CONTINUAL ENERGY BALANCE EQUATIONS AND ENTROPY OF A SUSPENSION OF ROTATING SPHERICAL PARTICLES

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Averaged equations of the kinetic energy balance of particle rotational motion and entropy are obtained on the basis of statistical methods developed in [1, 2].

Most universal for systems with a large number of degrees of freedom in an abbreviated description is the conception of statistical ensembles when a detailed picture of the behavior at the level of individual structures is not required and it is sufficient to know the evolution of certain average characteristics. Ensemble averaging can be used for suspensions of solid spherical particles if the space and time scales of the processes to be modeled are substantially greater than the dimensions of the individual particle and its relaxation time, respectively.

In the general case the distribution function of a statistical ensemble of states of a suspension depends on the coordinates of the centers of mass of all the particles and all their possible derivatives with respect to time, and is subject to the continuity equation in the phase space of these variables [3]. The number of components to which we should limit ourselves in the continuity equation will depend on the specific form of the equation of motion of an individual particle. For inertiafree motion, when the forces applied to a particle are equilibrated by a force acting from the fluid, the distribution function will depend only on the coordinates of the particle centers of mass [3]. Such an ensemble of possible spatial particle configurations is used in [1, 2]. Both phases are considered within the framework of the mechanics of continuous media. "Spreading" the properties of discrete particles over the volume of the whole system is realized by using a certain generalized function that equals one within the particle and zero in the fluid. In deducing the continual balance equations it is convenient to use the matrix form of writing the statistical averaging operator, which permits formal examination of a two-phase mixture as single-phased [4].

Statistical averaging of the balance equations of different kinds of energy, as well as the entropy of monodisperse suspensions of spherical particles, was examined in [4, 5], without taking account of their rotation and diffusion and chemical reaction processes within the phases. The balance equations are averaged in this paper with the effects noted above taken into account.

The kinetic energy balance of a continuum has the form [4]

$$\begin{aligned}\frac{\partial}{\partial t}\left(\frac{1}{2}\rho_N\rho_1 v_1^2+\frac{1}{2}\rho_1\langle\Theta_1\vec{V}'\cdot\vec{V}'\rangle\right)+\vec{\nabla}\cdot\Big[\frac{1}{2}\rho_N\rho_1 v_1^2\vec{v}_1+\\+\frac{1}{2}\rho_1\vec{v}_1\langle\Theta_1\vec{V}'\cdot\vec{V}'\rangle+\frac{1}{2}\rho_1\langle\Theta_1\vec{V}'(\vec{V}'\cdot\vec{V}')\rangle\Big]=-\vec{\nabla}(\sigma_1^*\cdot\vec{v}_1)\\+\vec{f}\cdot\vec{v}_1-\langle\Theta_1(\vec{\nabla}\cdot\Sigma)\cdot\vec{V}'\rangle-\rho_N\rho_1\vec{v}_1\cdot\vec{\nabla}\Pi_1-\rho_1\langle\Theta_1\vec{V}'\cdot\vec{\nabla}\Pi_1'\rangle.\end{aligned}\tag{1}$$

Using the relationships obtained in [1], we extract the kinetic energy of particle rotational motion in this equation. The mean of the local physical quantity $G(t, \vec{r}|C^N)$ (velocity, energy, etc.), dependent on the hydrodynamic $\vec{r}$ and phase $\langle G\rangle_{\vec{r}}$ variables, is expressed for the solid phase in the form of integrals of the conditional means

$$g_1=\langle\Theta_1 G\rangle\cong\frac{n(t,\vec{r})}{\rho_N}\int\limits_{x\leqslant a}\langle G\rangle_{\vec{r}}(t,\vec{r}+\vec{x})\,d\vec{x}=\frac{3}{4\pi a^3}\int\langle G\rangle_{\vec{r}}\,d\vec{x}.\tag{2}$$

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Using the known kinematic relationship $G \equiv \vec{V} = \vec{W}_1 + \vec{\Omega} \times \vec{x}$, by using (2) the mean velocity of the solid phase and the mean angular velocity of the particles can be found:

$$\vec{v}_1 = \frac{3}{4\pi a^3}\int(\langle \vec{W}_1 \rangle_{\vec{r}} + \langle \vec{\Omega} \rangle_{\vec{r}} \times \vec{x})\, d\vec{x} = \langle \vec{W}_1 \rangle_{\vec{r}}, \tag{3}$$

$$\vec{\omega} = \frac{3}{4\pi a^3}\int \langle \vec{\Omega} \rangle_{\vec{r}}\, d\vec{x} = \langle \vec{\Omega} \rangle_{\vec{r}}. \tag{4}$$

The fluctuating velocity components are connected by the relationship

$$\vec{V}' = \vec{W}_1' + \vec{\omega} \times \vec{x} + \vec{\Omega}' \times \vec{x}. \tag{5}$$

By using (2)-(5) the components in the left side of (1) are converted to the form

$$\begin{gathered}\frac{1}{2}\rho_1 \langle \Theta_1 \vec{V}' \cdot \vec{V}' \rangle = \frac{1}{2} n(t, \vec{r}) \int \langle \vec{V}' \cdot \vec{V}' \rangle_{\vec{r}}\, d\vec{x} = \frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1' \cdot \vec{W}_1' \rangle + \frac{1}{2} n(t, \vec{r}) Y \omega^2 + \frac{1}{2} n(t, \vec{r}) Y \langle \vec{\Omega}' \cdot \vec{\Omega}' \rangle_{\vec{r}}, \\ \frac{1}{2}\rho_1 \langle \Theta_1 \vec{V}' (\vec{V}' \cdot \vec{V}') \rangle = \frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1' (\vec{W}_1' \cdot \vec{W}_1') \rangle_{\vec{r}} + \frac{1}{2} n(t, \vec{r}) Y \langle \vec{W}_1' (\vec{\Omega}' \cdot \vec{\Omega}') \rangle_{\vec{r}} + n(t, \vec{r}) Y \langle \vec{W}_1' \vec{\Omega}' \rangle_{\vec{r}} \cdot \vec{\omega},\end{gathered} \tag{6}$$

where $Y = \frac{8}{15}\pi \rho_1 a^5$ is the moment of particle inertia. Transforming the right side with (2)-(4) taken into account, and also the expressions for the surface and external force moments $\vec{\lambda}^{(e)}$, $\vec{\lambda}^{(F)}$ and the interphasal interaction force $\vec{f}$:

$$\begin{gathered}\vec{\lambda}^{(F)} = n(t, \vec{r}) \int \vec{a} \times (\vec{n} \cdot \langle \Sigma \rangle_{\vec{r}})\, d\vec{a},\ \vec{\lambda}^{(e)} = n(t, \vec{r}) \int \langle \vec{\Lambda}^{(e)} \rangle_{\vec{r}}\, d\vec{x}, \\ \vec{f} = -n(t, \vec{r}) \int (\vec{n} \cdot \langle \Sigma \rangle_{\vec{r}})\, d\vec{a},\end{gathered} \tag{7}$$

we finally obtain

$$\begin{gathered}\frac{\partial}{\partial t}\left(\frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1 \rangle_{\vec{r}}^2 + \frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1' \cdot \vec{W}_1' \rangle_{\vec{r}} + \frac{1}{2} n(t, \vec{r}) Y \omega^2 + \right. \\ \left. + \frac{1}{2} n(t, \vec{r}) Y \langle \vec{\Omega}' \cdot \vec{\Omega}' \rangle_{\vec{r}}\right) + \vec{\nabla} \cdot \left[\frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1 \rangle_{\vec{r}}^2 \langle \vec{W}_1 \rangle_{\vec{r}} + \right. \\ + \frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1' \cdot \vec{W}_1' \rangle_{\vec{r}} \langle \vec{W}_1 \rangle_{\vec{r}} + \frac{1}{2} n Y \omega^2 \langle \vec{W}_1 \rangle_{\vec{r}} + \frac{1}{2} n Y \langle \vec{\Omega}' \cdot \vec{\Omega}' \rangle_{\vec{r}} \langle \vec{W}_1 \rangle_{\vec{r}} + \frac{1}{2}\rho_N \rho_1 \langle \vec{W}_1' (\vec{W}_1' \cdot \vec{W}_1') \rangle_{\vec{r}} \\ \left. + n Y \langle \vec{W}_1' \vec{\Omega}' \rangle_{\vec{r}} \cdot \vec{\omega} + \frac{1}{2} n Y \langle \vec{W}_1' (\vec{\Omega}' \cdot \vec{\Omega}') \rangle_{\vec{r}}\right] = -\vec{\nabla}[(\rho_N \rho_1 \langle \vec{W}_1' \vec{W}_1' \rangle_{\vec{r}} + \sigma^{(2)}) \langle \vec{W}_1 \rangle_{\vec{r}}] + \vec{f} \cdot \langle \vec{W}_1 \rangle_{\vec{r}} + \\ + \langle \vec{f}' \cdot \vec{W}_1' \rangle_{\vec{r}} - \vec{\lambda}^{(F)} \cdot \vec{\omega} + \langle \vec{\lambda}^{(F)\prime} \cdot \vec{\Omega}' \rangle_{\vec{r}} + \vec{\lambda}^{(e)} \cdot \vec{\omega} - \rho_N \rho_1 \langle \vec{W}_1 \rangle_{\vec{r}} \cdot \vec{\nabla}\Pi_1 - \rho_1 \langle \Theta_1 \vec{W}_1' \cdot \vec{\nabla}\Pi_1' \rangle_{\vec{r}}.\end{gathered} \tag{8}$$

Expressions for the effective stress fluctuations were taken into account in the derivation of (8) [1]:

$$\sigma_1^* = \rho_1 \langle \Theta_1 \vec{V}' \vec{V}' \rangle = \rho_1 \langle \Theta_1 \vec{W}_1' \vec{W}_1' \rangle + \sigma^{(2)}, \tag{9}$$

$$\sigma^{(2)} = -\frac{1}{2} Y n(t, \vec{r})[\vec{\omega}\vec{\omega} + \langle \vec{\Omega}' \vec{\Omega}' \rangle_{\vec{r}} - (\omega^2 + \langle \Omega' \rangle_{\vec{r}}^2)\,\mathbf{I}]. \tag{10}$$

To derive the transport equation for the kinetic energy of particle rotational motion, we consider the rotational energy balance of an individual particle

$$\frac{d}{dt}\left(\frac{1}{2} Y \Omega^2\right) = -\int \vec{\Omega} \cdot \vec{a} \times (\vec{n} \cdot \Sigma)\, d\vec{a} + \int (\vec{\Omega} \cdot \vec{\Lambda})\, d\vec{x}. \tag{11}$$

Taking the average of (11) term by term with (2) and (7) taken into account, we arrive at the desired equation

$$\begin{gathered}\frac{\partial}{\partial t}\left(\frac{1}{2} n Y \omega^2 + \frac{1}{2} n Y \langle \vec{\Omega}' \cdot \vec{\Omega}' \rangle_{\vec{r}}\right) + \vec{\nabla} \cdot \left[\frac{1}{2} n Y \omega^2 \langle \vec{W}_1 \rangle_{\vec{r}} + \right. \\ + \frac{1}{2} n Y \langle \vec{\Omega}' \cdot \vec{\Omega}' \rangle_{\vec{r}} \langle \vec{W}_1 \rangle_{\vec{r}} + n Y \langle \vec{W}_1' \vec{\Omega}' \rangle \cdot \vec{\omega} +\end{gathered} \tag{12}$$

$$+\frac{1}{2}nY\langle \vec{W}_1'(\vec{\Omega}'\cdot\vec{\Omega}')\rangle \Big] = -\vec{\lambda}^{(F)}\cdot\vec{\omega} - \langle \vec{\lambda}^{(F)\prime}\cdot\vec{\Omega}\rangle_{\vec{r}} + \vec{\lambda}^{(e)}\cdot\vec{\omega}.$$

Subtracting (12) term by term from (8), we obtain the balance equation for the translational energy of the disperse phase

$$\frac{\partial}{\partial t}\left(\rho_N\rho_1\langle\vec{W}_1\rangle^2_{\vec{r}}+\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1'\cdot\vec{W}_1'\rangle_{\vec{r}}\right)+\vec{\nabla}\cdot\Big[\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1\rangle^2_{\vec{r}}\langle\vec{W}_1\rangle_{\vec{r}}+\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1'\cdot\vec{W}_1'\rangle_{\vec{r}}\langle\vec{W}_1\rangle_{\vec{r}}+ +\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1'(\vec{W}_1'\cdot\vec{W}_1')\rangle_{\vec{r}}\Big]=-\vec{\nabla}\cdot[(\rho_N\rho_1\langle\vec{W}_1'\vec{W}_1'\rangle_{\vec{r}}+ +\sigma^{(2)})\cdot\langle\vec{W}_1\rangle_{\vec{r}}]+\langle\vec{f}'\cdot\vec{W}_1'\rangle_{\vec{r}}-\rho_N\rho_1\langle\vec{W}_1\rangle_{\vec{r}}\cdot\vec{\nabla}\Pi_1-\rho_1\langle\Theta_1\vec{W}_1'\cdot\vec{\nabla}\Pi_1'\rangle_{\vec{r}}. \tag{13}$$

By using (6) and (7) the kinetic energy of particle rotation is easily extracted from the equations of fluctuating motion [4]

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1'\cdot\vec{W}_1'\rangle_{\vec{r}}+\frac{1}{2}nY\omega^2+\frac{1}{2}nY\langle\vec{\Omega}'\cdot\vec{\Omega}'\rangle_{\vec{r}}\right)+\vec{\nabla}\cdot\Big[\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1'\cdot\vec{W}_1'\rangle_{\vec{r}}\langle\vec{W}_1\rangle_{\vec{r}}+ \frac{1}{2}nY\omega^2\langle\vec{W}_1\rangle_{\vec{r}}+\frac{1}{2}nY\langle\vec{\Omega}'\cdot\vec{\Omega}'\rangle_{\vec{r}}\langle\vec{W}_1\rangle_{\vec{r}}+\frac{1}{2}\rho_N\rho_1\langle\vec{W}_1(\vec{W}_1'\cdot\vec{W}_1')\rangle+nY\langle\vec{W}_1'\vec{\Omega}'\rangle_{\vec{r}}\cdot\vec{\omega}+ \frac{1}{2}nY\langle\vec{W}_1'(\vec{\Omega}'\cdot\vec{\Omega}')\rangle_{\vec{r}}\Big]=-\Big\{\rho_N\rho_1\langle\vec{W}_1'\vec{W}_1'\rangle_{\vec{r}}-\frac{1}{2}nY[\vec{\omega}\vec{\omega}+\langle\vec{\Omega}'\vec{\Omega}'\rangle_{\vec{r}}-(\vec{\omega}\cdot\vec{\omega}+\langle\vec{\Omega}'\cdot\vec{\Omega}'\rangle_{\vec{r}})\mathbf{I}\Big\}:\vec{\nabla}\langle\vec{W}_1'\rangle_{\vec{r}}+ +\langle\vec{f}'\cdot\vec{W}_1'\rangle_{\vec{r}}-\langle\vec{\lambda}^{(F)\prime}\cdot\vec{\Omega}'\rangle_{\vec{r}}-\rho_1\langle\Theta_1\vec{W}_1'\cdot\vec{\nabla}\Pi_1'\rangle_{\vec{r}}. \tag{14}$$

It is seen from this equation that the kinetic energy of rotational solid phase motion is of the same order of magnitude as the fluctuating kinetic energy of translational particle motion. Subtracting the equation for the balance of the averaged kinetic energy of particle rotation $nY\frac{D}{Dt}\frac{\omega^2}{2}=-\vec{\lambda}^{(F)}\cdot\vec{\omega}+\vec{\lambda}^{(e)}\cdot\vec{\omega}$, term by term from (12), we obtain the balance equation for the fluctuating kinetic energy of rotational motion

$$\frac{\partial}{\partial t}\left(\frac{1}{2}nY\langle\vec{\Omega}'\cdot\vec{\Omega}'\rangle_{\vec{r}}\right)+\vec{\nabla}\cdot\Big[\frac{1}{2}nY\langle\vec{\Omega}'\cdot\vec{\Omega}'\rangle_{\vec{r}}\langle\vec{W}_1\rangle_{\vec{r}}+ +nY\langle\vec{W}_1'\cdot\vec{\Omega}'\rangle_{\vec{r}}\vec{\omega}+\frac{1}{2}nY\langle\vec{W}_1'(\vec{\Omega}'\cdot\vec{\Omega}')\rangle_{\vec{r}}\Big]=-\langle\vec{\lambda}^{(F)\prime}\cdot\vec{\Omega}'\rangle_{\vec{r}}. \tag{15}$$

Finally, subtracting (12) from (14), the kinetic energy of the translational motion fluctuations of the disperse phase can be found. The influence of particle rotational motion on the behavior of the disperse system is also examined in [6].

Taking the average of the microscopic entropy balance equation [7] yields

$$\left\langle\Theta\rho\frac{ds}{dt}\right\rangle=\langle\Theta\vec{\nabla}\cdot\vec{J}_s\rangle+\langle\Theta\sigma_s\rangle,\quad \frac{\partial}{\partial t}(\bar{\rho}s)+\vec{\nabla}\cdot(\rho s\mathbf{V}+\rho\langle\Theta s'\vec{V}'\rangle)=-\mathbf{a}\vec{\nabla}\cdot\mathrm{Sp}(\theta\vec{J}_s)+(\mathbf{a}-\mathbf{b})\langle\Theta_1\vec{\nabla}\cdot\vec{J}_s\rangle+\theta\sigma_s, \tag{16}$$

where $\theta\sigma_s$ can be represented in the form $\theta\sigma_s=\mathrm{aSp}(\theta\sigma_s)+(\mathrm{b}-\mathrm{a})\langle\Theta_1\sigma_s\rangle$. Derivation of the specific mode of the entropy balance equation is based on the fundamental Gibbs equation [7] and the microscopic mass and internal energy balance equations at the phase level. Taking the average of the mass balance equation by using (2) results in the expression

$$\frac{\partial}{\partial t}(\bar{\rho}\mathrm{c}_k)+\vec{\nabla}\cdot(\rho\mathrm{c}_k\mathbf{V})=\mathbf{a}\vec{\nabla}\cdot\mathrm{Sp}(\theta\mathbf{J}_k)-\vec{\nabla}\cdot(\rho\langle\Theta c_k'\vec{V}'\rangle)+(\mathbf{a}-\mathbf{b})m_k+\theta\sigma_k^{(m)}, \tag{17}$$

where $m_k = n(t, \vec{r})\int\vec{n}\cdot\langle J_k\rangle_{\vec{r}}d\vec{a}$ is the flux of substance on the surface of the trial particle.

Taking (17) into account, taking the average of the Gibbs equation yields

$$\left\langle\Theta\rho T\frac{ds}{dt}\right\rangle=-\langle\Theta\vec{\nabla}\cdot[T^{-1}(\vec{J}_q-\sum_k\mu_k\vec{J}_k)]\rangle+\langle\Theta\vec{J}_q\cdot\vec{\nabla}T^{-1}\rangle-\langle\Theta\sum_k\vec{J}_k\cdot\vec{\nabla}(\mu_kT^{-1})\rangle-\langle\Theta T^{-1}\Sigma^{(i)}\vec{\nabla}\vec{V}\rangle-\langle\Theta\sum_k T^{-1}\mu_k\sigma_k^{(m)}\rangle. \tag{18}$$

Using the approximate equality $IT^{-1}=(\mathrm{T}+IT')^{-1}=\mathrm{T}^{-1}-0(T'\mathrm{T}^{-2})$, we extract the fluctuating components in the averaging operators. It is convenient to represent components of the form $\langle\Theta F\vec{\nabla}G\rangle$ thus

$$\langle\Theta F\vec{\nabla}G\rangle=\langle F\vec{\nabla}(\Theta G)\rangle-\langle FG\vec{\nabla}\Theta\rangle=\mathrm{f}[\vec{\nabla}(\theta\mathrm{g})+(\mathrm{b}-\mathrm{a})\langle G\vec{\nabla}\Theta_0\rangle]+\langle\Theta F'\vec{\nabla}G\rangle. \tag{19}$$

Setting $F = \vec{J}_q, \vec{J}_k, \tilde{\Sigma}^{(i)}$; $\vec{\nabla}G = \vec{\nabla}T, \vec{\nabla}(\mu_k T^{-1}), \vec{\vec{\nabla}}V$ in (19), and taking account of the symmetry of the viscous pressure tensor, we obtain an expression for the entropy production $(\langle \tilde{\Sigma}^{(i)} \rangle = \Sigma^{(i)},\ \langle \Sigma^{(i)} \rangle = \sigma^{(v)})$

$$\begin{aligned} \sigma_s^{\mathrm{eff}} = \theta\sigma_s = -\mathbf{q}\mathbf{T}^{-2}[\vec{\nabla}(\theta\mathbf{T}) + (\mathbf{b}-\mathbf{a})\ \langle T\vec{\nabla}\Theta_0 \rangle] - \sum_k \vec{\mathbf{J}}_k [\vec{\nabla}(\theta\mu_k\mathbf{T}^{-1}) + \\ + (\mathbf{b}-\mathbf{a})\mathbf{T}^{-1}\langle \mu_k\vec{\nabla}\Theta_0 \rangle] - \sigma^{(v)}\mathbf{T}^{-1} : [\vec{\nabla}(\theta\mathbf{V}) + (\mathbf{b}-\mathbf{a})\langle V(\vec{\nabla}\Theta_0) \rangle] - \\ - \sum_k \theta\mathbf{T}^{-1}\mu_k\sigma_k^{(m)} - \langle \Theta J_q T^{-1}\vec{\nabla}T \rangle - \sum_k \langle \Theta J_k' \vec{\nabla}(\mu_k T^{-1}) \rangle - \langle \Theta T^{-1}\Sigma^{(i)\prime} : \vec{\nabla}V \rangle - \sum_k \langle \Theta T^{-1}\mu_k\sigma_k^{(m)} \rangle. \end{aligned} \tag{20}$$

By using (2) we convert the divergence of the entropy flux determined by the first component in the right side of (18):

$$\begin{aligned} \vec{\nabla}\cdot\vec{J}_s^{\mathrm{efi}} = -\ \langle \Theta\vec{\nabla}\cdot[T^{-1}(\vec{J}_q - \sum_k \mu_k\vec{J}_k)] \rangle = -\mathbf{a}\vec{\nabla}\cdot\mathrm{Sp}(\theta\vec{J}_s) + \\ + (\mathbf{a}-\mathbf{b})\langle \Theta_1\vec{\nabla}\cdot\vec{J}_s \rangle = \mathbf{a}\vec{\nabla}\Big[\mathrm{Sp}\,\theta\mathbf{T}^{-1}\Big(\vec{\mathbf{q}} - \sum_k \mu_k\vec{J}_k\Big) + \langle \Theta T^{-1}\Big(\vec{J}_q' - \sum_k \mu_k\vec{J}_k'\Big) \rangle\Big] + (\mathbf{b}-\mathbf{a})Q_s, \end{aligned} \tag{21}$$

where $Q_s = \langle \Theta_1\vec{\nabla}\cdot\vec{J}_s \rangle = n(t,\vec{r})\int \vec{n}\cdot\langle T^{-1}(\vec{J}_q - \sum_k \mu_k\vec{J}_k) \rangle_{\vec{r}}\, d\vec{a}$ describes the interphasal entropy exchange.

If (20) and (21) are substituted into (16), then it will agree formally with the entropy balance equation for a single-phase medium

$$\frac{\partial}{\partial t}(\rho s) + \vec{\nabla}\cdot(\rho s\mathbf{V} + \rho\langle \Theta s'V' \rangle) = -\vec{\nabla}\cdot\vec{J}_s^{\mathrm{eff}} + \sigma_s^{\mathrm{eff}}. \tag{22}$$

In principle, the fluctuation components u_k', $\vec{V}'$ can be extracted in (20) and (21) and higher order infinitesimals in powers of TT^{-1} can be retained. However, this is not required for our purposes. We note that an alternative form of the expressions for σ_s^{eff} and $\vec{J}_s^{\mathrm{eff}}$ is presented in [5], but without the diffusion and chemical components. To obtain phenomenological laws, (20) is more convenient than σ_s^{eff} in [5].

Taking account of the complexity of the behavior of a disperse system, it is interesting to examine first the processes of pure heat conduction, viscous friction, and diffusion (without cross effects). As usual [7], the relationship between the fluxes and the generalized forces is assumed linear, and we can write for the heat conductivity in conformity with the first term in (20)

$$\theta\mathbf{q} = -\mathbf{L}_q\mathbf{T}^{-2}[\vec{\nabla}(\theta\mathbf{T}) + (\mathbf{b}-\mathbf{a})\ \langle T\vec{\vec{\nabla}}\Theta_0 \rangle]. \tag{23}$$

Rewriting (23) in terms of phases, we obtain the heat-conduction equations

$$\varepsilon\vec{\vec{q}}_0 = -\lambda_{0q}\vec{\nabla}(\varepsilon T_0) + \lambda_{0q}\langle T_{a+0}\vec{\vec{\nabla}}\Theta_0 \rangle, \tag{24}$$

$$\rho_N\vec{\vec{q}}_1 = -\lambda_{1q}\vec{\vec{\nabla}}(\rho_N T_1) - \lambda_{1q}\langle T_{a-0}\vec{\vec{\nabla}}\Theta_0 \rangle, \tag{25}$$

where $a + 0$, $a - 0$ denote the particle and the fluid, respectively. Adding (24) and (25) and taking account of the properties of the averaging operation, we obtain an expression for the mean heat flux with respect to the phases

$$\vec{\vec{q}} = \varepsilon\vec{\vec{q}}_0 + \rho_N\vec{\vec{q}}_1 = -\lambda_{0q}\vec{\vec{\nabla}}\overline{T} - (\lambda_{1q} - \lambda_{0q})\langle \Theta_1\vec{\nabla}T \rangle, \tag{26}$$

where $\overline{T} = \varepsilon T_0 + \rho_N T_1$ and $\langle \Theta_1\vec{\nabla}T \rangle$ can be represented, in conformity with (2), in the form of an integral over the surface of the trial particle.

The representation of the entropy production in the form (20) is convenient in that the linear phenomenological laws (24)-(26) for the mean heat fluxes in the phases and for the mixture obtained on the basis of (20) will agree with the results of taking the average of the local heat conductivity law which is valid at the level of the individual phases $\vec{J}_q = -\Lambda_q\vec{\nabla}T$.

Let us examine the effect of viscous friction in the suspension. The molecular viscosity appears only in the liquid phase. The particles yield a contribution to the viscous stresses in terms of the perturbations of the flux velocity field. The tensor of the molecular viscous pressures is antisymmetric when fluid particle rotation exists at the molecular level [7]. Rotation of the solid particles of the suspension is a supermolecular effect which does not yield a direct contribution to the energy dissipation, nor therefore, to the entropy production. Consequently, the irreversible part of the pressure tensor is a symmetric viscous tensor and we can write on the basis of (20)

$$\theta\sigma^{(v)} = -\mathrm{L}_v \mathrm{T}\,[\vec{\nabla}^s(\theta \mathrm{V}) + (\mathrm{b}-\mathrm{a})\langle V\vec{\nabla}\Theta_0\rangle]. \tag{27}$$

Since the normal velocity component on the particle surface is continuous, then $\langle\Theta_0\vec{\nabla}^s\vec{V}\rangle = \vec{\nabla}\cdot\langle\vec{V}\rangle - \langle\Theta_1\vec{\nabla}^s\cdot\vec{V}\rangle = \vec{\nabla}^s\cdot(\varepsilon\vec{v}_0 + \rho_N\vec{v}_1)$ and by calculating the trace in (27) we obtain

$$\sigma^{(v)} = \varepsilon\sigma_0^{(v)} + \rho_N\sigma_1^{(v)} = -2\overset{0}{\eta_0}\vec{\nabla}^s(\varepsilon\vec{v}_0 + \rho_N\vec{v}_1). \tag{28}$$

This same result can be obtained by taking the average of the local viscous pressure tensor [1]. The remaining tensor components $\sigma = \langle\Sigma\rangle$, related to the thermodynamic pressure and the mean with respect to the solid phase $\langle\Theta_1\Sigma\rangle$, are calculated in [1]. Let us note that the work of the deformation associated with the rotational component $\sigma^{(2)}$ of the pressure tensor can go into the change in energy of the translational motion of the continuous phase or be dissipated by means of viscous friction. In the absence of an external pair, the pressure tensor is symmetric [1].

Let us examine the simplest case of one-component diffusion in the liquid phase of a suspension at constant temperature and pressure. Taking into account that $\vec{J}_m = -L_m\vec{\nabla}\mu = -L_m\left(\frac{\partial\mu}{\partial c}\right)_{T,p}\vec{\nabla}c = -D\vec{\nabla}c$ [6], and replacing the chemical potential by the concentration formally in (20), we can write,

$$\theta \mathrm{J}_m = -\mathrm{D}[\vec{\nabla}(\theta \mathrm{c}) + (\mathrm{b}-\mathrm{a})\langle c\vec{\nabla}\Theta_0\rangle], \tag{29}$$

and the effective diffusion flux in the mixture can now be represented in the form

$$\vec{J}_m = \varepsilon\vec{J}_{0m} + \rho_N\vec{J}_{1m} = D_0\vec{\nabla}(\varepsilon c_0 + \rho_N c_1) + (D_0 - D_1)\langle\Theta_1\vec{\nabla}c\rangle. \tag{30}$$

This same expression can be obtained by taking the average of the local Fick law $\vec{J}_m = -D\vec{\nabla}c$. If diffusion in the solid phase ($D_1 = 0$) is neglected and taking the average over the conditional distribution function (2) is used, then it follows from (30) that

$$\vec{J}_m = -D_0\vec{\nabla}(\varepsilon c_0 + \rho_N c_1) + D_0 n(t,\vec{r})\int\vec{n}\langle c\rangle_{\vec{r}}d\vec{a},$$

from which it is seen that the presence of the solid phase can influence diffusion purely geometrically, firstly, because of distortion of the vector lines of flux $\vec{J}_m$, and secondly, because of chemical processes on the particle surface, i.e., in terms of the conditional mean concentration $\langle c\rangle_{\vec{r}}$.

Let us determine the energy dissipation due to the work of the viscous stresses, for which we take the average of the local dissipative function $T\frac{d_i s}{dt} = -\Sigma_{(i)}:\vec{\nabla}\vec{V}$ with respect to the phases:

$$W_{D0} = -\langle\Theta_0\Sigma^{(i)}:\vec{\nabla}\vec{V}\rangle = -(\varepsilon\sigma_0^{(v)}:\vec{\nabla}\vec{v}_0 + \rho_N\sigma_1^{(v)}:\vec{\nabla}\vec{v}_1) + \vec{f}\cdot\vec{v}_0 + \langle\Theta_1\vec{\nabla}\cdot(\Sigma^{(i)}\cdot\vec{V})\rangle - \langle\Sigma':\vec{\nabla}\vec{V}'\rangle - \langle\Theta_1\vec{V}'\cdot\vec{\nabla}\cdot\Sigma^{(i)}\rangle, \tag{31}$$

$$W_{D1} = -\vec{f}\cdot\vec{v}_1 - \langle\Theta_1\cdot(\Sigma^{(i)}\vec{V}')\rangle + \langle\Theta_1\vec{V}'\cdot\vec{\nabla}\cdot\Sigma^{(i)}\rangle. \tag{32}$$

Summing (31) and (32), we find

$$W_D = \left\langle T\frac{d_i s}{dt}\right\rangle = W_{D0} + W_{D1} = -(\varepsilon\sigma_0^{(v)}:\vec{\nabla}\vec{v}_0 + \rho_N\sigma_1^{(v)}:\vec{\nabla}\vec{v}_1) + \vec{f}\cdot(\vec{v}_0 - \vec{v}_1) - \langle\Sigma^{(i)\prime}:\vec{\nabla}\vec{V}'\rangle. \tag{33}$$

In a particular case this expression yields the results in [8]. We convert the first term in (33) as follows:

$$\begin{aligned}\varepsilon\sigma_0^{(v)}:\vec{\nabla}\vec{v}_0 + \rho_N\sigma_1^{(v)}\overleftrightarrow{:\nabla v_1} &= (\varepsilon\sigma_0^{(v)} + \rho_N\sigma_1^{(v)}):\vec{\nabla}\vec{v}_0 + \rho_N\sigma_1^{(v)}:\vec{\nabla}(\vec{v}_1 - \vec{v}_0) = \\ &= \sigma^{(v)}:(\vec{\nabla}\vec{v}_0) + \rho_N\vec{\nabla}[\sigma_1^{(v)}(\vec{v}_1 - \vec{v}_0)] - \rho_N(\vec{v}_1 - \vec{v}_0)\cdot\vec{\nabla}\cdot\sigma_1^{(v)}.\end{aligned} \tag{34}$$

If we limit ourselves to small Reynolds numbers, as in [8], and consider the flux of the suspension to be steady, then in conformity with [1]

$$-\rho_N\vec{\nabla}\cdot\sigma_1^{(v)}=(\overset{0}{\eta}-\overset{0}{\eta}_0)\nabla^2\vec{v};\quad \vec{v}=\varepsilon\vec{v}_0+\rho_N\vec{v}_1. \tag{35}$$

Taking account of (34) and (35), and the expression for the interphasal interaction force $\vec{f}=G(\vec{v}_1-\vec{v}_0)$ (34), then (33) is converted to the form

$$W_D=-\sigma^{(v)}:\overrightarrow{\nabla v_0}+\rho\vec{\nabla}\cdot[\sigma_1^{(v)}\cdot(\vec{v}_0-\vec{v}_1)]+(\overset{0}{\eta}-\overset{0}{\eta}_0)(\vec{v}_0-\vec{v}_1)\nabla^2\vec{v}+G(\vec{v}_0-\vec{v}_1)^2-\langle\Sigma^{(i)'}:\overrightarrow{\nabla V'}\rangle. \tag{36}$$

Approximating (36) by the expression $W_D=\tilde{W}_D+B(\vec{v}_0-\vec{v}_1)\nabla^2\vec{v}_0+G(\vec{v}_0-\vec{v}_1)^2$, where $\tilde{W}_D$ is the viscous dissipation in the liquid phase, we obtain the result in [8].

In principle, different cross effects can also be examined on the basis of the expression (20) for the entropy production. It is seen from the analysis presented that it is possible to take the average of local phenomenological laws which are valid at the phase level when solving practical problems. The expressions obtained as a result of taking the average correspond to linear relationships for the average fluxes and forces obtained by using (20).

Analysis of the fluctuating fields and the transport processes therin is a separate independent problem.

NOTATION

r, x, radius-vector and Cartesian coordinate; t, time; a, particle radius; Y, particle moment of inertia; ρ, density; T, temperature; s, entropy; μ_k, c_k, chemical potential and concentration of the k-component; ε, ρ_N, porosity and volume concentration of the particles, $n(\vec{r}, t)$, mean numerical particle concentration; $\bar{\rho}=\varepsilon\rho_0+\rho_N\rho_1$, disperse phase density; $G(t, \vec{r}|C^N)$, g, a local physical quantity and its mean value; C^N, a 3N-dimensional space of vectors $\vec{r}^{(i)}$; Σ, σ, local pressure tensor and its mean value; $\Sigma^{(i)}$, $\sigma^{(v)}$, local viscous pressure tensor and its mean value; $\Sigma^{(e)}$, reversible part of the pressure tensor; σ^*, effective fluctuating stress of the phase; Π, potential energy; $\vec{f}$, mean interphasal interaction force; $\vec{V}$, $\vec{v}$, local velocity and its mean value; $\vec{\Omega}$, $\vec{\omega}$, local angular velocity and its mean value; $\vec{W}$, translational motion velocity; $\Theta_1=\sum_i\eta_H(a-|\vec{r}-\vec{r}^{(i)}|)$, a generalized coordinate; $\Theta_0=1-\Theta_1$; η_H, Heaviside function; $\sigma_k^{(m)}$, bulk mass source; σ_s, entropy production; $\vec{q}$, $\vec{J}_q$, heat flux; $\vec{J}_k$, $\vec{J}_s$, diffusion flux and entropy flux; L, phenomenological coefficients; λ_q, heat-conduction coefficient; $\overset{0}{\eta}$, coefficient of dynamic viscosity; D, diffusion coefficient; $\Lambda_q=\Theta_0\lambda_{0q}+\Theta_1\lambda_{1q}$, generalized heat-conduction function. Subscripts: 0, 1, continuous medium and particle respectively; <...>, statistical average; eff, effective value; the prime denotes the fluctuating components of the quantities. The matrices introduced in [3, 4] are:

$$\mathbf{g}=\begin{pmatrix}g_0&0\\0&g_1\end{pmatrix};\ g\equiv c_k,\ \mu_k,\ s,\ T,\ \sigma_k^{(m)};\ \sigma_s,\ \sigma^{(v)};\ \vec{J}_k,\ \vec{J}_s;\ \mathbf{L}_q=$$
$$=\begin{pmatrix}L_{0q}&0\\0&L_{1q}\end{pmatrix}=\begin{pmatrix}\lambda_{0q}T_0^{-2}&0\\0&\lambda_{1q}T_1^{-2}\end{pmatrix};\ \mathbf{L}_v=\begin{pmatrix}2\overset{0}{\eta}_0T_0&0\\0&2\overset{0}{\eta}_1T_1\end{pmatrix};\ \mathbf{D}=\begin{pmatrix}D_0&0\\0&D_1\end{pmatrix};\ \mathbf{a}=$$
$$=\begin{pmatrix}1&0\\0&0\end{pmatrix};\ \mathbf{b}=\begin{pmatrix}0&0\\0&1\end{pmatrix};\ \mathbf{I}=\begin{pmatrix}1&0\\0&1\end{pmatrix};\ \langle\Theta\rangle=\theta=\begin{pmatrix}\varepsilon&0\\0&\rho_N\end{pmatrix}.$$

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PERIODIC MODES IN AN ISOTHERMAL TUBULAR REACTOR

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Nonstationary periodic conditions in an isothermal tubular reactor are considered. A study is made of the effects of the amplitude, frequency, and waveform of the input concentration signals on the average throughput.

A reactor with nonlinear kinetics is often better operated in nonstationary cyclic mode than in a stationary one. This was first pointed out in [1, 2], and then in [3] variational methods were used to formulate the optimization conditions. Since then, there have been very extensive studies on periodic modes of various types: for example, in [4] a study was made of the quasistationary state, while in [5] positive feedback was considered, in [6, 7] the study concerned systems was distributed parameters, in [8] periodic relaxation oscillations were examined, and [9] dealt with adiabatic reactors. In [10], very effective estimates were obtained by means of the π criterion, while in [11] differential inequalities were used for similar purposes. The results and problems in this area have been surveyed in [12, 13].

The published data relate primarily to completely mixed systems, or sometimes to models for ideal displacement, but very little is known about models characterizing intermediate mixing states. Here we may mention [7], in which an axial dispersion model was used to examine isothermal tubular reactors for the case of a second-order reaction, but only for a sinusoidal input signal and for parameters varying over a very narrow range.

Here we present some more general results for isothermal reactors, which can be described by means of an axial dispersion model. We consider irreversible reactions of order n and give data for limiting cases of mixing. Also, the results obtained previously for second-order reactions are extended to the effects of the frequency of the periodic input signals on the throughput, and we discuss the determination of the optimum period for sinusoidal inputs. The calculations were performed with an analog computer using perturbation methods.

Formulation. Consider an isothermal tubular reactor in which there is an irreversible reaction of order n, which is described mathematically by an axial dispersion model:

$$\frac{\partial c(x,\ t)}{\partial t} = L_a^n c(x,\ t),\ x \in (0,\ 1),\ t > 0; \tag{1}$$

$$L_a^n = \frac{1}{\mathrm{Pe}} \frac{\partial^2 (\cdot)}{\partial x^2} - \frac{\partial (\cdot)}{\partial x} - R\tau (\cdot)^n \tag{1a}$$

with the boundary conditions

$$c(x,\ t) - \frac{1}{\mathrm{Pe}} \frac{\partial c(x,\ t)}{\partial x} = u(t),\ x = 0,\ t > 0; \tag{2a}$$

$$\frac{\partial c(x,\ t)}{\partial x} = 0,\ x = 1,\ t > 0, \tag{2b}$$

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