NOTATION

V, liquid velocity averaged over cells equidistant from the column axis; $\bar{V}$, V_G, mean mass flow velocities of the liquid and gas, respectively; V_k, liquid local velocity in the k-th measuring cell obtained by dividing the liquid mass flow rate through this cell by its area; S^2, empirical dispersion.

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TOWARD A THEORY OF TRANSPORT PROCESSES IN BROWNIAN SUSPENSIONS

A. Yu. Zubarev

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Fluctuations in dispersed phase concentration increase the particle gradient diffusion coefficient and the effective viscosity of the suspension.

A large range of literature has been dedicated to the definition of effective properties of concentrated suspensions. A review of studies of the rheology of such suspensions can be found in [1]. The influence of collective effects on the gradient diffusion coefficient of Brownian particles in weak concentration suspensions was evaluated in [2-5], while in [6] the theory of [2] was generalized to concentrated suspensions. In all studies known to the present author the concentration of the dispersed phase was taken as a deterministically specified quantity, and the possibility of its fluctuation over time and space was neglected. However in suspensions in which the particles perform intense Brownian motion such fluctuations do occur and their amplitude increases with increase in external noise disturbance. Moreover, from the well known analogy between processes of colloid coagulation and molecular gas condensation [7] one can expect intense increase in fluctuations and their correlation radius in colloidal systems upon approach to the critical coagulation point, which within the framework of the indicated analogy corresponds to the critical gas-liquid phase transition point [8-10].

Below we will evaluate the effect of fluctuations in dispersed phase concentration on the effective diffusion coefficient of suspension particles and effective viscosity. A constructive description of the macroscopic behavior of suspensions can apparently only be given within the framework of the continuum approximation, which becomes inadequate if the amplitude of the fluctuations in porosity becomes comparable to the mean value of that quantity, while the correlation radius becomes comparable to the dimensions of the region occupied by the suspension. Therefore below we will assume the value of the fluctuations to be low in comparison to the mean concentration of the dispersed phase. We note that this limitation of smallness of the fluctuations is caused not only by the requirements of the continuum ap-

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A. M. Gor'kii Ural State University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 57, No. 5, 779-786, November, 1989. Original article submitted March 29, 1988.

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proximation, but also by the existing level of development of the theory of stochastic processes.

Gradient Diffusion Coefficient. We will consider a system of identical spheres of radius a, distributed homogeneously on the average within a Newtonian liquid with viscosity η_0. In accordance with [2] we use the Langevin equation describing motion of an individual particle in a medium fixed as a whole:

$$m\frac{d\mathbf{U}}{dt}=-\frac{\mathbf{U}}{B}-\frac{B}{1-R}\,\frac{\partial\mu}{\partial R}\cdot\mathbf{E},\ \mathbf{E}\equiv\nabla N;\ N=Rv^{-1};\ \ v=\frac{4}{3}\pi a^3. \tag{1}$$

Here μ is the chemical potential of the particle, as estimated, for example, in [2, 6], B is the hydrodynamic mobility of the particle under crowded conditions, R is the fluctuating volume concentration of the dispersed phase, which on the scale of some representative volume containing a large number of particles is assumed to be spatially homogeneous. The deterministic dependence of B on R has been evaluated in many studies (see, for example, [11]). Apparently B has been calculated most precisely in [11] using the general theory of [12]. Exact solution of the problem formulated in [11] is possible only by numerical methods, but good correspondence to experiment was achieved by the approximate expression

$$B=\frac{K(R)}{6\pi\eta_0 aL(R)}, \tag{2}$$

where K is defined by:

$$K=\frac{0.08L^2+0{,}96L+0{,}46}{0{,}58L+0{,}92}\,(1-R), \tag{3}$$

and L is a positive root of the equation:

$$L=1+\frac{1.6L^3+12.6L^2+12.4L+2.56}{1.6L^2+6{,}25L+3.82}\,R. \tag{4}$$

If the dispersed phase concentration is relatively low ($R \lesssim 0.25$) the expression [11]

$$B=\frac{(1-R)(1-2.5R)}{6\pi\eta_0 a}.$$

will produce satisfactory results.

Introduction of the chemical potential μ in Eq. (1) is justifiable only if the local equilibrium principle is satisfied. This principle requires that at all scales of time of interest to us in the representative volumes, local equilibrium is achieved, which we will assume below. In combination with the requirement of homogeneity of R in the representative volume this means that only coarse scale fluctuations including many particles will be studied. Estimates indicate that for real systems inhmogeneity diffusion relaxation times even at the scale of a are much greater than particle velocity viscous relaxation times $(Bm)^{-1}$, so that in the future we will take $d\mathbf{U}/dt=0$ in Eq. (1).

Considering this condition, we rewrite Eq. (1) as:

$$\mathbf{U}=-G\mathbf{E},\ G=\frac{B}{1-R}\,\frac{\partial\mu}{\partial R}. \tag{5}$$

By definition the local value of the diffusion flux density J is equal to:

$$\mathbf{J}=N\mathbf{U}=-GN\mathbf{E}. \tag{6}$$

Generally speaking the quantities figuring in Eq. (6) have a stochastic character. We will represent them in the form of a mean value denoted by the corresponding small letter and a fluctuation component, denoted by a prime, for example $\mathbf{J}=\mathbf{j}+\mathbf{J}'$, $R = \rho + R'$. Averaging the first identity of Eq. (6) over all possible states of the set of particles, and considering the relationship between R and N of Eq. (1), we obtain

$$\mathbf{j}\equiv\langle\mathbf{J}\rangle=n\mathbf{u}+v^{-1}\langle R'\mathbf{U}'\rangle,\ n=\rho v^{-1}, \tag{7}$$

where the angled brackets indicate the operation of averaging and it is considered that the mean of the fluctuations is equal to zero.

From the first equation of Eq. (5) we obtain

$$\mathbf{u}=-g\mathbf{e}+\langle G'\mathbf{E}'\rangle \tag{8}$$

and considering that $\mathbf{U}' = \mathbf{U} - \mathbf{u}$, we have

$$\mathbf{U}' = -G\mathbf{e} - g\mathbf{E}'. \tag{9}$$

Substituting Eqs. (8) and (9) in Eq. (7), we arrive at the following representation for the mean flux:

$$\mathbf{j} = -ng\mathbf{e} - v^{-1}\langle R'G' \rangle \mathbf{e} - n\langle G'\mathbf{E}' \rangle - gv^{-1}\langle R'\mathbf{E}' \rangle. \tag{10}$$

Assuming G to be a deterministic function of the random quantity R (this is possible, if, as assumed, the only variable fluctuating is R), we find g and G', for which, using the condition $R'/\rho \ll 1$, we write

$$G(R) = G(\rho + R') \approx G(\rho) + R'G^{(1)} + \frac{1}{2}R'^2G^{(2)}, \quad G^{(n)} \equiv \left.\frac{\partial^n G}{\partial R^n}\right|_{R=\rho}. \tag{11}$$

Averaging Eq. (11), we have

$$g \equiv \langle G(R) \rangle \approx G(\rho) + \frac{1}{2}G^{(2)}\langle R'^2 \rangle. \tag{12}$$

Considering that $G' = G - g$, subtracting Eq. (12) from EQ. (11), and neglecting the small quantity $G^{(2)}\langle R'^2 \rangle$, we obtain

$$G' = R'G^{(1)}. \tag{13}$$

Substituting Eq. (13) in Eq. (11), we arrive at a representation for the mean flux $\mathbf{j}$, containing the correlators $\langle R'R' \rangle$ and $\langle R'\mathbf{E}' \rangle$. Using the methods of the theory of random functions [13] and the definition $\mathbf{E}' = v^{-1}\nabla R'$, it can be shown that $\langle R'\mathbf{E}' \rangle = 0$. As a result we have

$$\mathbf{j} = -D_e\mathbf{e}, \quad D_e = D^\circ + D', \tag{14}$$

where

$$D^\circ = nG(\rho); \quad D' = \left(G^{(1)} + \frac{1}{2}\rho G^{(2)}\right)\langle R'R' \rangle. \tag{15}$$

The derivatives $G^{(1)}$ and $G^{(2)}$ can be calculated from the definition of G in Eq. (5), the explicit definitions of B in Eqs. (2)-(4), and expressions for μ which were obtained for a system of rigid spheres in [6], while for interacting colloidal particles they can be determined from the equations of state of dense gases [9] by a method proposed in [6]. We will not present explicit expressions for $G^{(1)}$ and $G^{(2)}$ because of their cumbersomeness. Calculations show that for a system of rigid spheres the sum $G^{(1)} + (1/2)\rho G^{(2)}$ takes on only positive values. The correlator $\langle R'R' \rangle$ in its physical meaning of the mean square of the R fluctuations is nonnegative. Therefore porosity fluctuations increase the diffusion coefficient of neutral particles. For the final definition of D' it is necessary to calculate the correlator $\langle R'R' \rangle$. It will be shown below that the effective viscosity of the suspension η_e is functionally dependent on $\langle R'R' \rangle$. Therefore we will first calculate η_e to the accuracy of this correlator and then in the final portion of the study calculate $\langle R'R' \rangle$ and determine explicit values of D_e and η_e with consideration of concentration fluctuations of the dispersed phase.

Effective Viscosity of the Suspension. The relationship between the values of the deviator portions of the hydrodynamic stress tensors $\mathbf{\Sigma}$ and the shear flow velocity $\mathbf{E}$ can be written in the standard form

$$\mathbf{\Sigma} = 2H(R)\mathbf{E}. \tag{16}$$

Again representing the stochastic quantities in the form of the sum of mean and fluctuation components, we have

$$\mathbf{\Sigma} = \boldsymbol{\sigma} + \mathbf{\Sigma}', \quad H = \eta + H', \quad \mathbf{E} = \boldsymbol{\varepsilon} + \mathbf{E}', \tag{17}$$

while for η and H, after manipulations analogous to those used in deriving Eqs. (12), (13), we obtain

$$\eta = H(\rho) + \frac{1}{2}H^{(2)}\langle R'R' \rangle, \quad H' = R'H^{(1)}, \tag{18}$$

where the quantities denoted by superscripts 1 and 2 again have the meaning of the corresponding derivatives of H with respect to R at $R = \rho$.

To establish the form of the quantities appearing in Eq. (18), it is necessary to have explicit expressions for the effective viscosity H(R). Such relationships are widely found in the literature (see, for example, [1]). A detailed analysis of the dependence of H upon R based on the exact theory of [12] was given in [11, 14], where for a system with arbitrary concentration of identical spherical particles the expression $H = \eta_0 L(R)$ was obtained, while L(R) is defined by Eq. (4). For moderately concentrated suspensions ($R \lesssim 0.25$) the theory of [11, 12, 14] leads to an approximate expression $H = \eta_0(1 - 2.5R)^{-1}$, coinciding with the well known Lundgren expression.

Substituting Eq. (17) in Eq. (16) and averaging, we obtain

$$\sigma = 2[\eta\varepsilon + \langle H'\mathbf{E}' \rangle]. \tag{19}$$

Again using Eq. (17) in Eq. (16), subtracting Eq. (19) from the expression thus obtained, considering Eq. (18) and neglecting quantities quadratic in the fluctuations, we arrive at an expression for the fluctuation of the hydrodynamic stress

$$\Sigma' = 2(\eta\mathbf{E}' + H'\varepsilon) = 2(\eta\mathbf{E}' + H^{(1)}\varepsilon R). \tag{20}$$

Simple estimates show that for real systems the suspension hydrodynamic perturbation relaxation times on the whole are much less than the diffusion dissipation times of fluctuations over these spatial intervals. Therefore we write the Navier–Stokes equations linearized with respect to fluctuations in the steady state form

$$\nabla P' = \nabla\Sigma', \quad \operatorname{div}\mathbf{V}' = 0, \tag{21}$$

where $\mathbf{V}'$ is the fluctuation in suspension velocity as a whole, related to the components of the tensor $\mathbf{E}'$ in the normal manner:

$$\mathrm{E}'_{ij} = \frac{1}{2}\left(\frac{\partial V'_j}{\partial r_i} + \frac{\partial V'_i}{\partial r_j}\right), \quad i,\ j = x,\ y,\ z. \tag{22}$$

The goal of the following analysis is to determine the correlator $\langle \mathbf{E}'H' \rangle$ and to establish the form of the rheological equation of state of the suspension from Eq. (19). Below we will make use of the methods of correlation theory of random functions [13], in accordance with which the random quantity $h(t, \mathbf{r})$ can be represented as a Fourier–Stilties integral with Winer metric dZ_h:

$$h(t,\ \mathbf{r}) = \int e^{i\omega t + i\mathbf{k}\mathbf{r}}\, dZ_h(\omega,\ \mathbf{k}), \quad i = \sqrt{-1}, \tag{23}$$

while we write the correlator of the two random quantities h and ℓ in the form

$$\langle h(t+\tau,\ \mathbf{r}+\mathbf{x})\, l(t,\ \mathbf{r}) \rangle = \int e^{i\omega\tau + i\mathbf{k}\mathbf{x}}\, \Phi_{gh}(\omega,\ \mathbf{k})\, d\omega d\mathbf{k}, \tag{24}$$

where integration is performed over the entire frequency axis Ω and all wave space $\mathbf{k}$. The spectral density Φ_{gh} is related to the metrics dZ_h and dZ_ℓ as follows:

$$\Phi_{gh}(\omega,\ \mathbf{k})\, d\omega d\mathbf{k} = \langle dZ_h dZ_l^* \rangle, \tag{25}$$

where the asterisk denotes the complex conjugate.

Applying the Fourier–Stilties transform of Eq. (23) to Eqs. (21) and (22) we obtain

$$\mathbf{k}dZ_P = \mathbf{k}d\mathbf{Z}_\Sigma; \quad \mathbf{k}d\mathbf{Z}_\mathbf{V} = 0; \quad d\mathbf{Z}_\Sigma = 2(\eta d\mathbf{Z}_\mathbf{E} + \varepsilon H^{(1)} d\mathbf{Z}_R), \tag{26}$$

$$dZ_{\mathrm{E}_{lj}} = \frac{i}{2}(k_j dZ_{V_l} + k_l dZ_{V_j}), \quad j,\ l = x,\ y,\ z; \ i = \sqrt{-1}.$$

In calculating Eq. (26) it was considered that the linear scale of the mean quantities is much greater than that of fluctuation quantities, and therefore in substituting Eq. (20) in Eq. (21) derivatives of $H^{(1)}$ and ε were neglected.

The problem now consists of determining the tensor metric $d\mathbf{Z}_\mathrm{E}$, which when used in Eq. (24) together with the metric $dZ_H = H^{(1)}dZ_R$ allows us to determine the correlator $\langle H'\mathbf{E}' \rangle$, figuring in Eq. (19), thus evaluating the effect of porosity fluctuations on the rheological properties of the suspension.

For a concrete solution of such a problem it is convenient to specify the tensor ε in the form $\varepsilon_{xx} = -\varepsilon_{yy} = \varepsilon$($\varepsilon$ = const), taking its remaining components equal to zero. In this case, after cumbersome computations we obtain from Eq. (26)

$$dZ_{E_{xx}} = \varepsilon \frac{2H^{(1)}}{\eta} \frac{k_x^2}{k^2} \left(\frac{k_x^2 - k_y^2}{k^2} - 1 \right) dZ_R ,$$
$$dZ_{E_{yy}} = \varepsilon \frac{2H^{(1)}}{\eta} \frac{k_y^2}{k^2} \left(\frac{k_x^2 - k_y^2}{k^2} + 1 \right) dZ_R . \quad (27)$$

Substituting Eq. (27) together with $dZ_H = H^{(1)}dZ_R$ in Eq. (25) and then in Eqs. (24) and (19), after simple calculations we obtain

$$\sigma = 2\eta_e \varepsilon, \quad \eta_e = \eta^\circ + \eta', \quad (28)$$

where $\eta^0 = H(\rho)$, and

$$\eta' = 2H^{(1)} \int \frac{k_x^2}{k^2} \left(\frac{k_x^2 - k_y^2}{k^2} - 1 \right) \Phi_{RR} d\omega d\mathbf{k} + \frac{1}{2} H^{(2)} \int \Phi_{RR} d\omega d\mathbf{k}. \quad (29)$$

For the final determination of η' it is necessary to calculate the spectral density Φ_{RR}. We will note that as follows from Eqs. (15) and (24), the parameter D', defining the contribution of porosity fluctuations to the particle diffusion coefficient, can be defined in the form

$$D' = \left(G^{(1)} + \frac{1}{2} \rho G^{(2)} \right) \int \Phi_{RR} d\omega d\mathbf{k}. \quad (30)$$

Determination of Spectral Density Φ_{RR}. To determine Φ_{RR} we will make use of the treatment of [15] and write

$$\Phi_{RR} = 3C \frac{D^\circ k^2}{\omega^2 + D^{\circ 2} k^4} F(k). \quad (31)$$

As in [16], the cofactor $D^\circ k^2(\omega^2 + D^{\circ 2}k^4)^{-1}$ in Eq. (31) can be obtained from point particle models. The function F(k) introduced in [1] considers the finite dimensions of the particles. The constant C will be determined below.

Using the concept of [15], we arrive at the following expression for the function F(k):

$$F(k) = \frac{\sin 2ka - 2ak \cos 2ak}{(2ak)^3}. \quad (32)$$

We note that in [15], in place of 2ak the quantity kb, $b = a\rho^{-1/3}$, was used. It was thus assumed that the correlation radius between particle positions is b. However, from the form of the spherical particle binary distribution function [9, 11, 14] it follows that this radius is approximately equal to 2a, which is considered in Eq. (32).

As in [15], to determine the constant C, we calculate the mean square of the fluctuations M' of the total number of particles M in some fixed volume W. By considerations fully analogous to those of [15], using Eq. (32) we obtain

$$\langle M'^2 \rangle = \frac{8\pi^4}{3v^2} CW. \quad (33)$$

On the other hand, as is well known, the square of impurity particle fluctuations can be found from the following expression [8]:

$$\langle M'^2 \rangle = \frac{T}{\partial\mu/\partial m|_{T,m_0}}, \quad m = \langle M \rangle , \quad (34)$$

where m_0 is the mean number of liquid molecules in the region under consideration, and T is the temperature in energy units. Considering that $\rho = mv(mv + m_0v_0)^{-1}$ (v_0 is the volume occupied by one molecule of solvent), assuming the particles and liquid incompressible, i.e., v, v_0 = const, from Eq. (34) we obtain

$$\left. \frac{\partial\mu}{\partial m} \right|_{T,m_0} = \frac{\partial\mu}{\partial\rho} \frac{\rho(1-\rho)}{m}.$$

Hence from Eqs. (33), (34) it follows that

$$C = \frac{3v}{8\pi^4} \frac{T}{(1-\rho)\partial\mu/\partial\rho}. \quad (35)$$

Now substituting Eqs. (31), (32), and (35) in Eqs. (29), (30) and calculating the integrals, we arrive at the following expressions for D' and η':

$$D' = \frac{3}{8}\,\frac{T}{(1-\rho)\,\partial\mu/\partial\rho}\left(G^{(1)} + \frac{1}{2}\,\rho G^{(2)}\right),$$
$$\eta' = \frac{3}{8}\,\frac{T}{(1-\rho)\,\partial\mu/\partial\rho}\left(\frac{1}{2}H^{(2)} - \frac{4}{5\eta^{\circ}}\,H^{(1)^2}\right). \tag{36}$$

Calculations show that $H^{(2)}/2 > (4/5\eta_0)H^{(1)2}$ and therefore $\eta' > 0$. Thus, the effective viscosity of the suspension $\eta^{\circ} = H(\rho)$ proves to be greater than the value η_e, calculated without consideration of porosity fluctuations. This fact is possibly one of the reasons behind the large scattering in known experimental data on effective viscosity of suspensions [1, 11, 14], since in different experiments porosity fluctuations may manifest themselves to a different degree.

We will now consider the behavior of the derivative $\partial\mu/\partial\rho$. If the particles interact as rigid spheres, the chemical potential μ is a monotonically increasing function of ρ [6], and therefore $\partial\mu/\partial\rho > 0$ everywhere. However the situation changes if, as is the case in colloidal systems, there are attractive forces between the particles. In such a case μ can be calculated by the methods of [6] from the equations of state of dense gases (for example, see [9]). Although final results are lacking, we will note that in such situations there exists a critical value of ρ at which $\partial\mu/\partial\rho = 0$. As is evident from Eq. (36), the parameters D' and η' then diverge. The value of Eq. (34) also diverges, and thus the theory developed herein becomes inapplicable. However, in analogy to dense gases, we can expect the appearance of anomalies in the behavior of suspensions and colloids near the critical point. Theoretical analysis of the behavior of dispersions in such a situation is quite difficult at present, since the dynamic scaling aparatus used for determination of critical properties of molecular systems relies on the experimental results of [10, 17]. But experimental studies of the behavior of suspensions and colloids near the sol-gel transition critical point are apparently lacking. In addition study of the critical behavior of dispersed systems may be of interest for clarifying general principles of phase transition.

NOTATION

a, particle radius; D_e and D°, effective and deterministically defined particle gradient diffusion coefficients; E and e, random and mean values of particle concentration gradient; g, mean value of G; H, random value of suspension viscosity in some local region; $\mathbf{k}$, wave vector; m, particle mass in Eq. (1), mean number of particles in volume W in Eq. (34); ρ, mean volume particle concentration; $\mathbf{U}$ and $\mathbf{u}$, random and mean particle diffusion velocities; $\mathbf{E}$ and $\boldsymbol{\varepsilon}$, random and mean shear flow velocity tensor values; η_0, η°, η and η_e, viscosity of dispersed liquid, deterministically determined, mean and effective viscosities of suspension; $\boldsymbol{\Sigma}$ and $\boldsymbol{\sigma}$, random and mean values of values of suspension hydrodynamic stress tensor; $\Phi_{\ell h}$, spectral density; Ω, frequency.

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DYNAMIC NONLINEAR PROPERTIES OF VISCOELASTIC LIQUIDS FROM THE RHEOLOGICAL FLOW CURVE

V. G. Pivovarov, S. V. Vasil'chenko,
and A. G. Potapov

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A method is developed for prediction and calculation of nonlinear properties of viscoelastic liquids solely by measurement of tangent stresses during flow in a rheometer.

A method was proposed in [1] for calculation of elastic characteristics of non-Newtonian liquids from their rheological flow curve, based on the fact that the viscosity measured in a rotation viscosimeter η_m differs from the true inelastic viscosity η_m, due to the effect of the elastic properties of the liquid. The relationship between η_m and η_m has the form [1]

$$\frac{1}{\eta_m^2}=\frac{1}{\eta_t^2}+\frac{\tau^2}{4G^2\eta_m^2}. \tag{1}$$

For a linear viscoelastic liquid (η_t and G constant) the relationship between $1/\eta_m^2$ and τ^2 is linear in character and can serve to define the modulus of elasticity G, and thus, the liquid relaxation time. In [1] good agreement between calculation results and direct measurements with a Weissenberg rheogoniometer was demonstrated.

If the dependence of $1/\eta_m^2$ on τ^2 is nonlinear, this means that the viscosity or the modulus of elasticity (one, the other, or both together) depends on shear velocity. In the "inelastic" flow region, where $\tau^2 \ll 4G^2$ and $\eta_m \approx \eta_t$ (for low shear rates) one can establish the form of η_t, γ) and calculate the value of $G(\gamma)$ from Eq. (1) transformed in the following manner:

$$\left(\frac{\eta_t}{\eta_m}\right)^2=1+\frac{\tau^2}{4G^2}. \tag{2}$$

To evaluate the applicability of the proposed method, relaxation times were calculated for several polymers from their rheological flow curves as presented in [2]. The results obtained are presented in Table 1.

The quite satisfactory agreement of the results obtained indicates the possibility of using the proposed method for operative evaluation of liquid relaxation characteristics.

A practical realization of this approach can be illustrated by results of calculating

TABLE 1. Comparison of Calculated Relaxation Times for Polymers

Polymer	Sprigs model	Meister model	Bog model	Present method
PEVP	78,96	23,27	29,70	27,55
PENP	2,80	0,94	5,82	4,21
PS	1,85	1,72	1,02	1,41
PP	1,03	0,72	0,94	1,25

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