MACROSCOPIC-MICROSCOPIC PARADOX IN DYNAMIC EQUILIBRIUM FOCUSING

Josef JANČA

Université de La Rochelle, Pôle Sciences et Technologie, Avenue Michel Crépeau, 17042 La Rochelle Cedex 01, France; e-mail: jjanca@univ-lr.fr

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Dedicated to Professor Pavel Kratochvíl on the occasion of his 70th birthday.

Recent theoretical and experimental findings concerning equilibrium focusing in density gradient (isopycnic focusing) indicate that the density gradient forming liquid should not necessarily behave as a continuum regarding the focused species. The size of the focused species can be commensurate with the size of the density gradient forming species. Consequently, the microscopic interactions among the gradient forming and focused species must be taken into account while the macroscopic density gradient loses its physical meaning with regard to the mechanism of the focusing. As a result, a paradox appears as concerns the macroscopic and microscopic approaches to explain the focusing phenomenon.
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Dynamic equilibrium focusing is a physical phenomenon exploited for the separation purposes. The isopycnic[1,2] focusing represents one of the methods of this category. It is based on the concentrating transport leading to an equilibrium distribution of the focused species established in a density gradient forming fluid. The gravitational or centrifugal forces generate a formation of both the density gradient and isopycnic focused zones. It has been assumed that the density gradient forming fluid must behave as a continuum with respect to discrete colloidal species undergoing focusing. Paradoxically, recent theoretical predictions[3,4] and experiments[5,6] showed that the focusing of larger size particles appears in a suspension of smaller colloidal particles even if the particle size ratio of both particles is low. Moreover, the focusing phenomenon was generated not only by single centrifugal forces[5] but also by a coupled action of the electrical and gravitational fields[6].

THEORY

The basic equation describing the thermodynamic sedimentation equilibrium of two component solvent system is[7,8]:

$$\mathrm{d}\Delta\mu_i = M_i g\left(1 - v_i \rho(x)\right)\mathrm{d}x \ , \tag{1}$$

where $\Delta\mu_i$ is the chemical potential, M_i is the molar mass, v_i is the partial specific volume of the i-th component (i = 1, 2), $\rho(x)$ is the density of the complex liquid at a position x, and g is the gravitational or centrifugal acceleration. The concentration (density) distribution of any species obeying Eq. (*1*) resulting from a solution to this differential equation is a kind of the Boltzmann exponential function[9,10]. According to this approach, none of sedimenting species of different molar masses (or different sizes) can focus but each exhibits its proper exponential concentration distribution.

Dynamic transport model[3,4] allowed to calculate an accurate concentration distribution of larger size focused particles in a suspension of density gradient forming smaller size particles although no *a priori* condition of the continuity of the density gradient with respect to the size of the focused species was imposed. Accordingly, the focusing of larger size particles should appear in a suspension of smaller particles even if the particle size ratio is low, as mentioned above, and it should disappear only when this ratio approaches to 1. The driving force generating the focusing phenomenon $F_\mathrm{f}(x)$ results from Archimedes principle

$$F_\mathrm{f}(x) = \left(\rho(x) - \rho_\mathrm{f}\right) v_\mathrm{f}\, g \ , \tag{2}$$

where ρ_f and v_f are the density and the volume, respectively, of the focused particles. The resulting concentration distribution of the focused species is described by[3,4]:

$$\begin{aligned} c_\mathrm{f}(x) = c_\mathrm{f}(x_{\mathrm{f,max}}) \exp\Bigg\{ & \left[\left[\frac{v_\mathrm{f}\, g \phi_{\mathrm{m,ave}} \Delta\rho_\mathrm{m}\, h}{kT\left(1 - \exp\left(-hF_{\mathrm{I,m}} / kT\right)\right)}\right]\right] \times \\ & \times \Big[\exp\left(-x_{\mathrm{f,max}} F_{\mathrm{I,m}} / kT\right) - \exp\left(-x F_{\mathrm{I,m}} / kT\right) + \\ & + \exp\left(-x_{\mathrm{f,max}} F_{\mathrm{I,m}} / kT\right)\left(\frac{F_{\mathrm{I,m}}\left(x_{\mathrm{f,max}} - x\right)}{kT}\right)\Big]\Bigg\} \ , \end{aligned} \tag{3}$$

where $\phi_{m,ave}$ is the average volume fraction of the density gradient forming (modifier) particles, $\Delta\rho_m$ is the density difference between the modifier particles and the suspending liquid, h is the height of the liquid in sedimentation cell, k is Boltzmann constant, T is the temperature, $x_{f,max}$ is the position of the maximal concentration of the focused particles, and $F_{I,m}$ is the force acting on the modifier particles in the case of the centrifugation or sedimentation in the gravitation field. The force $F_{I,m}$ is proportional to the volume of the modifier particles. As a result, Eq. (*3*) allowed to calculate the concentration distribution of the focused species as a function of the size ratio of the focused to the density modifier particles[4].

The experiments[5,6] were in good agreement with the theoretical predictions. Regardless this positive result, the dynamic transport model is based on the macroscopic approach without a possibility of a detailed insight into the microscopic scale particle–particle interactions which are at the origin of the focusing phenomenon.

A microscopic kinetic model presented here assumes the existence of a suspension of uniform size colloidal particles dispersed in a homogeneous liquid in which particle–particle collisions are frequent events. Larger uniform size colloidal particles are dispersed in this suspension. The system is exposed to the action of two physical fields of different nature. Smaller particles interact exclusively with the primary field and form an exponential concentration distribution. Larger particles interact only with the secondary field which generates constant driving force displacing larger particles in the same direction. The modifier particles are in permanent collisions with the focused particles. The force acting on the focused particle per unit area of its surface and resulting from the collisions with the modifier particles is proportional to the partial osmotic pressure of the modifier particles[11].

The equilibrium concentration distribution of modifier particles creates a partial osmotic pressure gradient which produces an unidirectional and position dependent "lift" force (generated by the collisions with the modifier particles) acting on the focused particles and displacing them to the extreme limit of the system. A spherical particle exerts the action of the force which is due to the difference between the integral osmotic pressures on the upper and lower hemispheres. By considering only the x-axis component of the osmotic pressure gradient, this "lift" force can be calculated from

$$F_f(x) = 2\pi r_f kT \left[\int_{x-r_f}^{x} n_m(x)\,dx - \int_{x}^{x+r_f} n_m(x)\,dx \right], \qquad (4)$$

where r_f is the radius of the focused particles and $n_\mathrm{m}(x)$ is the spatial distribution of modifier particles along the x-axis. The displacing "lift" force $F_\mathrm{f}(x)$ must be counteracted to yield the resulting focusing force $\mathsf{F}_\mathrm{f}(x)$ which can appear only under the condition that it is position dependent, converging, changing the sign at the position $x_\mathrm{f,max}$ and vanish at this focusing point

$$\mathsf{F}_\mathrm{f}(x) = F_\mathrm{f}(x) - F_\mathrm{II,f} \ , \tag{5}$$

where $F_\mathrm{II,f}$ is the counteracting force generated by the secondary field. Whenever $F_\mathrm{II,f} = 0$, the focused particles are unidirectionally displaced without being focused, as mentioned above.

The force $\mathsf{F}_\mathrm{f}(x)$ can be composed of three contributing forces. The "lift" force $F_\mathrm{f}(x)$ generated by the interactions of the focused particles with the modifier ones, the volume force $F_\mathrm{I,f}$ which can be generated by the primary field due to the effective bulk property of the suspending liquid (such as the Archimedes force), and the force $F_\mathrm{II,f}$ due to the secondary field

$$\mathsf{F}_\mathrm{f}(x) = F_\mathrm{f}(x) - F_\mathrm{II,f} \pm F_\mathrm{I,f} \ . \tag{6}$$

At least one of the contributing forces must be position dependent and balanced by the counteracting force at the focusing point. The long range interactions (*e.g.*, electrostatic repulsions) and, consequently, the elastic collisions among the modifier and focused species can also be effective. (see FIG. 1)

The resulting concentration distribution of the focused species based on this kinetic model is

$$c_\mathrm{f}(x) = c_\mathrm{f}(x_\mathrm{f,\,max})\exp\left\{\frac{2\pi r_\mathrm{f}\, kTc_\mathrm{m,\,ave}hf(r_\mathrm{f})}{m_\mathrm{m}\, F_\mathrm{I,\,m}\left(1-\exp\left(-hF_\mathrm{I,\,m}\ /\ kT\right)\right)}\times \right.$$
$$\left.\times\left[\exp\left(-x_\mathrm{f,\,max}F_\mathrm{I,\,m}\ /\ kT\right)-\exp\left(-xF_\mathrm{I,\,m}\ /\ kT\right)\right]+\frac{F_\mathrm{II,\,f}}{kT}\left(x_\mathrm{f,\,max}-x\right)\right\} . \tag{7}$$

Previous dynamic transport model can be considered as a special case of the kinetic model presented in this work. The principal difference consists in the fact that the main focusing force $\mathsf{F}_\mathrm{f}(x)$ in the dynamic transport model is a macroscopic volume force while the $F_f(x)$ is the surface force and the character of the forces $F_{I,f}$ and $F_{II,f}$ is not specified. It can be either a volume force (such as the Archimedes force) or a surface force (*e.g.*, electrostatic charge in electrical field) which can be effective. As a result, operational variables can have rather complex impact on the equilibrium focusing phenomenon and the whole system behaviour.

CONCLUSION

Summarizing the above, the new microscopic kinetic approach describes the concerned transport phenomena on an accurate physical basis. Although it was elaborated for two fields interacting separately and independently with two different sizes but uniform particle populations, an extension is possible to a simultaneous action of several effective fields (when applying, *e.g.*, the coupling of thermophoretic and electrophoretic effects). On the other hand, upon reduction this solution describes the action of a single field interacting with both populations (as, *e.g.*, in centrifugal isopycnic focusing).

Nevertheless, as far as only the gravitational or centrifugal field forces generate the formation of the concentration gradient of the modifier as well as the focusing of other species, a paradox between the macroscopic dynamic model and the microscopic kinetic model emerges. The question is, whether the focusing phenomenon is principally driven by volume or

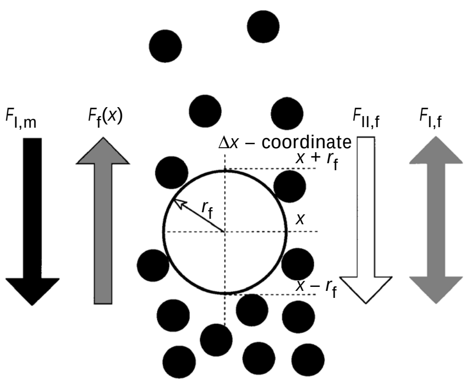

FIG. 1
Schematic representation of effective forces if a focused particle (❍) is exposed to collisions with smaller modifier particles (●). $F_f(x)$, position dependent "lift" force generated by the collisions with the modifier particles; $F_{I,m}$, primary field force acting on the modifier particles; $F_{I,f}$, primary field force acting on the focused particle; $F_{II,f}$, counteracting force generated by the secondary field acting on the focused particle only

surface forces or by a combination of both. It seems that an accurate answer in favour of only volume forces, based on macroscopic experience does not exist, on the other hand, microscopic scale experiments should, logically, support the kinetic model and the dominating role of surface forces. If future experiments confirm the hypothesis on dominating role of surface forces at least on the microscopic scale, the analytical impact of the results of the “isopycnic” focusing separations should seriously be reconsidered.

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