


# Physicochemical Mechanics and Colloid Science

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## Abstract

Suggested by us physicochemical mechanics is based on mechanical ideas simple and intuitive unifying approach to describe all major laws of equilibrium and nonequilibrium thermodynamics including kinetics of elementary chemical reactions far from equilibrium. In this paper we suggest a new equation for chemical transport that generalizes the equilibrium Gibbs-Duhem equation. Using physicochemical mechanics we further demonstrate how it is possible to derive many classical equations of colloid science, including the Gibbs adsorption isotherm, the relationship between surface energy and curvature, the Young-Laplace equation, Kelvin's equation for partial vapor pressure above a curved surface, the Ostwald equation describing the solubility of solid particles in liquid, the Gibbs-Thomson equation describing the increase of boiling temperature as a function of curvature, the Clausius-Clapeyron equation for vaporization, sublimation and fusion, Rehbinder's effect for materials mechanics, the relation of the applied electric potential with the surface tension and the Lippmann and Frumkin electrocapillary equations. In all cases, we use the same mobility suggested by Einstein to describe Brownian motion. Now, based on mobility or the rate of any one transport process, using known molecular constants we can calculate the rates of all other transport processes and their equilibrium without additional experiments and computer simulations.

**Keywords:** Physicochemical mechanics; Equilibrium and nonequilibrium thermodynamics; Colloid phenomena fundamentals; Mobility

## Introduction to Physicochemical Mechanics

As is clear from its name, Gibbs equilibrium thermodynamics deals with equilibrium states, initial and final, therefore it does not tell how fast equilibrium is reached. Time is not present as a variable in equilibrium thermodynamics [1]. Linear nonequilibrium thermodynamics is based on the rate of entropy production, and its main postulate tells that not far from equilibrium the flux is a linear function of so-called "thermodynamic forces" [2]. These "forces" have different units, not Newtons and cannot be added. As a result, it is not a trivial task to derive classical equilibrium relations. The major achievement of nonequilibrium thermodynamics is the statement known as the Onsager reciprocity relation. According to it, if there are several fluxes  $i$  driven by the same set of thermodynamic forces  $j$ , in the matrix of equations describing all fluxes mutually symmetric phenomenological coefficients in front of the forces are equal, i.e.,  $L_{ij} = L_{ji}$  [3,4]. When  $i \neq j$ , nonsymmetrical coefficients  $L_{ii}$  and even their signs are often not known.

Previously we suggested another approach, which we call physicochemical mechanics. This approach is based on well-known mechanical principles and suggested by Einstein mobility. It allows for a simple derivation of all major classical physicochemical equations, both for the rates of transport processes, and their equilibrium [5]. It easily leads to the Onsager reciprocal relations, and it also gives the relation of all phenomenological transport coefficients [6]. Moreover, far from equilibrium it leads to equations similar to the theory of the activated complex for elementary chemical reactions [7]. Chemical transport is often driven by one driving factor such as concentration, pressure, voltage, etc. Specifics of colloid processes are that they may be driven by three additional driving factors, such as gradients of surface tension, specific molar surface and even curvature. In this paper we briefly remind the reader of the major ideas of physicochemical mechanics and then we demonstrate how to use it in the derivation of major equations of colloid science, which has not been done before.

According to the Newton's second law, acceleration of a moving body of  $i$ -th type driven by  $j$  forces is described by  $m_i \mathbf{a}_i = \sum_j \mathbf{F}_{ij}$ . Dealing with molecules, it is convenient to use molar concentration  $c_i$  (mol/L), so that each of the terms  $\mathbf{F}_{ij}$  is a molar force with the same units of Newton/mol. In a condensed system there is also a friction force. It has the direction opposite to the sum of the other forces, and usually it is proportional to velocity, which is known as Stokes' law,  $\mathbf{F}_{friction} = -k_i \mathbf{v}_i$ . Transport very quickly reaches the steady state where the friction force balances the total of the other forces, and thus  $\mathbf{a}_i = 0$ , and  $\mathbf{v}_i = \frac{1}{k_i} \sum_j \mathbf{F}_{ij}$ .  $k_i$  is proportional to viscosity and depends on body's size and shape. The flux of many particles of the same type with the units of mol/area  $\times$  time is  $\mathbf{J}_i = c_i \mathbf{v}_i = \frac{c_i}{k_i} \sum_j \mathbf{F}_{ij} = U_i c_i \sum_j \mathbf{F}_{ij}$ . Thus, it is the flux, and not the acceleration, which is proportional to the total acting force.

All  $j$  terms in the total force are multiplied the same mobility coefficient  $U_i$ , suggested by Einstein to describe Brownian motion. It is inversely proportional to viscosity and may be interpreted as the velocity per unit of molar force. Taking each of these  $j$  terms separately leads to related transport equations. For example, the flux (mol/cm<sup>2</sup>sec) in the  $x$ -direction of an ion with the molar charge  $\bar{q}_i$ , driven by a gradient of an electric field  $d\psi/dx$ , is  $\mathbf{J}_i = -U_i c_i \bar{q}_i d\psi/dx$ . This relation is the differential form of Faraday's law, and the molar electric force is  $\mathbf{F}_{ie} = -d(\bar{q}_i \psi)/dx$ , i.e., the negative gradient of molar electric energy. Positive ions move towards the decrease of electric potential. In its turn, an electric current density due to this ion is  $I_i = \mathbf{J}_i \bar{q}_i = -U_i c_i \bar{q}_i^2 d\psi/dx$ , which is the differential form of Ohm's law and electric conductivity due to each ion in the solution is  $U_i c_i \bar{q}_i^2$ .

Classical thermodynamics gives the relation of changes of chemical potential and molar entropy. At constant temperature it is  $d\mu_i(x) = -Td\bar{s}_i(x)$  [1] and after substitution we have well-known  $\mathbf{J}_i = U_i c_i T d\bar{s}_i(x) = -U_i c_i d\mu_i/dx$  [5]. Thermal Brownian motion is important for molecules and the total driving molar force is  $\mathbf{F}_{ist} = d(\bar{s}_i T)/dx = \bar{s}_i dT/dx + T d\bar{s}_i/dx$ . Thus we can talk about both thermal and entropic forces. Any molecule without additional driving factors moves towards increase of molar entropy  $\bar{s}_i$ , so we do not need a minus sign in this expression. In the ideal solution, the molar entropy changes as  $-R \ln c_i$ , and  $\mu_i = \mu_{0i} + RT \ln c_i$ , where  $\mu_{0i}$  is the standard chemical potential of  $i$ -th component. In isothermal conditions after substitution this gives not only Fick's law  $\mathbf{J}_i = -RTU_i dc_i/dx$ , but also the Einstein relation of mobility and diffusion coefficient:  $D_i = RTU_i$ . Note that even for ideal gases, the molar entropy depends on temperature [1]. Because of that if the process is not isothermal, and temperature also is a function of coordinate, transport equations become more complicated, but this explains the much less understood phenomenon of thermos diffusion [8].

For one component in non-isolated system instead of traditional chemical potential we may introduce more general physicochemical potential  $\mu_{gi}$  such as:  $d\mu_{gi} = d\mu_{fi} + \bar{v}_i dP - \bar{s}_i dT - T d\bar{s}_i$ . The additional terms included into  $\mu_{fi}$  are due to external fields (e.g.,  $\bar{q}_i \psi$  with molar charge  $\bar{q}_i$ ) plus all other driving factors, but excluding pressure and temperature. Molar volume  $\bar{v}_i$  is usually constant and  $d\bar{v}_i = 0$ . In a simple case for ions only concentration

and electric field are important, and other driving factors including temperature are constant. Based on previous analysis the flux of one component will be

$$\mathbf{J}_i = -U_i c_i d\mu_{gi}/dx = -U_i c_i \frac{d\mu_{fi} + \bar{v}_i dP - \bar{s}_i dT - T d\bar{s}_i}{dx} \quad (1)$$

It includes entropy-related and fields-related terms. Thus, we see that suggested previously and based on physicochemical potential approach [5] is closely related to molar entropy-based description. Each term in the nominator of equation 1 has units of molar energy and its negative derivative over coordinate has the units of force. In most common cases the energy components may be presented as a product of an intensive molar property by an extensive variable, such as constant molar charge by electric potential or constant molar volume by pressure. The situation is more complicated for a product molar entropy by temperature. In the presence of temperature gradient molar entropy also is a function of coordinate and the two last terms describe thermal and entropic forces.

Now consider transport driven by two driving factors simultaneously, for example, by a concentration gradient and the gradient of electric field. Without equilibrium, the molar transport driven by the gradients of chemical and electric potentials may be presented as  $\mathbf{J}_i = -U_i c_i d\mu_i/dx - U_i c_i \bar{q}_i d\psi/dx$  and the expression for electric current is  $I_i = \bar{q}_i \mathbf{J}_i = -U_i \bar{q}_i c_i d\mu_i/dx - U_i c_i \bar{q}_i^2 d\psi/dx$ . It is easy to see that the transport coefficients in front of  $d\psi/dx$  in the first equation, and in front of  $d\mu_i/dx$  in the second equation are equal, i.e., they follow Onsager reciprocity relations. The same is valid for symmetric coefficients for other fluxes carried by the species with the same mobility,  $L_{ij} = L_{ji}$ . All transport coefficients are equal to the product of mobility, concentration and conjugated to the driving force molar property, such as molar charge for electric field- and molar volume for pressure-driven processes. Usually, these molar properties are known and this means that if we measure one transport coefficient, we can easily calculate mobility and all other coefficients for the same species. Simultaneously it becomes clear that if fluxes of different properties are carried by different species with different mobility, such as molecules, ions and electrons, the Onsager relations are not necessarily valid for multicomponent diffusion [6].

In simple equilibrium, the two fluxes due to two driving factors should balance one another. For concentration and potential gradients this means  $-U_i c_i \bar{q}_i d\psi/dx = RTU_i dc_i/dx$ . After integration this leads to the Nernst equation describing the relation of electrode potential and concentration. All terms of transport equations are proportional to the same mobility, which disappears in equilibrium expressions. A similar approach may be used for any pair of driving forces. As a result, we were able to suggest a table, summarizing all transport and equilibrium equations for different pairs of major driving factors [5]. Similar analysis may be used for several driving factors acting simultaneously.

### Transport and inversed Gibbs-Duhem equation

The variables held constant in a process are termed the natural variables. With adequately chosen natural variables related

thermodynamic functions decrease in a spontaneous process. For example, Gibbs free energy  $G$  has natural variables  $T$  and  $P$ . It is easy to control temperature and pressure, which makes  $G$  an especially valuable function, which decreases in isobaric-isothermal processes in an isolated system. In the presence of electric and other fields, including pressure and temperature gradients, for multicomponent system we may introduce a new general function,  $G_g$ , such as  $G_g = E + \sum_i \mu_{fi} N_i + PV - TS$ . Internal energy  $E$  does not change for transport without chemical reactions. The complete differential  $G_g$  for transport is

$$dG_g = \sum_i \mu_{fi} dN_i + \sum_i N_i d\mu_{fi} + PdV + VdP - TdS - SdT \quad (2)$$

In transport the role of intensive natural variables and their conjugated molar properties changes to the opposite in comparison to chemical processes. It is possible to apply a pressure gradient, temperature gradient, or electric field to a solid membrane and observe chemical transport, though extensive system volume or charge of transported ions do not change. To describe transport in space, we need only a part of equation 1 with differentials of intensive variables, i.e.,

$$dG_g = \sum_i N_i d\mu_{fi} + VdP - SdT \quad (3)$$

In addition, transport leads to changes of local concentrations, and it means local entropy. Thus, the correct equation should have an additional term  $-TdS$ :

$$dG_g = \sum_i N_i d\mu_{fi} + VdP - SdT - TdS \quad (4)$$

Together with the previous equation this means that

$$\sum_i \mu_{fi} dN_i + PdV = 0 \quad (5)$$

After comparison with the complete differential (equation 1), this equation simply tells that the changes of composition due to  $dN_i$  lead to changes of volume and *vice versa*. There is no contradiction between this and the well-known for chemical thermodynamics Gibbs-Duhem equation  $\sum_i N_i d\mu_i - VdP + SdT = 0$  because the first is the result of a  $G_g$ -related vectorial transport process and the second describes equilibrium of internal scalar chemical processes.

### Derivation of basic equations of colloid chemistry

The possibility of using conventional non-equilibrium thermodynamics for interfaces is not obvious, which was recognized by Prigogine [9] and later in [10]. We suggest adding an additional term to physicochemical potential, which is the product of effective local surface tension  $\sigma$  by molar surface area  $\bar{a}$ . The specifics of interface processes are that both the gradients of surface tension and curvature may be driving factors. In addition, in some processes  $\bar{a}$  also may change. All these factors may be easily included in physicochemical mechanics-based description. For simplicity we neglect possible hydrodynamic effects, and assume that heat transport does not change the temperature distribution, though both these effects may be important for colloid systems [11-13]. If all other driving factors are also constant, the rate of lateral transfer of an adsorbed component due to the gradient of surface tension should be

$$J = -Uc\bar{a} \frac{\partial \sigma}{\partial x} \quad (6)$$

Here  $c$  is local concentration near the surface.

It is easy to describe the equilibrium of processes driven by surface tension and any other driving factor, such as concentration, pressure, electric field and temperature. In the first case, balance with the described by Fick's law flux if curvature and molar surface area  $\bar{a}$  is constant gives

$$\ln \frac{c_2}{c_1} = -\frac{\bar{a}\Delta\sigma}{RT} \quad (7)$$

This equation can be rewritten in a differential form, known as Gibbs adsorption isotherm:

$$-\frac{cd\sigma}{RTdc} = \frac{1}{\bar{a}} = \Gamma \quad (8)$$

Here  $\Gamma$  is the surface concentration.

For a pair pressure and surface tension as driving factors at equilibrium

$$\bar{a}d\sigma / dx = -\bar{v}dP / dx \quad \text{and} \quad \frac{d\sigma}{dP} = -\frac{\bar{v}}{\bar{a}} = -\bar{v}\Gamma \quad (9)$$

After integration for a spherical droplet with radius  $r$  this gives an analog of Young-Laplace equation [12]:

$$\Delta P = -\frac{\bar{a}\Delta\sigma}{\bar{v}} = -\frac{2\Delta\sigma}{r} \quad (10)$$

For a droplet of arbitrary shape, one has to use a tensor-based description with three coordinates [13]. In this case one could introduce invariants of a tensor, i.e., scalar functions of the tensor components which remain constant under a basis change. This invariant has the same value when computed in two arbitrary bases, a Cartesian and some other basis. A symmetric second order tensor always has three independent invariants, but they do not help analysis of transport in condensed systems where pressure and external forces depend on coordinate.

Adsorption of a surface-active substance and its subsequent penetration decreases  $\sigma$  on the surfaces of solid granules and in preexisting minor cracks inside the solid. This leads to smaller inter-particle interactions, disjoining pressure and finally, reduces the material's mechanical strength. It is even possible to break a wedding gold ring simply by covering it with thin films of Hg. This mechanical phenomenon induced by physicochemical interactions is known as the Rehbinder's effect, who also called it physicochemical mechanics [14]. Similar description is valid for a balance of surface tension and gravity. Onboard the International Space Station the weightless water can form big floating drops and even films/membranes, which are stable inside a wire ring for many hours.

Balance of surface tension and electric potential gives the Lippmann equation, usually used to analyze an electric double layer and electrocapillary maximums

$$\frac{\partial \sigma}{\partial \psi} = -\frac{\bar{q}_i}{\bar{a}_i} \quad (11)$$

In a solution we have  $q_i = c_i \bar{q}_i = c_i z_i F$ . For electrocapillary phenomena  $\bar{q}_i$  is generated by one ion charge of unit surface and  $\psi$  - its electric potential. Changes in applied electric potential lead to the changes of surface tension, and the negative slope reaches its zero maximum when the surface charge is zero. This zero-



charge potential is an essential characteristic of electrode kinetics, especially for polarography with dropping mercury electrodes.

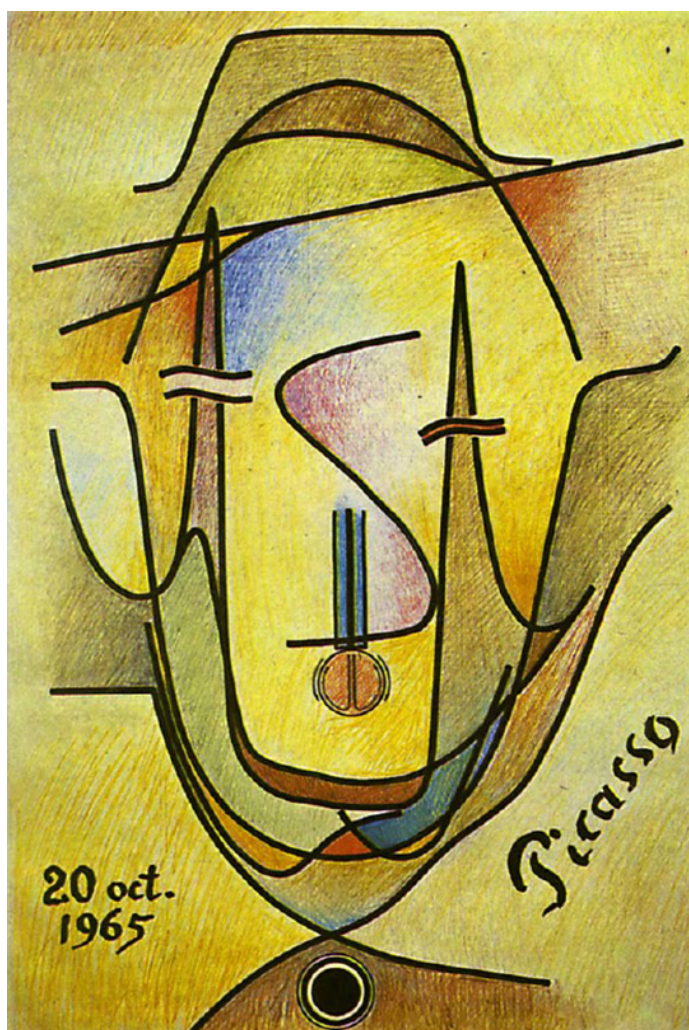
When  $\bar{a}$  changes at constant  $\sigma$ , balance of surface curvature effects and electrical forces is described by

$$\frac{d\psi}{d\bar{a}} = -\frac{\sigma}{zF} \quad (12)$$

Further, we will consider major processes due to the surface curvature when the surface tension is constant. After integration for a sphere, we have

$$\psi_2 - \psi_1 = -\frac{2\sigma\bar{v}}{zF} \left( \frac{1}{r_2} - \frac{1}{r_1} \right) \quad (13)$$

Changes in electric potential with size play a crucial role in colloid stability, nanoparticle electro-separation, electrocapillary effects and polarography with dropping mercury electrodes. In a multicomponent system where noncharged species  $j$  may be also adsorbed on the surface, we should talk about reversible work  $dA$  to increase surface area by one unit. In this case in equilibrium, we have a balance of three driving factors, and  $dA = -q_i d\psi - \frac{q_i}{z_i F} d\mu_i - \sum_j \Gamma_j d\mu_j$ .  $z_i F$  and  $\mu_i$  are molar charge and chemical potential for surface charges of one type. This suggested by Frumkin (Figure 1) equation is useful in description of electrocapillary phenomena and adsorption of molecules on charged surfaces [15].



**Figure 1:** A la Picasso portrait of A. N. Frumkin, made by his pupil O. Petrii and R. Marvet at Lomonosov Moscow State University, electrochemistry department. All major curves and a capillary with mercury drop are taken from Frumkin's electrochemical papers.

Here we should mention that electrophoresis of colloid particles is described based on electrophoretic mobility  $U_e$ , which is the particle velocity for a field strength 1 volt/cm. In this case an assumption that an electric force is balanced by viscous drag force described by Stokes equation leads to the Hückel equation

$$U_e = \frac{2}{3} \frac{\epsilon \zeta}{\eta} \quad (14)$$

Note that when electrophoretic mobility is presented as a function of  $\zeta$ -potential, it does not explicitly depend on the particle size, which is different to Einstein's mobility. The coefficient is not necessary  $2/3$  and it is sensitive to particle shape and double layer thickness [12].

In general, it is the ratio  $2\sigma/r$ , which plays the role of a driving factor for a sphere. In this case, small changes  $\delta$  of this ratio are

$$\delta(2\sigma/r) = \frac{2}{r} \delta\sigma - \frac{2\sigma}{r^2} \delta r \quad (15)$$

The flux due to the changes of  $r$  should be proportional to  $-U\bar{c}\frac{2\sigma}{r^2}$ . A species has higher energy on the surface with higher curvature and will move to the flat area. This effect is essential for transport along nonhomogeneous and bent bio-membranes. For a flat surface, the curvature  $1/r$  is zero, and the flux disappears. In equilibrium, this flux must be counterbalanced by concentration-driven flux. After substitution into two expressions for fluxes mobility cancels giving

$$RT \frac{dc}{dr} = \frac{2\sigma\bar{c}}{r^2} \quad (16)$$

Integration from  $r$  to  $\infty$  using partial pressure for vapor instead of concentration (at equilibrium they are proportional) gives Kelvin equation for partial vapor pressure above the curved surface:

$$RT \ln \frac{p_r}{p_\infty} = \frac{2\sigma\bar{v}}{r} \quad (17)$$

A similar equation, known as the Ostwald equation, describes the solubility of solid particles in liquid. The plus sign refers to a convex surface, while a concave surface should have the minus sign. For a pair pressure and temperature as driving factors at equilibrium we have Clausius-Clapeyron equation  $\frac{dP}{dT} = \frac{Q_L}{T\Delta v} = \frac{\Delta s}{\Delta v}$ . The equation describes the relation of pressure and temperature along the coexistence curve of two phases. The process can be vaporization, sublimation, fusion, or transition between two solid phases of a pure substance. Here  $dP/dT$  is the slope of the tangent to the coexistence curve at any point,  $Q_L$  is the specific latent heat,  $\Delta v$  is the specific volume change for the phase transition, and  $\Delta s$  is the specific entropy change of the phase transition.

Balance surface structure gradients and surface effects is essential for evaporation or condensation through the drop surface. If molar entropy and temperature gradient does not change with time, the rate of mass transfer from the liquid phase to vapor is:

$$J_{\bar{s}} = U\bar{c}\bar{s} \frac{dT}{dr} \quad (18)$$

In equilibrium it is balanced by the surface tension-driven flux, which gives

$$-\bar{s} \frac{dT}{dr} = \frac{2\sigma\bar{v}}{r^2} \quad (19)$$

At constant surface tension and using the approximate relation  $\bar{s} = \Delta H_{vap}/T$ , after integration from initial  $r$  to  $\infty$  and from  $T$  to the boiling temperature  $T_b$ , we have an analog of the Gibbs-Thomson equation describing the increase of boiling temperature as a function of curvature:

$$\ln \frac{T_b}{T} = \frac{2\sigma\bar{v}}{\Delta H_{vap} r} \quad (20)$$

A similar equation describes the melting point decrease for nanocrystals or crystals in pores. If the surface tension changes with  $r$ , which is also important for nanomaterials, we can use an approximate relation

$$\bar{a} \frac{d\sigma}{dr} = \bar{s} \frac{dT}{dr} \quad (21)$$

In equilibrium,

$$\frac{d\sigma}{dT} = \frac{\bar{s}}{\bar{a}} = \Gamma\bar{s} \quad (22)$$

giving a simple method to measure molar entropy  $\bar{s}$ .

## Conclusion

Albert Einstein in Herbert Spencer Lecture, "On the Method of Theoretical Physics", given in Oxford, June 1933, wrote: "The supreme goal of all theory is to make the irreducible basic elements as simple and as few as possible." Later in 1936, the paper "Physics and Reality" he wrote: "The whole of science is nothing more than a refinement of everyday thinking" [16]. Here we demonstrated that a few simple ideas from physicochemical mechanics lead to many well-known classical laws of colloid chemistry and related transport processes. One does not have to memorize many different laws. It becomes possible not only to easily derive them but also see their interrelations. More specific examples of other applications in colloid chemistry, including kinetics of colloid coagulation and micelle extraction, phase rule in the presence of fields, kinetics of the first order phase transitions and formation of a new phase embryos and kinetics of the second order phase transitions and critical phenomena are described in our book [17].

Suggested by Einstein to explain Brownian motion mobility and forces-based physicochemical mechanics give well-known and experimentally proven equilibrium equations in colloid science. This shows that the same mobility applies to the volume near the surface and surface processes. If the proportionality coefficient were different in front of the gradients of different driving factors, we would not get the correct equations for equilibrium states. Based on the rate of just one transport process we can calculate mobility, and then, using molecular constants we can calculate the rates of other transport processes without experiments and computer simulations.

## Declaration of Interest

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