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Heat and mass transfer phenomena

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Abstract

The paper deals with the main problems of heat and mass transfer in magnetic colloids. The following problems are briefly discussed: the equation of energy conservation accounting for new adiabatic effects and dissipation due to internal rotation, the thermomagnetic and magnetosolutal instabilities, the specifics of magnetic convection in fluids of non-uniform temperature and concentration, the thermodiffusion of magnetic particles under the effect of a magnetic field and some phenomena of the combined thermal and Soret-driven convection.

Keywords: Magnetic fluids; Convection; Mass transfer; Thermodiffusion; Soret effect

1. Introduction

In the first applications the magnetic fluids mostly had been used to position a colloid at a certain point by means of magnetic forces. Therefore, the most important research problems were the increase of fluid magnetization, the specific properties of ferrofluid surfaces in the presence of an external field and the magnetoviscous and magnetorheological effects. Presently the research field undergoes a serious transition taking into account the non-potential bulk forces in magnetically non-uniform fluids. They open the promising design of new challenging applications (intensification of the heat transfer for cooling the high power electric transformers, magnetically controlled thermosyphons, etc.). Besides, the temperature or concentration gradients cause new thermo- and magnetophoretic transport processes, which can influence the long-time stability of the ferrocolloids in many technical devices. In the present paper the main problems of the heat and mass transfer in the presence of a magnetic field are briefly discussed.

2. Energy conservation

Many authors have analyzed the energy conservation equation in magnetizable media. From the second law of thermodynamics for quasi-equilibrium model of ferrofluids it becomes [1]

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}t} = T\frac{1}{\bar{V}}\frac{\partial \bar{V}}{\partial T}\frac{\mathrm{d}p}{\mathrm{d}t} - T\frac{\partial \mathbf{M}}{\partial T}\mu_0\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t} + Q - \mathrm{div}\,\mathbf{j}_q \times \left(\frac{d}{\mathrm{d}t} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right). \tag{1}$$

The left part of Eq. (1) characterizes the thermal energy of the fluid, the first two terms of the right side reflect the adiabatic effects of fluid compression and magnetization ($\bar{V}$ and $\mathbf{M}$ are specific volume and magnetization), Q represents the internal heat source density and the last term describes the conductive heat input or output. Temperature gradients can be applied externally by a heat flux:

$$\mathbf{j}_q = -\lambda\,\mathrm{grad}\,T \tag{2}$$

(λ is the fluid thermal conductivity) or are generated adiabatically (under the effect of compression and magnetization of the fluid) or by Q due to the viscous dissipation of energy in flows under the shear stress.

The temperature changes in liquids due the compression as well as the magnetic demagnetization effects are

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very small [1]. Only close to the Curie temperature, the adiabatic magnetization can cause a considerable change in fluid temperature. This phenomenon at an early stage of the magnetic fluid research was proposed for use for a thermomagnetic energy conversion [2].

In colloids containing magnetically "hard" particles, the fluid magnetoviscosity can significantly effect the thermal dissipation of flow energy Q. For example, in cobalt ferrite containing ferrofluids a rotating field 40 kA/m of frequency $\omega = 1.75$ kHz generates the heat density up to 600 W/kg [3]. In principle, the micro-convection under the effect of field rotation induces also some changes in thermal conductivity. Microvortices alter the magnitude of heat flux along the temperature gradient and cause a transversal heat flux in the plane of rotation axis. Still, the numerical estimates show [4] that this magnetic analog of Rigi-Leduc effect in colloids is usually negligible.

For practical needs the thermal conductivity λ of colloids of spherical particles can be calculated using the classical dependence [5]:

$$\frac{\lambda}{\lambda_0} = \frac{2\lambda_0 + \lambda_p - \varphi(\lambda_p - \lambda_p)}{2\lambda_0 + \lambda_p + \varphi(\lambda_p - \lambda_p)}. \tag{3}$$

Here λ_0 and λ_p are the thermal conductivities of the carrier liquid and of the particles, φ is the particle volume concentration. Only for dispersions of non-spherical particles or if the aggregate formation takes place, the thermal conductivity depends on magnetic field. In the presence of an orthogonal field $\mathbf{B} \perp \nabla T$ the thermal conductivity decreases and in its absence, in a longitudinal field $\mathbf{B} \| \nabla T$ it increases [1].

The specific heat of colloid c_p and density ρ can be calculated under the assumption of additivity, employing the known coefficients of particles and those of a carrier liquid.

3. Thermomagnetic convection

To analyze the convective processes, the energy conservation equation should be considered together with the equation of a fluid motion. Let us consider the fluids assuming the physical properties and the transfer coefficients (with exception of the density in the gravitation force $\rho\mathbf{g}$ and the magnetization) constant. The equation of motion contains a new term of magnetostatic force:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla p + \eta \Delta \mathbf{v} + \rho \mathbf{g} + \mu_0 (\mathbf{M}\nabla)\mathbf{H}. \tag{4}$$

If the magnetic susceptibility χ is dependent solely upon the field and $\rho = \text{const}$, then on an equilibrium approximation $\mathbf{M} = \chi \mathbf{H}$ both the gravitation and the magnetic forces are potential and there cannot arise internal convective flows in the fluid. The non-potentiality of bulk forces appears only if a fluid possesses spatial non-uniformity of ρ and M due to their dependence on temperature or on particle concentration φ. From Eq. (4) it follows that the free convection develops spontaneously if

$$\nabla \rho \times \mathbf{g} + \mu_0 \nabla \chi \times \nabla H^2 \neq 0. \tag{5}$$

We can see that there exists a certain analogy between the thermogravitational and the thermomagnetic convection. The difference is only the spatial non-uniformity of magnetic acceleration ∇H^2 while the gravitation acceleration $\mathbf{g}$ is constant. There are many works published in which the magnetic convection under various field distributions are calculated and measured (see the review in Ref. [1]).

If Eq. (5) equals zero, a problem of thermoconvective instability appears. The stability criterion is the Rayleigh number Ra. Eqs. (1) and (4), linearized with respect to small perturbations of velocity, temperature and pressure, have the same form as in the conventional convection problems. The only difference lies in appearance of a different form of Ra (coordinate $\mathbf{z} \downarrow \downarrow \mathbf{g}$) [6]:

$$Ra = \left(\beta_T \rho g + \mu_0 \alpha_T M \frac{dH}{dz}\right) \times \left[\frac{dT}{dz} - \frac{T}{\rho c_p}\left(\beta_T g \rho + \mu_0 \alpha_T M \frac{dH}{dz}\right)\right] \frac{c_p l^4}{\nu \lambda}. \tag{6}$$

Here β_T and α_T are the expansion and the pyromagnetic coefficients of the fluid (according to the definition they are positive); l is the characteristic length.

From Eq. (6) it follows that without applying external temperature gradients the fluid with respect to adiabatic compression and magnetization is always stable (Ra is negative). The temperature gradients necessary to attain the critical value of Ra are so large that the adiabatic terms (the second part in the square brackets in Eq. (6)) can usually be neglected. In such approximation the Rayleigh number contains two additive terms reflecting the thermogravitational (Ra_T) and the thermomagnetic (Rm_T) buoyancy forces:

$$Ra = Ra_T + Rm_T = \left(\beta_T \rho g + \mu_0 \alpha_T M \frac{dH}{dz}\right) \frac{dT}{dz} \frac{c_p l^4}{\nu \lambda}. \tag{7}$$

Convective instability can develop ($Ra > 0$) if the temperature gradient is directed along the gravitation or the magnetic force.

An interesting situation appears when the non-isothermic ferrofluid layer is subjected to a homogeneous magnetic field $\mathbf{B} = \text{const}$. From the equation $\text{div}\,\mathbf{H} = -\text{div}\,\mathbf{M}$ it follows that thanks to the pyromagnetic properties of the fluid, a gradient of internal magnetic field appears in the layer. Instead of Eq. (7) the

Ra_T now is the following:

$$Ra = Ra_T + Rm_T = \left(\beta_T \rho g + \mu_0 \frac{\alpha_T^2 M^2}{(1+\chi)} \frac{dT}{dz}\right) \frac{dT}{dz} \frac{c_p l^4}{\nu \lambda}. \quad (8)$$

(Here $\chi = \partial M / \partial H$ is the differential magnetic susceptibility.) As a result, the magnetic Rayleigh number becomes square dependent on the temperature gradient and is positive. It means that the thermal perturbations of the magnetizing field always lead to the thermoconvective fluid destabilization.

The critical conditions for onset of the convection in a flat horizontal layer can be represented by [7]

$$\frac{Ra^*}{R_0} = \frac{Rm^*}{Rm_0}. \quad (9)$$

Here $R_0 = 1708$ (flat layer of rigid boundaries), whereas Rm_0 is the critical Rm value when the gravitation is absent. The latter depends on the magnetic properties of channel walls and is slightly influenced also by the nonlinearity of the fluid magnetization curve.

The general conclusions of thermoconvective stability theories (the pioneering one, obviously, is Ref. [8]) are confirmed experimentally (see, for example Ref. [9]). If the external gradient of magnetic field is applied nonparallel to the ∇T, the intensity of magnetic convection can significantly exceed the thermogravitational one. It means that magnetic control of the heat transfer in ferrofluids is an interesting problem of applications.

4. Mass transfer

Considering stable colloids without chemical reactions, the mass conservation equation for two component systems (particles of a mass concentration ρ_i and a carried liquid) is the following:

$$\frac{d\rho_i}{dt} = -\,\mathrm{div}\,\mathbf{j}_i. \quad (10)$$

Ultra-fine particles in magnetic fluids obey an intensive Brownian motion. Therefore, the mass transfer in colloids can be considered similar to that in molecular liquids. The diffusion coefficient of nanoparticles is determined by the relation $D = kT/f_v$, where f_v is the coefficient of the hydrodynamic drag force (for spherical particles of radius r $f_v = 6\pi\rho\nu r$). The diffusion coefficient for colloidal particles is several orders of magnitude less than that for molecules in liquids. The mass flux [1]

$$\mathbf{j}_i = -D\nabla\rho_i + \frac{m_g}{f_v}\left[(\bar{V}_i - \bar{V}_0)\rho\mathbf{g} + \mu_0(\bar{M}_i - \bar{M}_0)\nabla H\right]\rho_i(1-n_i) - \rho_i(1-n_i)DS_T\nabla T \quad (11)$$

contains a new barodifusion term. Besides the conventional gravitational sedimentation (m_g is the mass of the particle, $\bar{V}_i$ and $\bar{V}_0$ are the specific volume of the solid phase and that of the carrier liquid) it is necessary to take into account also the magnetic sedimentation ($\bar{M}_i = M_i/\rho_i$ and $\bar{M}_0 = M_0/\rho_0$ are correspondingly the specific magnetization of the particles and the carrier). The thermodiffusion term in Eq. (11) is retained for the purpose of generality, S_T is the Soret coefficient of particles, $n_i = \rho_i/\rho$ is the mass fraction of the particles.

The conditions of the fluid convective instability in isothermal liquids also are determined by relation (5). The corresponding solute Rayleigh number now is the following:

$$Ra = Ra_c + Rm_c = -\left(\beta_c \rho g + \mu_0 \alpha_c M \frac{dH}{dz}\right) \frac{d\rho_i}{dz} \frac{l^4}{\eta D}. \quad (12)$$

(The solute expansion (β_c) and magnetic (α_c) coefficients are positive). It is important to note that there is a principal difference between the thermal and the solutal convective stability. In stable colloids the concentration boundary conditions are the unpermeability of the surfaces. It means that the concentration gradients cannot be applied independently, the internal sedimentation forces form near the walls in the form of diffusive boundary layers. From Eq. (12) it can be seen that the gravitational or the magnetic stratification of particles always causes the increase of the fluid convective stability. If the fluid layer is placed in a homogeneous magnetic field $\mathbf{B} = \mathrm{const}$, the action of internal field gradients is quite different. The magnetic Rayleigh number now becomes a square dependent on concentration gradient and it is positive:

$$Rm_c = \left(\alpha_c M \frac{d\rho_i}{dz}\right)^2 \frac{\mu_0 l^4}{(1+\chi)\eta D}. \quad (13)$$

This means that the internal field gradients always cause a destabilization of the fluid layer.

The magnetic force usually is not homogeneous. As a result, the magnetic sedimentation forms the nonuniform distribution of particles also outside the boundary layers. These bulk gradients of the concentration are always oriented opposite to the magnetic driving force. Thus, the magnetic stratification of fluids is unstable. In Ref. [10] the convective stability of fluid in a coaxial gap subjected by the non-uniform azimuthal magnetic field of an axial central electric current is analyzed. Reaching the critical solute Rayleigh number value, the onset of a specific diffusion-magnetic convection should be observed even in isothermal colloid. This effect is confirmed experimentally [11]. If $\nabla\rho \times \nabla H \neq 0$, the solute-driven convection starts to develop monotonously and immediately after the field is switched on. Considering the magnetophoretic particle transfer near a transversally magnetized cylinder, in Ref. [12] it is shown that around the cylinder a system of intensive convection rolls should develop. This effect is conformed experimentally by holographic measurements of unsteady concentration distribution around the cylinder; the results coincide very well with the concentration profiles calculated under the assumption of the solute-driven magnetic convection [13].

5. Heat and mass transfer problems

Recent experiments refer to high thermodiffusion coefficients of nanoparticles in ferrocolloids. Using two different methods—the separation measurements in thermodiffusion column [14], and the measurements of diffraction signal from optically induced particle grating in thin films [15,16]—it is shown that the surfacted ferrite particles in hydrocarbons are transferred towards decreasing temperatures, the Soret coefficients reach values approximately equal to $S_T = +0.15\,K^{-1}$ (several orders of magnitudes higher than these in molecular liquids!). Electrically stabilized particles in ionic colloids usually have negative Soret coefficients [15,16]. The separation effect is so strong, that in the thermodiffusion column experiments almost complete educing of ferroparticles from the carrier liquid can be achieved [17].

The theory of the Soret effect in colloids is not well developed yet. Some general ideas of the theory of the slip velocity at a solid–liquid interface resulting from tangential temperature gradient are reviewed in Ref. [18]. Analyzing the enthalpy flux carried by forced convection of fluid across a porous barrier and applying Onsager's reciprocal theory for the slip velocity, in Ref. [19] it is predicted that free particles in surfacted colloids should move towards decreasing temperatures. According to the recent theoretical considerations the Soret coefficient of surfacted particles is proportional to the Gibbs absorption and the length of surfactant molecules as well as to the size of particles [20]. The measured values S_T qualitatively well agree with this theory. In recent experiments we have measured very high Soret coefficients in ferrofluid emulsions up to $S_T = 480\,K^{-1}$ [21]. We suspect that such a high thermodiffusive mobility of droplets is a result of Marangoni-type transfer. According to Ref. [22], the droplet velocity in a non-isothermal fluid follows the expression

$$u_\sigma = \frac{d}{2(3\eta + 2\eta_0)}\left(-\frac{\partial\sigma}{\partial T}\right)\nabla T. \tag{14}$$

Here η and η_0 are the viscosities of the ferrofluid droplet and the surrounding liquid, $\partial\sigma/\partial T$ is the dependence of the surface tension on temperature and d is the diameter of the droplet. The experimental results agree qualitatively well with the value of S_T calculated from the dependence given by Eq. (14).

Theory [23] tries to explain the reason of negative Soret coefficients in ionic ferrofluids [15]. It is shown that the direction of thermodiffusive transfer of charged particles depends on electrochemical parameters of the colloid. If the Debye layer is very thin, independent of the surface potential value, the particles are transferred in a direction opposite to the temperature gradient, $S_T > 0$. Increasing the thickness of double layer, at high values of ζ-potential it is possible to observe a reverse direction of particle transfer. The parameters of ionic ferrofluid used in the experiment [15] correspond to such requirements.

Let us consider a homogeneous magnetic field $\mathbf{B} = \text{const}$ directed along the temperature gradient. From the equation $\text{div}\,\mathbf{H} = -\text{div}\,\mathbf{M}$ we obtain (we assume $M_0 = 0$)

$$\begin{aligned}\nabla H &= -\nabla M_i \\ &= -\frac{\partial M_i}{\partial \rho_i}\nabla\rho_i - \frac{\partial M_i}{\partial T}\nabla T - \frac{\partial M_i}{\partial H}\nabla H.\end{aligned} \tag{15}$$

Mass flux (11) with respect to Eq. (15) can be rewritten in the form

$$\begin{aligned}\mathbf{j}_i = &-\left(D + \frac{\mu_0\alpha_c M^2 m_g}{f_v(1+\chi)}(1+n_i)\right)\nabla\rho_i \\ &-\left(S_T - \frac{\mu_0\alpha_T M^2 m_g}{f_v D\rho_i(1+\chi)}\right)\rho_i D(1-n_i)\nabla T.\end{aligned} \tag{16}$$

Respectively, the magnetic stratification of ferroparticles can be considered as an increase of the mass diffusion coefficient and as a reduction (in surfacted colloids) of Soret coefficient. More detailed analysis performed accounting for the particle interaction leads to the conclusion, that the change in coefficient D should be observed also in the case when the field is oriented normally to the temperature gradient [24,25]. The only difference is that now (at $\mathbf{B}\perp\nabla T$) the field causes a reduction of the mass diffusion coefficient. Both effects are confirmed experimentally recently [25].

The Soret effect of magnetic particles in the presence of uniform magnetic field is considered in Ref. [26]. Analyzing the hydrodynamic Stokes problem for spherical magnetic particle effected by the mean field of the colloid, it is shown, that if $\mathbf{B}\parallel\nabla T$, the magnetophoretic motion of particles is oriented along the temperature gradient in accordance with the dependence given by Eq. (16). On the contrary, in the presence of a transversal field $\mathbf{B}\perp\nabla T$ the particles are transferred towards decreasing temperatures. This so-called "magnetic Soret effect" and its anisotropy have been confirmed recently experimentally from the separation measurements in thermodiffusion column [27].

The very high Soret coefficient of ferroparticles is not only an important practical problem for ferrofluid applications but also brings up new research tasks. The most important problems are: the combined thermal and Soret-driven convection in thermodiffusion columns [28], the stability of convective shear flow in channels under the effect of transversal magnetic forces in non-isothermic and stratified colloids, the stability of convection in vertical fluid layer with an adverse density gradient due to negative Soret coefficient of heavy particles [29], etc. There also appears a new class of the stability problems of double diffusive magnetic convection in stratified colloid [30].

6. Conclusions

Magnetic convection in non-isothermic and stratified ferrocolloids can be used to develop new effective cooling systems (for loudspeakers, electric transformers, magnetically controlled thermosyphons, etc.). Magnetic and thermodiffusional stratification of colloids should be taken into account considering the long-time working ability of magnetofluid devices.

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