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Linear stability of Rayleigh–Benard–Poiseuille convection for electrochemical system

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ABSTRACT

The effect of Poiseuille flow on the convective stability of electrochemical system is considered. It is found that the effect is destabilizing in the case of oscillatory instability in the system. It is shown that this effect is caused by the fact that the problem is not self-conjugate, because the system is multicomponent. In addition, it is found that the effect of Reynolds number on the stability of these systems is linear at small Reynolds number, in contrast to the self-conjugate Rayleigh–Benard problem, where the effect is quadratic.

1. Introduction

The effect of forced convection in horizontal plane channel on natural-convective flows, which are caused by nonuniform heating of liquid, has been studied from the beginning of 20th century, predominantly, in connection with geophysical applications [1]. This problem is a combination of Rayleigh–Benard problem (the stability of liquid with nonuniform density) and the problem of stability of plane flow (the Orr–Sommerfeld problem).

Classical Rayleigh–Benard problem involves the study of convective systems, in which stable equilibrium can be reached, and the determination of conditions, under which the equilibrium is violated. The problem is reduced to the determination of critical Rayleigh number Ra_{cr}. If the Rayleigh number Ra of the system is lower than the critical one ($Ra < Ra_{cr}$), liquid remains stagnant and convection does not occur; at $Ra > Ra_{cr}$, natural convection occurs in the system [2].

When a complex system with applied shear flow in the X direction, which is characterized by the Reynolds number Re, is considered (Fig. 1), the problem is posed to determine the critical Rayleigh number as a function of Reynolds number $Ra_{cr}(Re)$. If the shear flow has a parabolic rate profile in the undisturbed state, the study of the system for stability is called the Rayleigh–Benard–Poiseuille (RBP) problem [3]. The linear stability of RBP was first studied by Gage and Reid [3]. This problem is characterized by three dimensionless parameters: the Rayleigh number, the Prandtl (Schmidt) number, and the Reynolds number. The determination of critical Rayleigh numbers at small Reynolds numbers and arbitrary Prandtl number was considered in [4]. In addition, the case of small Reynolds numbers and constant Prandtl number was considered in [5].

It can be readily shown that the shear flow has an effect only on the perturbations, whose convective rolls are perpendicular to the flow (transversal perturbations). Perturbations, whose convective rolls are parallel to the flow (longitudinal perturbations) remain invariant. This means that, in the case of plane liquid layer, to the linear approximation, forced convection only directs convective rolls and does not change the convective stability of system as a whole. However, in more complex geometric conditions, when transversal and longitudinal perturbations are not equally favored by influence of the sidewalls, shear flow can has a determining effect on the system stability [6].

In electrochemistry, the Rayleigh–Benard–Poiseuille problem has some peculiarities. Firstly, the Prandtl (Schmidt) number in the electrochemical systems is much higher (about 1000) than in the heat systems. Secondly, the electrochemical systems are commonly multicomponent, and this can complicate significantly the system's behavior. The transfer equations in the electrochemical systems and the boundary conditions are often more complicated.

2. Statement of problem

A system of two horizontal plane electrodes of the same metal is considered. The space between the electrodes is filled with electrolyte solution. An external constant pressure, which causes longitudinal liquid flow, is applied to the system.

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Nomenclature

c_{m}	concentration of ions of *m*th type
C_1	dimensionless concentration of electroactive ion, $C_1 = \frac{c_1}{2c_{1_{\mathrm{b}}}}$
C_4	dimensionless concentration of fictitious ion, $C_4 = \frac{z_3 c_4}{2\alpha c_{1_{\mathrm{b}}(z_3 - z_2)}}\beta_2$
D_m	diffusion coefficient of ions of *m*th type
D_4	dimensionless parameter, which is proportional to the diffusion coefficient of fictitious ion, $D_4 = \frac{D_2 D_3 (z_3 - z_2)}{z_3 D_3 - z_2 D_2}$
$\overline{D}_4$	dimensionless parameter, $\overline{D}_4 = \frac{D_4}{D_1}$
D^*	coefficient of cross effect of concentration of electroactive ion on the fictitious ion transfer, $D^* = \frac{D_1}{D_2}\left[\frac{n_2}{n_1}D_1 - \frac{D_3(z_3 - z_2) + (D_3 - D_2)z_1}{z_3 D_3 - z_2 D_2}D_2 - \frac{n_2 - n_1}{n_1}D_4\right]$
$\overline{D}^*$	dimensionless parameter, $\overline{D}^* = \frac{z_3 D^*}{\alpha d_1 (z_3 - z_2)}\beta_2$
$\mathbf{e}_{\mathrm{X}}$	unit vector collinear with *X* axis
$\mathbf{e}_{\mathrm{Z}}$	unit vector collinear with *Z* axis
F	Faraday number
g	gravitational acceleration
h	distance between electrodes
M_{m}	designation of ions of *m*th type
n_{m}	stoichiometric coefficient of ions of *m*th type
n	number of electrons, which are transferred in the electrode reaction, $n = z_1 n_1 - z_2 n_2$
p	pressure
P	dimensionless pressure, $P = \frac{h^2}{\rho_{\mathrm{b}} \nu D_1} p$
R	gas constant
Ra	Rayleigh number, $Ra = \frac{2gh^3 c_{1_{\mathrm{b}}}\alpha}{\rho_{\mathrm{b}} \nu D_1}$
Re	Reynolds number, $Re = \frac{V_{\max} h}{\nu}$
Sc	Schmidt number, $Sc = \frac{\nu}{D_1}$
t	time
T	temperature
$\mathbf{U}$	perturbation of electrolyte flow velocity
$\mathbf{v}$	electrolyte flow velocity
$\mathbf{V}$	dimensionless electrolyte flow velocity, $\mathbf{V} = \frac{\nu}{D_1}\mathbf{v}$
$\bar{v}$	velocity profile of the Pioseuille flow in direction of *x* axis, $\bar{v} = v_{\max}\left[1 - 4(z/h)^2\right]$
$\mathbf{v}_{\max}$	maximum velocity of the Poiseuille flow
$\mathbf{V}_0$	vector of velocity profile of the Poiseuille flow, $\mathbf{V}_0 = \mathbf{e}_{\mathrm{X}} \mathbf{V}_0$
V_0	velocity profile of the Poiseuille flow, $V_0 = 1 - 4Z^2$
W	component of perturbation of electrolyte flow velocity along the *Z* axis
w	amplitude of component of perturbation of electrolyte flow velocity along the *Z* axis
x, y, z	Cartesian coordinates (the origin of coordinates is placed at the lower electrode (cathode), *z* axis is directed vertically upward from the cathode to the anode)
X, Y, Z	dimensionless Cartesian coordinates, $X = \frac{x}{h}$, $Y = \frac{y}{h}$, $Z = \frac{z}{h}$
Z_{m}	charge number of ions of *m*th type

Greek symbols

α	mass coefficient of electrolyte with three types of ions, $\alpha = \beta_1 + \frac{z_1 - z_3 n_2 D_1 / n_1 D_2}{z_3 - z_2}\beta_2$
β_{m}	mass coefficient of ions of *m*th type, $\beta_{\mathrm{m}} = \partial p / \partial c_{\mathrm{m}}$
Δ_{H}	horizontal Laplacian (in the $X - Y$ plane), $\Delta_H = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}$
Θ_1	perturbation of electroactive ions
Θ_4	perturbation of fictitious ions
θ_1	amplitude of perturbation of electroactive ions
θ_4	amplitude of perturbation of fictitious ions
λ	eigenvalue
ν	electrolyte kinematic viscosity
Π	perturbation of pressure
ρ	electrolyte density
φ	electric potential
Φ	dimensionless electric potential, $\Phi = \frac{F\varphi}{RT}$
τ	dimensionless time, $\tau = \frac{\nu}{h^2}t$

Subscript

b	corresponds to the bulk electrolyte

Overbar

–	undisturbed state

Within the Boussenesq approximation, the equations describing convective mass transfer for binary electrolyte (for example, for $CuSO_4$ solution between two copper electrode) will coincide with the heat-transfer equations [2,7,8], and equations for the system containing three types of ions with an excess of supporting electrolyte excluding the migration current (for example, $CuSO_4 + H_2SO_4$ (in excess) solution between two copper electrodes) can be presented as follows (see Appendix):

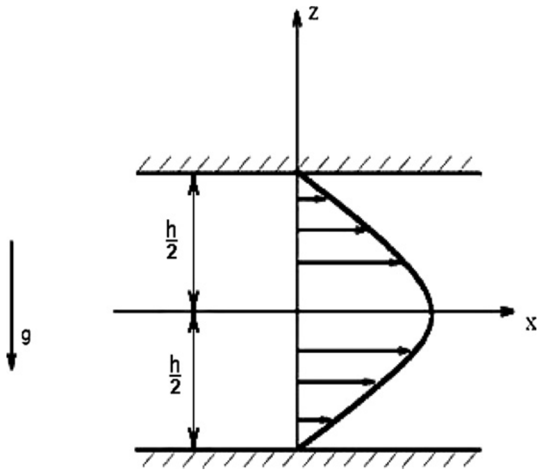

Fig. 1. Plane horizontal layer. Axes and profile of main flow (cathode: $z = -1/2$; anode: $z = 1/2$).

$$\frac{\partial \mathbf{V}}{\partial \tau} + \frac{1}{Sc}(\mathbf{V}.\nabla)\mathbf{V} = -\nabla P + \Delta \mathbf{V} - \mathbf{e}_z Ra(C_1 - 0.5 + C_4) \tag{1}$$

$$\operatorname{div}(\mathbf{V}) = 0 \tag{2}$$

$$Sc\frac{\partial C_1}{\partial \tau} = \Delta C_1 - \mathbf{V}\nabla C_1 \tag{3}$$

$$Sc\frac{\partial C_4}{\partial \tau} = \overline{D}_4 \Delta C_4 - \mathbf{V}\nabla C_4 + \overline{D}^* \Delta C_1 \tag{4}$$

$$\mathbf{V}|_{Z=-\frac{1}{2},\ Z=\frac{1}{2}} = 0 \tag{5}$$

$$C_1|_{Z=-\frac{1}{2}} = 0, \quad C_1|_{Z=\frac{1}{2}} = 1 \tag{6}$$

$$\left.\frac{\partial C_4}{\partial Z}\right|_{Z=-\frac{1}{2},\ Z=\frac{1}{2}} = 0 \tag{7}$$

Here, (1) is the Navier–Stokes equation that accounts for the buoyancy forces, (2) is the condition of incompressibility, (3) is the equation of electroactive ion transfer (Cu^{2+} in the above examples), (4) is the transfer equation of fictitious electrolyte, which is introduced in order to eliminate the migration current [9,10], (5) is the condition of liquid adhesion to the cell walls, boundary conditions (6) show that the electrochemical reaction on the lower electrode proceeds in the limiting-current mode and leads to a decrease in the solution density, (7) are the boundary conditions for fictitious electrolyte.

As is easy to see, at $\overline{D}^* = 0$, due to zero boundary conditions (7), the problem is reduced to the well-known heat-transfer problem.

At nonzero longitudinal gradient of pressure in the system with plane electrodes (Fig. 1), the Poiseuille flow arises. Its profile in the dimensionless form is

$$\overline{\mathbf{V}} = Re\cdot Sc\mathbf{V}_0 = \mathbf{e}_X Re\cdot Sc(1-4Z^2) \qquad (8)$$

To investigate the stability of undisturbed state, that is, a solution of system (1)–(7) for the Poiseuille flow of electrolyte, the perturbations of dependent variables are introduced

$$C_1 = \overline{C}_1 + \Theta_1, \quad C_4 = \overline{C}_4 + \Theta_4, \quad \mathbf{V} = \overline{\mathbf{V}} + \mathbf{U}, \quad P = \overline{P} + \Pi \qquad (9)$$

Equations for linear perturbations of velocity and concentration are as follows:

$$\frac{\partial \mathbf{U}}{\partial \tau} + Re(\mathbf{V}_0\cdot\nabla)\mathbf{U} + Re(\mathbf{U}\cdot\nabla)\mathbf{V}_0 = -\nabla\Pi + \Delta\mathbf{U} - \mathbf{e}_Z Ra(\Theta_1+\Theta_4) \qquad (10)$$

$$\mathrm{div}(\mathbf{U}) = 0 \qquad (11)$$

$$Sc\frac{\partial\Theta_1}{\partial\tau} = \Delta\Theta_1 - Re\cdot Sc\cdot\mathbf{V}_0\cdot\nabla\Theta_1 - W\frac{\partial\overline{C}_1}{\partial Z} \qquad (12)$$

$$Sc\frac{\partial\Theta_4}{\partial\tau} = \overline{D}_4\Delta\Theta_4 - Re\cdot Sc\cdot\mathbf{V}_0\cdot\nabla\Theta_4 + \overline{D}^*\Delta\Theta_1 - W\frac{\partial\overline{C}_4}{\partial Z} \qquad (13)$$

In the absence of natural convection system of Eqs. (3) and (4) has a steady-state solution dependent only on vertical coordinate Z:

$$\overline{C}_1 = 1/2 + Z, \quad \overline{C}_4 = 0, \qquad (14)$$

Let us twice apply rot to Eq. (10) and project the result onto Z axis. Then, taking into account relations (14), Eqs. (10), (12) and (13) can be written as follows:

$$\frac{\partial\Delta W}{\partial\tau} + Re\left(\mathbf{V}_0\Delta - \frac{\mathrm{d}^2V_0}{\mathrm{d}Z^2}\right)\frac{\partial W}{\partial X} = \Delta^2 W - Ra\cdot\Delta_H(\Theta_1+\Theta_4) \qquad (15)$$

$$Sc\frac{\partial\Theta_1}{\partial\tau} = \Delta\Theta_1 - Re\cdot Sc\cdot V_0\frac{\partial\Theta_1}{\partial X} - W \qquad (16)$$

$$Sc\frac{\partial\Theta_4}{\partial\tau} = \overline{D}_4\Delta\Theta_4 - Re\cdot Sc\cdot V_0\frac{\partial\Theta_4}{\partial X} + \overline{D}^*\Delta\Theta_1 \qquad (17)$$

Problem (15)–(17) has a solution in the form of so-called normal perturbations:

$$\begin{aligned} W(X,Y,Z,\tau) &= w(Z)\exp(-\lambda\cdot\tau + \mathrm{i}k_X\cdot X + \mathrm{i}k_Y\cdot Y)\\ \Theta_1(X,Y,Z,T) &= \theta_1(Z)\exp(-\lambda\cdot\tau + \mathrm{i}k_X\cdot X + \mathrm{i}k_Y\cdot Y)\\ \Theta_4(X,Y,Z,T) &= \theta_4(Z)\exp(-\lambda\cdot\tau + \mathrm{i}k_X\cdot X + \mathrm{i}k_Y\cdot Y)\end{aligned} \qquad (18)$$

Substituting (18) into (15)–(17), we obtain the system of equations for amplitudes:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)^2 w + \mathrm{i}k_x Re\left[\frac{\mathrm{d}^2V_0}{\mathrm{d}Z^2}w - V_0\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)w\right] + k^2 Ra(\theta_1+\theta_4) = -\lambda\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)w \qquad (19)$$

$$\frac{1}{Sc}\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)\theta_1 - w\right] - \mathrm{i}k_x ReV_0\theta_1 = -\lambda\theta_1 \qquad (20)$$

$$\frac{1}{Sc}\left[D_4\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)\theta_4 + D^*\left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - k^2\right)\theta_1\right] - \mathrm{i}k_x ReV_0\theta_4 = -\lambda\theta_4 \qquad (21)$$

with the boundary conditions for amplitudes:

$$w = \frac{\partial w}{\partial Z} = \theta_1 = \frac{\mathrm{d}\theta_4}{\mathrm{d}Z} = 0 \quad \text{at } Z = \pm 1/2 \qquad (22)$$

This boundary-value problem is not self-conjugate and, therefore, its eigenvalues λ can be real or complex. If decrement λ is real, perturbation varies monotonically (until the perturbation can be considered as small, and linear expansion in terms of this perturbation is valid; at $\lambda > 0$, the perturbation damps out, and at $\lambda < 0$, it increases.

3. Results and discussion

The eigenvalue problem (19)–(21) was solved using the Galerkin method that has been proven in the problems of hydrodynamic stability [7]. Solutions were obtained for various magnitudes of parameter $\overline{D}^*$. At zero cross (mutual) parameter $\overline{D}^*$, solution of

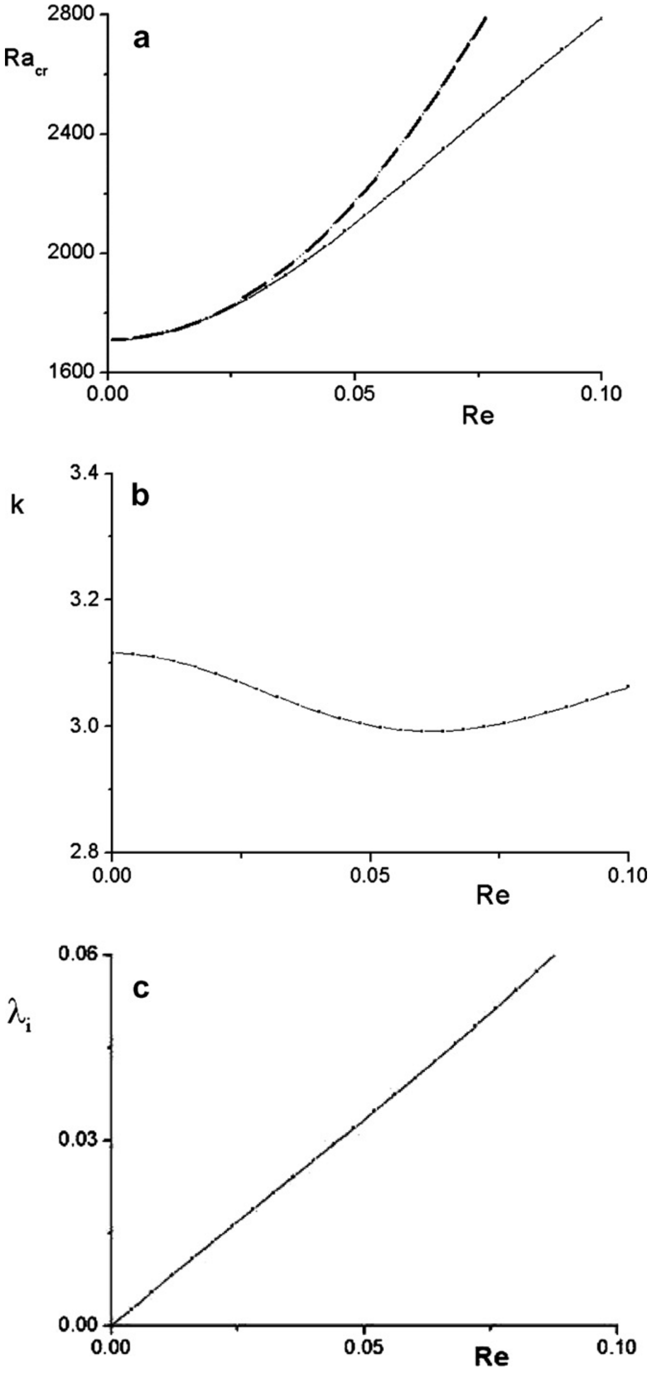

Fig. 2. Dependences of (a) critical Rayleigh number Ra_{cr} (the asymptotic Miller solution [1] is shown with a fine line), (b) critical wave Rayleigh number, and (c) the frequency of arising perturbations on the Reynolds number for systems with $\overline{D}^* = 0$, $Sc = 1000$.

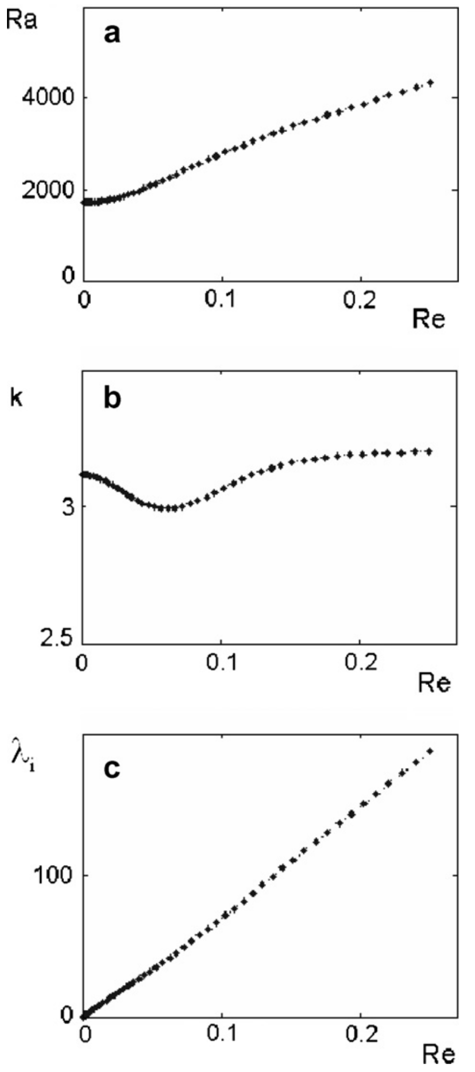

Fig. 3. Dependences of (a) critical Rayleigh number Ra_{cr} (b) critical wave Rayleigh number, and (c) the frequency of arising perturbations on the Reynolds number for systems with $\overline{D}^* = 0.001, \overline{D}_4 = 1$, Sc = 1000.

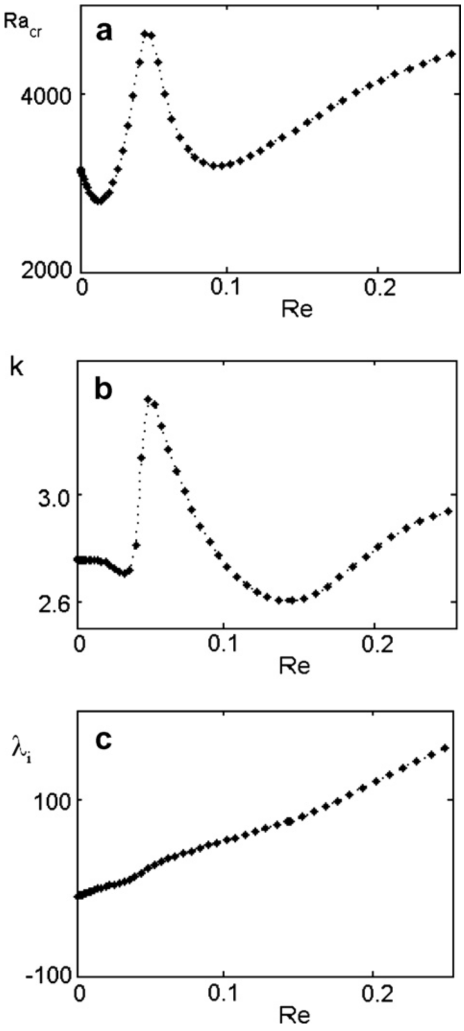

Fig. 4. Dependences of (a) critical Rayleigh number Ra_{cr}, (b) critical wave Rayleigh number, and (c) the frequency of arising perturbations on the Reynolds number for systems with $\overline{D}^* = 4, \overline{D}_4 = 1$, Sc = 1000.

the problem is similar to the solution of heat problem, which is available from the literature (Fig. 2).

As is seen from Fig. 2a, at small Reynolds numbers, the plot of critical Rayleigh number vs. *Re* coincides with the asymptotic solution [4]. The flow makes the system more stable, i.e. the critical Rayleigh number increases with increasing Reynolds number. Moreover, frequency of perturbations linearly depends on the Reynolds number (Fig. 2c). The wave number decreases at small *Re*, the shear flow as if extends convective cells; however, at higher Re, smaller cells become more beneficial (advantageous, profitable, efficient), because the flow, which is nonuniform along *Z* axis, has no time to (hollow out) blur them; this corresponds to an increase in the wave number (Fig. 2b). If $\overline{D}^*$ is slightly different from zero, but insufficiently high for critical perturbations to become oscillatory, the dependences of critical parameters on Re qualitatively differ from the heat case (Fig. 3).

Much more complicated dependences of critical parameters on the Reynolds number are observed when the cross parameter $\overline{D}^*$ is sufficiently high for perturbations to become oscillatory (Fig. 4). As is seen from Fig. 4a, at small *Re*, the critical Rayleigh number initially decreases with increasing *Re*, then increases, then, again, steeply decreases, and only with further increase in the flow velocity, again increases. In contrast to the case of monotonic instability, which is typical for the Rayleigh–Benard convection, weak forced flow has a destabilizing effect on the oscillatory stability. The forced flow converts the monotonic perturbations into oscillatory ones (the action of forced flow on the monotonic perturbations makes them oscillatory) and stabilizes the system by making perturbations to damp. A system with initially oscillatory perturbations, conversely, becomes more unstable under the action of weak forced flow.

Within the theory of perturbations, this phenomenon can be explained as follows. According to [4], for the case of Rayleigh–Benard convection with imposed weak shear Poiseuille flow, the problem can be stated as determining the spectrum of operator **A**+i*kReU*, where **A** is a self-adjoined operator (it will be termed the Rayleigh–Benard operator) and i*kReU* is the operator of Poiseuille flow perturbation. If *Re* is small, by using the perturbation theory for self-conjugate operators, it can be easily seen that the correction to zero eigenvalue in the leading order will be purely complex. (The correction will be $\lambda^1 = \mathrm{i}Rek(\varphi^* U\varphi)$, where φ are the eigenvalues of Rayleigh–Benard operator **A**.) This means that small *Re* make the critical perturbations oscillatory with a frequency linearly dependent of *Re*, but stability depends on Re^2. When an effect of weak forced flow on convective stability of system under consideration is studied, the problem is in determining the spectrum of operator **B**+i*kReU*, where **B** is not self-conjugate operator (the non self-conjugation is the reason for oscillatory instability). As-

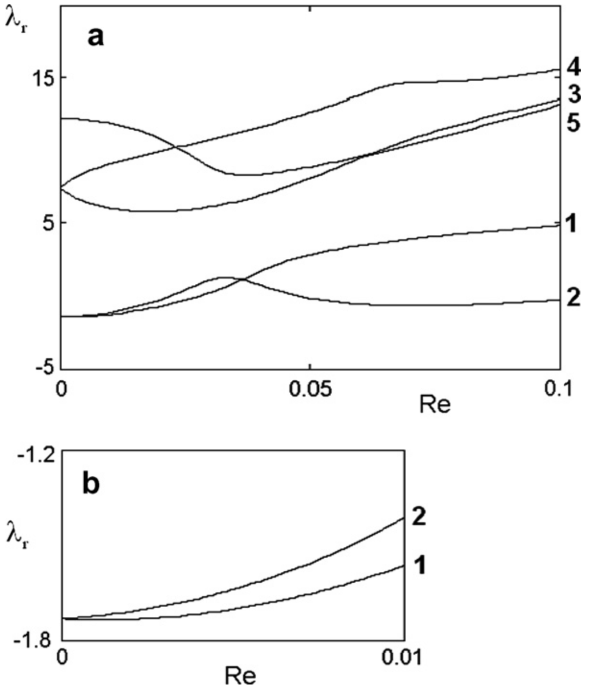

Fig. 5. Dependences of real part of spectrum on the Reynolds number (the first five levels 1–5) for system with $\overline{D}^* = 1, \overline{D}_4 = 1$, $Sc = 1000$, $k = 3$, $Ra = 4000$. (a) Intersections of lower levels and (b) initial divergence of lower complex conjugate level at a larger scale.

sume that undisturbed system corresponding to operator **B** is in the critical state of oscillatory convection, i.e. $\lambda_r = 0$, and $\lambda_i \neq 0$. Operator **B** is equal to its complex-conjugate operator; therefor, the lower oscillatory level will be double $\pm\lambda_i$. First-order correction of perturbation theory for these two values will be written using the theory for not self-conjugate operators [11]:

$$+ : ikRe(\psi^{-^*} U\varphi^{+}) \tag{23}$$

$$- : ikRe(\psi^{+^*} U\varphi^{-}) \tag{24}$$

where φ^+ and φ^- are eigenvectors of operator B corresponding to eigenvalues $i\lambda_i$ and $-i\lambda_i$, ψ^+ and ψ^- are eigenvalues of conjugate operator B^* corresponding to eigenvalues $i\lambda_i$ and $-i\lambda_i$ Due to the fact that operators B and B^* are equal to their own complex conjugates, it is easy to see that $\overline{(\psi^{-^*} U\varphi^{+})} = (\psi^{+^*} U\varphi^{-})$. This means that corrections (23) and (24) can be written as $i\bar{z}$ and iz, where z is a complex number, i.e. if, after a small perturbation is imposed, one of eigenvalues $\pm\lambda_i$ becomes damping, another, inversely, becomes growing. In addition, as is seen (Fig. 4a), for this system, the effect of *Re* on stability is not quadratic in *Re*, as in the case of Rayleigh–Benard convection, but is linear in *Re*.

An inflection in stability (Fig. 4a, I) is caused by the fact that two lower levels, which initially came apart due to the linear correction, intersect again, i.e. previously second level exchanges places with the first level; therefore, the critical wave number also changes jumpwise (Fig. 4b I). The intersection of levels is illustrated on Fig. 5a. Fig. 5a gives the evolution of first five levels of real part of spectrum λ under the action of flow and, in addition, Fig. 5b shows the initial divergence of the lower level at a larger scale.

As well as in all of cases under consideration, for oscillatory instability, a further increase in the Reynolds number has a stabilizing effect.

4. Conclusions

The effect of Poiseuille flow on the convective stability of model electrochemical system is considered. It is found that the effect is destabilizing in the case of oscillatory instability in the system. This is a new result, which is not available from the literature. It is shown that this effect is caused by the fact that the problem is not self-conjugate, because the system is multicomponent. In addition, it is found that the effect of Re on the stability of these systems is linear in *Re* at small *Re*, in contrast to the self-conjugate Rayleigh–Benard problem, where the effect is quadratic in *Re*. A decrease in the stability of oscillatory systems, which is found here, is of practical importance, because it can be observed immediately in the experiments, in contrast to the classical Rayleigh–Benard–Poiseuille problem, where it cannot be observed without crating nonuniform geometrical conditions for rolls of various types. A decrease in stability can have a pronounced effect on the generation of convective noises in the electrochemical devices and should be taken into account, when they are developed.

It should be noted that a possibility of decreasing stability of multicomponent Rayleigh–Benard systems by imposing external hydrodynamic flow is typical of not only electrochemical systems. For instance, in geophysics, a similar effect of a decrease in stability is observed in the binary convection under the conditions of nonuniform temperature and salinity in sea water. In addition, as follows from the analysis of the reasons for a decrease in stability, it will take place in the case of hydrodynamic flow of another nature (the Couette flow, for example).

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Appendix. Mathematical model

Within the Boussinesq approximation, the theory of dilute electrolytes and taking into account the assumption of electroneutrality, the equations of incompressible viscous liquid flow and ion transfer in the electrolyte layer between two horizontal electrodes can be written as follows [12]:

$$\begin{aligned}
&\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{1}{\rho_b}\nabla p + \nu \triangle \mathbf{v} - \frac{\mathbf{e}_z g}{\rho_b}(\rho - \rho_b) \\
&\mathrm{div}(\mathbf{v}) = 0 \\
&\frac{\partial c_1}{\partial t} = D_1 \triangle c_1 + \frac{F z_1 D_1}{RT}(\nabla c_1 \nabla \varphi + c_1 \triangle \varphi) - \mathbf{v}\nabla c_1 \\
&\frac{\partial c_2}{\partial t} = D_2 \triangle c_2 + \frac{F z_2 D_2}{RT}(\nabla c_2 \nabla \varphi + c_2 \triangle \varphi) - \mathbf{v}\nabla c_2 \\
&\frac{\partial c_3}{\partial t} = D_3 \triangle c_3 + \frac{F z_3 D_3}{RT}(\nabla c_3 \nabla \varphi + c_3 \triangle \varphi) - \mathbf{v}\nabla c_3 \\
&z_1 c_1 + z_2 c_2 + z_3 c_3 = 0
\end{aligned} \tag{A.1}$$

For three-component electrolyte, which is produced of two source substances, the electrolyte density can be always expressed in terms of concentrations of two types of ions, because the concentration of ions of the third type is uniquely determined by the electroneutrality condition. For the sake of definiteness, we assume that the electrolyte density is expressed as follows:

$$\rho - \rho_b = \beta_1(c_1 - c_{1_b}) + \beta_2(c_2 - c_{2_b}) \tag{A.2}$$

Assume that the following reaction proceeds on the electrodes:

$$n_1 M_1^{z1} + ne \leftrightarrow n_2 M_2^{z2} \tag{A.3}$$

Eq. (A.3) describes both redox reactions ($n_2 \neq 0$) and the reactions of cathodic deposition (anodic dissolution) ($n_2 = 0$).

The boundary conditions for set of equation (A.1) for the limiting-current mode, i.e. at zero concentration of electroactive ion on the cathode surface, can be written as follows:

$$\mathbf{v}|_{z=-h/2,z=h/2} = 0 \tag{A.4}$$

$$\left(\frac{\partial c_3}{\partial z} + \frac{Fz_3c_3}{RT}\frac{\partial \varphi}{\partial z}\right)\bigg|_{z=-h/2,z=h/2} = 0 \tag{A.5}$$

$$\left[n_2D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1c_1}{RT}\frac{\partial \varphi}{\partial z}\right) = -n_1D_2\left(\frac{\partial c_2}{\partial z} + \frac{Fz_2c_2}{RT}\frac{\partial \varphi}{\partial z}\right)\right]\bigg|_{z=-h/2,z=h/2} \tag{A.6}$$

$$c_1|_{z=-h/2} = 0, \quad c_1|_{z=h/2} = 2c_{1_b} \tag{A.7}$$

We assume that the concentration of supporting electrolyte is significantly higher than the concentration of electroactive electrolyte

$$\varepsilon = \frac{c_{1_b}}{c_{3_b}} \ll 1 \tag{A.8}$$

Let us estimate the relative diffusion and migration terms in the equations of ion transfer and the corresponding boundary conditions at $\varepsilon \ll 1$. The difference between the concentrations of the first electrolyte component at the anode and at the cathode is denoted as $\delta c_1 (\delta c_1 \sim \varepsilon c_{3_b})$. From the electroneutrality condition, for the second and the third electrolyte components, we obtain:

$$\begin{aligned} &\delta c_2 \sim \delta c_1 \sim \varepsilon c_{3_b} \\ &\delta c_3 \sim \delta c_1 \sim \varepsilon c_{3_b} \end{aligned} \tag{A.9}$$

Thus, the diffusion terms for all electrolyte components have identical relative values proportional to ε. To estimate the derivatives of electric potential, the condition of charge conservation is used

$$\sum_{m=1}^{3} z_mD_m\Delta c_m + \nabla\varphi\sum_{m=1}^{3}\frac{Fz_m^2D_m}{RT}\nabla c_m + \nabla\varphi\sum_{m=1}^{3}\frac{Fz_m^2D_mc_m}{RT} = 0, \tag{A.10}$$

which follows from the equations of ion transfer (1) and the electroneutrality condition.

Taking into account that $\sum_{m=1}^{3} z_mD_m\Delta c_m \sim \varepsilon c_{3_b}\left|\sum_{m=1}^{3}\frac{Fz_m^2D_m}{RT}\nabla c_m\right| \sim \varepsilon c_{3_b}$ $\sum_{m=1}^{3}\frac{Fz_m^2D_mc_m}{RT} \sim c_{3_b}$ and $\Delta\varphi \sim |\nabla\varphi|$, we obtain: $\Delta\varphi \sim \varepsilon$, $|\nabla\varphi| \sim \varepsilon$.

In the approximation linear in parameter ε, set of equation (A.1) will take the following form:

$$\begin{aligned} &\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\frac{1}{\rho_b}\nabla p + \nu\Delta\mathbf{v} - \frac{\mathbf{e}_zg}{\rho_b}[\beta_1(c_1 - c_{1_b}) + \beta_2(c_2 - c_{2_b})] \\ &\operatorname{div}(\mathbf{v}) = 0 \\ &\frac{\partial c_1}{\partial t} = D_1\Delta c_1 - \mathbf{v}\nabla c_1 \\ &\frac{\partial c_2}{\partial t} = D_2\Delta c_2 + \frac{Fz_2D_2c_{2_b}}{RT}\Delta\varphi - \mathbf{v}\nabla c_2 \\ &\frac{\partial c_3}{\partial t} = D_3\Delta c_3 + \frac{Fz_3D_3c_{3_b}}{RT}\Delta\varphi - \mathbf{v}\nabla c_3 \\ &z_1c_1 + z_2c_2 + z_3c_3 = 0 \end{aligned} \tag{A.11}$$

From boundary conditions (A.6) and (A.7) and the electroneutrality condition, taking into account that $\varepsilon \ll 1$, we obtain:

$$\frac{\partial}{\partial z}\left(\frac{n_2D_1}{n_1D_2}c_1 + c_2 + c_3\right)\bigg|_{z=-h/2,z=h/2} = 0 \tag{A.12}$$

Introducing new variable (concentration of fictitious ion)

$$c_4 = \frac{n_2D_1}{n_1D_2}(c_1 - c_{1_b}) + c_2 - c_{2_b} + c_3 - c_{3_b} \tag{A.13}$$

and expressing concentrations c_2 and c_3 in terms of c_1 and c_4

$$\begin{aligned} &c_2 = c_{2_b} + \frac{z_3}{z_3 - z_2}c_4 + \frac{z_1 - z_3n_2D_1/n_1D_2}{z_3 - z_2}(c_1 - c_{1_b}) \\ &c_3 = c_{3_b} + \frac{z_2}{z_3 - z_2}c_4 + \frac{z_1 - z_2n_2D_1/n_1D_2}{z_3 - z_2}(c_1 - c_{1_b}) \end{aligned} \tag{A.14}$$

set of equation (A.11) can be presented as follows:

$$\begin{aligned} &\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\frac{1}{\rho_b}\nabla p + \nu\Delta\mathbf{v} - \frac{\mathbf{e}_zg}{\rho_b}\left[\alpha(c_1 - c_{1_b}) + \frac{z_3}{z_3 - z_2}\beta_2c_4\right] \\ &\operatorname{div}(\mathbf{v}) = 0 \\ &\frac{\partial c_1}{\partial t} = D_1\Delta c_1 - \mathbf{v}\nabla c_1 \\ &\frac{\partial c_4}{\partial t} = D_4\Delta c_4 + D^*\Delta c_1 - \mathbf{v}\nabla c_4 \end{aligned} \tag{A.15}$$

with the boundary conditions:

$$\mathbf{v}|_{z=-h/2,z=h/2} = 0 \tag{A.16}$$

$$c_1|_{z=-h/2} = 0, \quad c_1|_{z=h/2} = 2c_{1_b} \tag{A.17}$$

$$\frac{\partial c_4}{\partial z}\bigg|_{z=-h/2,z=h/2} = 0 \tag{A.18}$$

In the dimensionless form, set of equation (A.15) will take the following form:

$$\begin{aligned} &\frac{\partial \mathbf{V}}{\partial \tau} + \frac{1}{Sc}(\mathbf{V}\cdot\nabla)\mathbf{V} = -\nabla P + \Delta\mathbf{V} - \mathbf{e}_zRa(C_1 - 0.5 + C_4) \\ &\operatorname{div}(\mathbf{V}) = 0 \\ &Sc\frac{\partial C_1}{\partial \tau} = \Delta C_1 - \mathbf{V}\nabla C_1 \\ &Sc\frac{\partial C_4}{\partial \tau} = \overline{D}_4\Delta C_4 - \mathbf{V}\nabla C_4 + \overline{D}^*\Delta C_1 \end{aligned} \tag{A.19}$$

with the boundary conditions:

$$\begin{aligned} &\mathbf{V}|_{Z=-\frac{1}{2},Z=\frac{1}{2}} = 0 \\ &C_1|_{Z=-\frac{1}{2}} = 0, \quad C_1|_{Z=-\frac{1}{2}} = 1 \\ &\frac{\partial C_4}{\partial Z}\bigg|_{Z=\frac{1}{2},Z=\frac{1}{2}} = 0 \end{aligned} \tag{A.20}$$

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