyd formula is explicit for the shear modulus

$$\mu^* = \mu_0 \frac{(2+3\phi)\mu+3(1-\phi)\mu_0}{2(1-\phi)\mu+(3+2\phi)\mu_0} \quad (10)$$

where μ^*, μ and μ_0 are the shear moduli referring to the colloid system, the dispersed material and the continuous phase, respectively. Introducing complex viscosity, equation (10) becomes

$$\eta^* = \eta_0 \frac{(2+3\phi)\mu+3(1-\phi)\eta_0 p}{2(1-\phi)\mu+(3+2\phi)\eta_0 p}. \quad (11)$$

Hence, the coefficients in equation (7) are

$$\eta = \frac{2+3\phi}{2(1-\phi)}\eta_0; \quad \tau_t = \frac{3+2\phi}{2(1-\phi)}\frac{\eta_0}{\mu};$$

$$\tau_d = \frac{3(1-\phi)}{2+3\phi}\frac{\eta_0}{\mu}. \quad (12)$$

The inequalities in equation (7) can be checked.

In the following we discuss some simple solutions of equation (7).

RECTILINEAR SHEARING FLOW

To determine the viscometric functions, suppose that the velocity field in a Cartesian frame of reference is given by

$$v_x = \kappa y, \quad v_y = v_z = 0. \quad (13)$$

The calculations are done in matrix notation. The matrices of $\underset{\circ}{\underline{d}}$ and $\underline{\omega}$ (the skew symmetric part of the velocity gradient) are

$$[\underset{\circ}{\underline{d}}] = \frac{\kappa}{2}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \quad \text{and}$$

$$[\underline{\omega}] = \frac{\kappa}{2}\begin{bmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \quad (14)$$

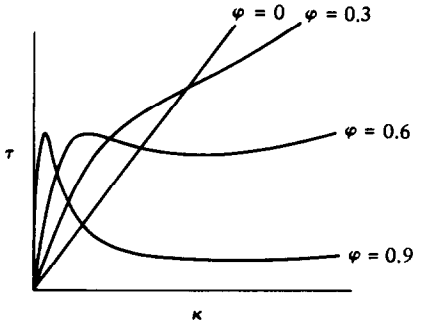

FIG. 1. Shear stress vs shear rate.

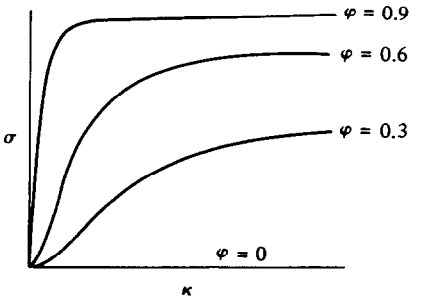

FIG. 2. Normal stress vs shear rate.

while the matrices of $\mathring{\underline{d}}$ and $\mathring{\underline{t}}$ can be calculated by

$$\underline{d} = \mathring{\underline{d}}\cdot\underline{\omega} - \underline{\omega}\cdot\mathring{\underline{d}} \qquad \text{(steady)}$$

and

$$\mathring{\underline{t}} = \underline{t}\cdot\underline{\omega} - \underline{\omega}\cdot\underline{t}. \qquad \text{(steady)}$$

Inserting the matrices into equation (7), we get for the deviatoric part of the stress tensor

$$[\underline{t}] = \begin{bmatrix} \sigma(\kappa) & \tau(\kappa) & 0 \\ \tau(\kappa) & -\sigma(\kappa) & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{15}$$

with

$$\tau(\kappa) = \frac{\tau_d}{\tau_t}\eta\kappa + \frac{\tau_t - \tau_d}{\tau_t}\frac{\kappa}{1+\tau_t^2\kappa^2} \tag{16}$$

and

$$\sigma(\kappa) = \frac{\eta(\tau_t - \tau_d)\kappa^2}{1+\tau_t^2\kappa^2}. \tag{17}$$

The shearing stress function $\tau(\kappa)$ and the normal stress difference function $\sigma(\kappa)$ are plotted in Figs. 1 and 2, respectively. Examination of the shearing stress function plotted in Fig. 1 leads to the conclusion that the colloid system at hand has plastic properties if the volume fraction of the dispersed phase is greater than 50%.

UNIAXIAL TENSION

In the case of rather concentrated solutions, the viscosity at small loads is high enough to prepare specimens for tension tests. The behaviour of globular colloids in tension and compression is studied next.

Suppose that the stress tensor is given by the matrix

$$[\underline{t}_{\text{total}}] = \begin{bmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

The deviatoric part of it is

$$[\underline{t}] = \frac{\sigma}{3}\begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \tag{18}$$

The line elements parallel to the x-axis (the direction of traction) are supposed not to rotate, moreover, for stationary motions, the y-axis is chosen such that $\omega_{13} = 0$. These result in

$$[\underline{\omega}] = \begin{bmatrix} 0 & -\omega_3 & 0 \\ \omega_3 & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{bmatrix}$$

$$[\mathring{\underline{d}}] = \begin{bmatrix} \mathring{d}_{11} & -\omega_3 & 0 \\ -\omega_3 & \mathring{d}_{22} & \mathring{d}_{23} \\ 0 & \mathring{d}_{23} & \mathring{d}_{33} \end{bmatrix}. \tag{19}$$

Furthermore

$$[\mathring{\underline{t}}] = \sigma\begin{bmatrix} 0 & -\omega_3 & 0 \\ -\omega_3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

and

$$[\mathring{\underline{d}}] = \begin{bmatrix} -2\omega_3^2 & \omega_3(\mathring{d}_{22} - \mathring{d}_{11}) & \omega_3(\omega_1 + \mathring{d}_{23}) \\ \omega_3(\mathring{d}_{22} - \mathring{d}_{11}) & 2\omega_3^2 + 2\omega_1\mathring{d}_{23} & -\omega_1(\mathring{d}_{11} + 2\mathring{d}_{22}) \\ \omega_3(\omega_1 + \mathring{d}_{23}) & -\omega_1(\mathring{d}_{11} + 2\mathring{d}_{22}) & -2\omega_1\mathring{d}_{23} \end{bmatrix}.$$

Inserting these in equation (7) yields

$$\frac{\sigma}{\sigma\eta\tau_d}\begin{bmatrix} 2 & -3\tau_t\omega_3 & 0 \\ -3\tau_t\omega_3 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} =$$

$$\begin{bmatrix} \frac{1}{\tau_d}\mathring{d}_{11}-2\omega_3^2 & \omega_3\left(-\frac{1}{\tau_d}+\mathring{d}_{22}-\mathring{d}_{11}\right) & \omega_3(\omega_1+\mathring{d}_{23}) \\ \omega_3\left(-\frac{1}{\tau_d}+\mathring{d}_{22}-\mathring{d}_{11}\right) & \frac{1}{\tau_d}\mathring{d}_{22}+2\omega_3^2+2\omega_1\mathring{d}_{23} & \frac{1}{\tau_d}\mathring{d}_{23}-\omega_1(\mathring{d}_{11}+2\mathring{d}_{22}) \\ \omega_3(\omega_1+\mathring{d}_{23}) & \frac{1}{\tau_d}\mathring{d}_{23}-\omega_1(\mathring{d}_{11}+2\mathring{d}_{22}) & \frac{1}{\tau_d}\mathring{d}_{33}-2\omega_1\mathring{d}_{23} \end{bmatrix}. \quad (20)$$

Remember that the motion is volume preserving, hence $\mathring{d}_{11}+\mathring{d}_{22}+\mathring{d}_{33}=0$. The solution of the matrix equation is a bit easier if we assume σ, $\mathring{d}_{11}$, $\mathring{d}_{22}$, $\mathring{d}_{33}$ and $\mathring{d}_{23}$ as functions depending on ω_1 and ω_3 temporarily. This way the scalar equations are linear and the solution is obtained in parametric form. For further considerations we write the scalar equations as follows:

$$\begin{aligned} \mathring{d}_{11} &= \frac{\sigma}{3\eta}+2\tau_d\omega_3^2 \\ \mathring{d}_{22} &= -\frac{\sigma}{6\eta}-2\tau_d\omega_3^2+\frac{4\tau_d^3\omega_1^2\omega_3^2}{1+4\tau_d^2\omega_1^2} \\ \mathring{d}_{23} &= -\frac{2\tau_d^2\omega_1\omega_3^2}{1+4\tau_d^2\omega_1^2} \\ \omega_3\left[\frac{\sigma}{2\eta}(\tau_t-\tau_d)-1-4\tau_d^2\omega_3^2+\frac{4\tau_d^4\omega_1^2\omega_3^2}{1+4\tau_d^2\omega_1^2}\right] &= 0 \\ \omega_3\cdot\omega_1\left(1-\frac{2\tau_d^2\omega_3^2}{1+4\tau_d^2\omega_1^2}\right) &= 0. \end{aligned} \quad (21)$$

The last two equations show clearly that three different cases can be distinguished. In the first case $\omega_1=\omega_3=0$, in the second case $\omega_3\neq 0$ but $\omega_1=0$ and in the third case both the components of angular velocity differ from zero ($\omega_1\neq 0$, $\omega_3\neq 0$). The discussion of the first case is rather simple, and the solution is given in tensorial notation as

$$\underline{\mathring{d}}=\frac{1}{2\eta}\underline{t}. \quad (22)$$

We mention here that this solution remains valid when $\omega_1\neq 0$ but this circumstance has no physical significance, it simply means that the system rotates around the direction of traction. The second case is much more interesting. The actual value of ω_3 is determined from equation $(21)_4$ and the components of the tensor $\underline{\mathring{d}}$ are given in the first, the second and the third equation. To save time and room, we write the equation for $\mathring{d}_{11}$ only

$$\mathring{d}_{11}=\frac{\sigma}{12\eta\tau_d}(3\tau_t+\tau_d)-\frac{1}{2\tau_d}. \quad (23)$$

The condition of existence of the second case is

$$\frac{\sigma}{2\eta}(\tau_t-\tau_d)-1=4\tau_d^2\omega_3^2\geqslant 0. \quad (24)$$

This third case is similar to the second one, but this time equation $(21)_5$ is also involved. That is

$$\mathring{d}_{11}=\frac{\sigma\tau_t}{3\eta\tau_d}-\frac{1}{\tau_d} \quad (25)$$

and the condition of case 3 is

$$\frac{\sigma}{2\eta}(\tau_t-\tau_d)-3=6\tau_d^2\omega_1^2\geqslant 0. \quad (26)$$

In summary the rate of stretching $\mathring{d}_{11}$ is given by the following function of σ:

$$\mathring{d}_{11}=\begin{cases} \dfrac{\sigma}{3\eta} & \text{if} \quad \sigma\leqslant\dfrac{2\eta}{\tau_t-\tau_d} \\ \dfrac{\sigma(3\tau_t+\tau_d)}{12\eta\tau_d}-\dfrac{1}{2\tau_d} & \text{if} \quad \dfrac{6\eta}{\tau_t-\tau_d}\geqslant\sigma\geqslant\dfrac{2\eta}{\tau_t-\tau_d} \\ \dfrac{\sigma\tau_t}{3\eta\tau_d}-\dfrac{1}{\tau_d} & \text{if} \quad \sigma\geqslant\dfrac{6\eta}{\tau_t-\tau_d}. \end{cases} \quad (27a)$$

The graph of the function is a broken line, which is steepest for case 3 and flattest for case 1 (Fig. 3). The occurrence of ω_1 in the third case can be interpreted as follows: if the load of traction increases over the value of $6\eta/(\tau_t-\tau_d)$, then the angular velocity, which was steady in case 2, begins to rotate around the direction of traction, with angular velocity ω_1. Hence the motion is steady in a frame spinning also around the same axis with the same angular velocity. Here we repeat this function using the properties of the constituent

$$\mathring{d}_{11}=\begin{cases} \dfrac{2(1-\phi)}{3(2+3\phi)}\dfrac{\sigma}{\eta_0} & \\ \dfrac{8+9\phi+8\phi^2}{12(2+3\phi)(1-\phi)}\cdot\dfrac{\sigma}{\eta_0}-\dfrac{2+3\phi}{6(1-\phi)}\dfrac{\mu}{\eta_0} & \\ \dfrac{3+2\phi}{9(1-\phi)}\dfrac{\sigma}{\eta_0}-\dfrac{2+3\phi}{3(1-\phi)}\dfrac{\mu}{\eta_0} & \end{cases} \quad (27b)$$

$$\sigma\leqslant\frac{2(2+3\phi)^2}{25\phi}\mu$$

$$\frac{2(2+3\phi)^2}{25\phi}\mu\leqslant\sigma\leqslant\frac{6(2+3\phi)^2}{25\phi}\mu$$

$$\sigma\geqslant\frac{6(2+3\phi)^2}{25\phi}\mu.$$

A simple analysis of stability based on equation (7) shows that the conditions indicated in equation (27a) are in accordance with the physical possibilities. The behaviour of the colloid medium under uniaxial compression is very similar. Now it is supposed that the planes perpendicular to the direction of compression do not change their orientation. The tensors in equations (19) are

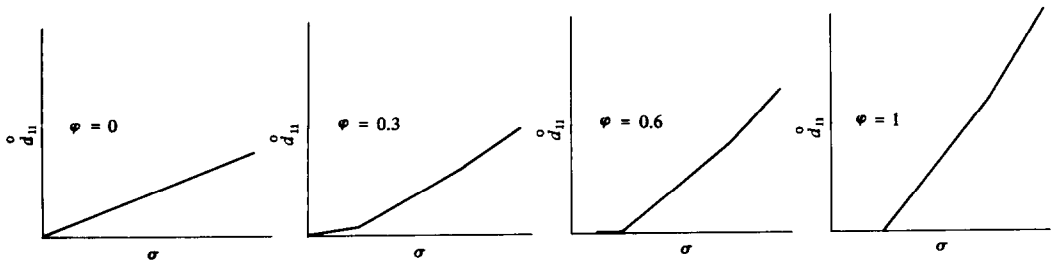

FIG. 3. Stretching vs normal stress.

$$[\omega] = \begin{bmatrix} 0 & -\omega_3 & 0 \\ \omega_3 & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{bmatrix} \quad \text{and}$$

$$[\mathring{d}] = \begin{bmatrix} \mathring{d}_{11} & \omega_3 & 0 \\ \omega_3 & \mathring{d}_{22} & \mathring{d}_{23} \\ 0 & \mathring{d}_{23} & \mathring{d}_{33} \end{bmatrix}.$$

Furthermore, the stress tensor obeys equation (18) but, now, σ is negative. If the notations

$$\sigma^1 = -\sigma, \quad \mathring{d}^1_{11} = -\mathring{d}_{11}, \quad \mathring{d}^1_{22} = -\mathring{d}_{22}, \quad \mathring{d}^1_{33} = -\mathring{d}_{33}, \quad \mathring{d}^1_{23} = -\mathring{d}_{23}$$

are applied, we get the same equations for the primed quantities as before, consequently, the function given in equation (27) has to be continued in an odd manner for negative values of σ.

SMALL LOADS

In the case of rather concentrated colloid solutions, the rate of deformation at small loads is slow, hence it can be called 'creep'. If we neglect this slow motion equation (7) can be reduced for small loads.

Introducing

$$\underline{\mathring{d}} = \frac{1}{2\eta}\underline{t} + \underline{\mathring{d}}^* \tag{28}$$

into equation (7) we obtain

$$(\tau_t - \tau_d)\underline{\mathring{t}} = 2\eta(\underline{\mathring{d}}^* + \tau_d \underline{\mathring{\mathring{d}}}^*). \tag{29}$$

If the creep term in equation (28) is omitted, the asterisk can be dropped and a first integral of the equation is evaluated for small loads as follows:

$$(\tau_t - \tau_d)\underline{t} = 2\eta[\tau_d \underline{\mathring{d}} + \underline{d} - \underline{d}_0] \tag{30}$$

where $\underline{d}_0$ is a tensor constant in the corotating frame. We have obtained the constitutive equation of a Kelvin body with the material constants

$$\mu_K = \frac{\eta}{\tau_t - \tau_d} = \frac{(2+3\phi)^2}{25\phi}\mu;$$

$$\eta_K = \frac{\eta\tau_d}{\tau_t - \tau_d} = \frac{3(1-\phi)(2+3\phi)}{25\phi}\eta_0. \tag{31}$$

The model we obtained takes into account elastic deformations before or after plastic flow. Finally, we mention that all the considerations above can be extended over emulsions. In that case, the effect of interfacial tension is taken into account by considering the stored energy which defines an apparent modulus of elasticity. Formulae become especially simple if the viscosity of the dispersed material is negligible as, e.g. in the case of foams. The apparent shear modulus is given as

$$\mu = \frac{4\gamma}{5r} \tag{32}$$

where γ is the interfacial tension and r the radius of the drops or bubbles. Its value depends on the size of the colloid particles, hence the heterodispersity causes some difficulties.

CONCLUSIONS

It is worth noting that the intricate mechanical behaviour of globular colloids has been described by the strictly linear Onsager theory. The nonlinearity of the differential equations is not due to a non-linear constitutive equation but to rotations. The nonlinearity of our equations is similar to that of the Navier–Stokes equations.

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THERMODYNAMIQUE IRREVERSIBLE POUR LES PROPRIETES RHEOLOGIQUES DES COLLOÏDES

Résumé—Les propriétés viscoélastiques et plastiques des colloïdes globulaires sont traitées sur la base de la théorie linéaire d'Onsager des mécanismes irréversibles. Dans le cas des émulsions, on prend aussi en compte l'effet de la tension interfaciale. Le comportement très complexe des colloïdes est relié à la thermodynamique hors équilibre avec seulement trois constantes matérielles.

IRREVERSIBLE THERMODYNAMIK FÜR DIE RHEOLOGISCHEN EIGENSCHAFTEN VON KOLLOIDEN

Zusammenfassung—Die viskoelastischen und plastischen Eigenschaften kugelförmiger Kolloide wurden auf der Basis der streng linearen Onsager-Theorie für irreversible Prozesse behandelt. Im Fall von Emulsionen wurde der Einfluß der Grenzflächenspannung berücksichtigt. Das komplizierte mechanische Verhalten der Kolloide wurde mittels der klassischen Nicht-Gleichgewichts-Thermodynamik mit nur drei Materialkonstanten dargestellt.

ТЕРМОДИНАМИКА НЕОБРАТИМЫХ ПРОЦЕССОВ ПРИ ОПИСАНИИ РЕОЛОГИЧЕСКИХ СВОЙСТВ КОЛЛОИДОВ

Аннотация—Из линейной теории необратимых процессов Онзагера выведены вязкопластичные и пластичные характеристики сферических коллоидов. Для эмульсий кроме того учитывается эффект межфазного натяжения. Сложное механическое поведение коллоидов описывается классической неравновесной термодинамикой с использованием только трех материальных констант.