

Anomalous field-induced particle orientation in dilute mixtures of charged rod-like and spherical colloids

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Charged colloids in aqueous suspension often reconfigure counter-intuitively in the presence of an external electric field^{1–7}. Despite decades of substantial theoretical effort, a clear understanding of such electrokinetic phenomena is only available for the electric polarization and migration of diluted spheres in low fields⁸. The interpretation of the electric response of charged rod-like particles is far less advanced. Here we report that diluted rod-like particles suspended in a sea of smaller spherical particles having similar charge align perpendicular to the external electric field. This ‘anomalous’ orientation, which contradicts the notion that charged rods in dilute suspensions always align parallel to external electric fields⁹, seems to be universal in dilute mixtures of charged rod-like and spherical colloids. The dependence of the perpendicular orientation on frequency and particle charge, size and concentration indicates the presence of field-induced asymmetric crowding of spherical particles around each rod, which gives rise to asymmetric electro-osmotic flows that induce a negative torque.

Rod-like colloids made of homogeneous isotropic materials whose conductivity and/or dielectric constant differ from those of the suspending medium, orient their longest axis along external electric fields. Apart from hydrodynamic contributions certainly present at low frequencies in the case of dispersions of charged particles¹⁰, the orientation is explained by basic electrostatics and appropriate boundary conditions where the particles’ surface charge is mapped onto an effective conductivity^{11,12}. As the field is turned on, free (and/or polarization) charges accumulate on the particle–solvent interface, thus making the particle’s dipole moment grow, either in the direction of the field or opposite to it. The growth proceeds until the fields produced by the accumulated charges counterbalance the conduction (and/or dielectric) mismatch between interior and exterior of the particle, yielding continuous free-charge currents (and/or electric displacement) across the interfaces. As the charges on the interface in the parallel configuration are on average farther apart from the particle interior than in the perpendicular configuration, they produce a weaker internal field and a stronger external field.

Hence, the dipole required to sufficiently decrease the internal field in highly conductive particles, such as charged colloids, is larger for parallel alignment, which is thus energetically favoured. A dual argument applies when the particle’s conductivity (and/or dielectric constant) is lower than the solvent, demonstrating that parallel alignment always minimizes the electric energy. So far, the only exceptions to the expected parallel orientation in colloidal rods are found at high particle concentrations^{1,2}. However, as reported in this paper, simple homogenous rod-like colloids with normal parallel orientation in a diluted condition show instead anomalous perpendicular orientation when spherical particles are added to the dispersion.

We studied low-field electrically induced orientation in dilute suspensions of charged rod-like ‘primary particles’ (PPs) in the presence of smaller ‘secondary particles’ (SPs) by measuring the electrically induced optical birefringence (EB) and extracting the Kerr constant spectra $B(\nu)$ (where B is the Kerr constant and ν is the frequency). We investigated bidisperse mixtures of well-studied colloids: latex rods, oxide rods and bioparticles as PPs; latex spheres, silica nanoparticles, linear polyelectrolyte coils and ionic micelles as SPs. In Fig. 1a (green line) we show a typical $B(\nu)$ spectrum of a dilute suspension of polytetrafluoroethylene (PTFE) particles, the features of which are general for all PPs investigated here. $B(\nu)$ is relatively flat up to a frequency of about 1 MHz, indicating that the anisotropy of the electric polarization of the particles, mostly due to ion-cloud polarization, is basically constant. Above 1 MHz, the field-induced orientational order decreases and reaches an asymptotic value around 200 MHz, mirroring the diminished displacement allowed the ions by the high-frequency field. In this regime $B(\nu)$ is well described by the Maxwell–Wagner theory for polarization^{8,12}. For dilute suspensions of PPs, $B(\nu)$ is always positive (with the possible exception of a small frequency interval in the megahertz range¹²) indicating that the rods are oriented with the field (Fig. 1b). The red line in Fig. 1a represents $B(\nu)$ of a solution of polystyrene spheres, showing that the SP signal is negligible with respect to the PP signal. This ratio between the relative contributions of the two EB signals is confirmed for all

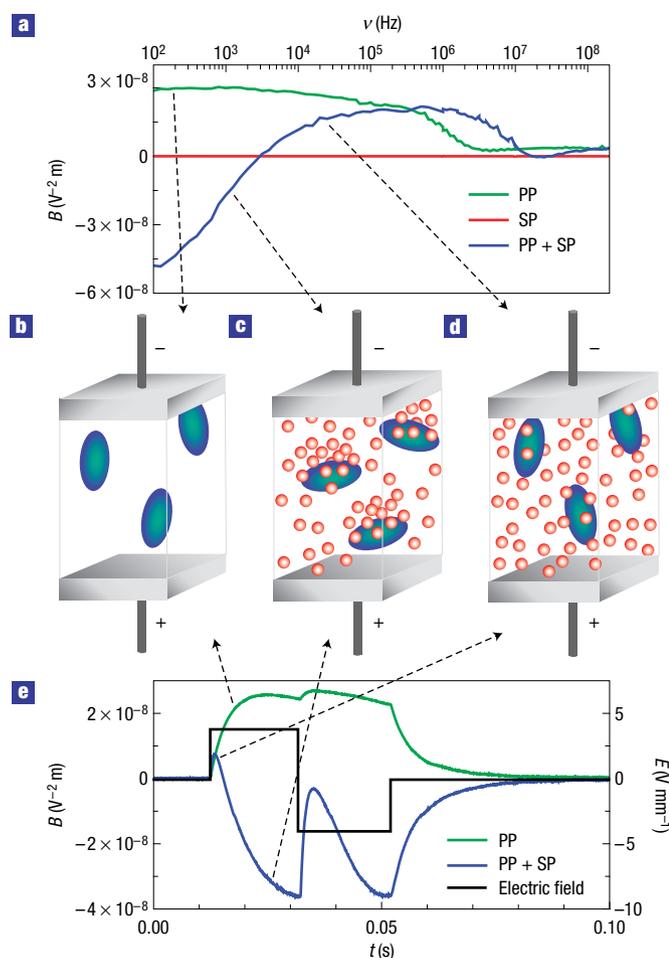


Figure 1 Normal and anomalous Kerr constant B measured as a function of frequency ν and time t for monodisperse or bidisperse mixtures of PPs and SPs. **a**, Green line: $B(\nu)$ of diluted PTFE (negatively charged, long semiaxis $b = 240$ nm, axial ratio 3, $\phi_{PP} = 0.001$). Red line: $B(\nu)$ of mildly concentrated polystyrene spherical particles, here indicated as P18 (negatively charged, $R = 18$ nm, $\phi_{SP} = 0.01$). Blue line: $B(\nu)$ of PTFE + P18 mixture ($\phi_{PP} = 0.001$, $\phi_{SP} = 0.01$). **b–d**, Schematic representation of the geometrical arrangement of rod-like PPs (blue ellipsoids) and spherical SPs (red spheres) in different conditions of frequency and mixture composition. The anomalous orientation is depicted in **c**. **e**, $B(t)$ (left axis) measured in response to an electric bipolar pulse (black line, right axis) for the same samples shown in **a**. Green line: normal behaviour (PTFE). Blue line: anomalous EB (PTFE + P18). The slight decrease of B with t at longer times when the field is on is due to electrode polarization effects.

SPs and PPs at the explored volume fractions ($\phi_{SP} = 0.005–0.05$, $\phi_{PP} = 0.0002–0.01$). However, the EB spectrum goes through a pronounced change when PPs are mixed with SPs (Fig. 1a, blue line). The large negative values of $B(\nu)$ at low frequencies indicate that the rods are oriented perpendicular to the applied field (Fig. 1c); whereas at higher frequencies the PPs recover their normal behaviour (Fig. 1d). Although most of the SPs have spherical symmetry, this is not strictly required for the anomalous effect as it is observed even when irregular silica Ludox particles or random coils were used. The sphericity of SPs better highlights the effect, as in this case the EB signal of the SPs is much lower than the signal of the PPs.

In Fig. 1e we show the time dependence of B measured when a bipolar electric pulse $E(t)$ (where t is time; black line) is applied to

the same samples shown in Fig. 1a, showing normal (green line) and anomalous response (blue line). The non-monotonicity of the anomalous $B(t)$ clearly reflects the non-monotonic behaviour of the anomalous $B(\nu)$. Of particular interest is the positive spike following the field inversion, demonstrating that whatever property is at the origin of the anomalous orientation, it is not symmetric for $E \rightarrow -E$ inversion and requires a significant time to be re-established after the field sign is changed. The transient behaviour of B after the field is turned off is due to PP rotational diffusion, and the comparison of relaxation measurements in the presence and absence of SPs confirms that the PPs are monomerically dispersed, thus ruling out the possibility that the anomaly is a result of field-induced particle aggregation.

The exploration of various PP + SP dispersions indicates the anomalous response as a universal feature of the low-frequency electric behaviour of mixtures of charged rods and spheres. The data in Fig. 2a refer to suspensions of various PPs with polystyrene SPs. Analogous results (see Fig. 2b) have been obtained by measuring solutions of the same PPs mixed with different SPs. Indeed, the only exceptions to the anomaly were found with uncharged or weakly charged SPs, for example, neutral PEO (water-soluble polyethylene oxide) or weakly charged silica nanoparticles (Ludox TMA).

The anomalous birefringence of the mixed systems cannot be ascribed to SP-mediated anisotropic interactions between the rods, such as those due to depletion forces. This is demonstrated by the perfect collapse of several $B(\nu)/\phi_{PP}$ curves measured at constant ϕ_{SP} and various ϕ_{PP} (Fig. 2c). The anomalous behaviour is definitely a property of each single rod-like PP surrounded by charged spheres.

The data obtained with PTFE PPs, whose surface charge can be controlled by means of non-ionic surfactant adsorption¹³, at the same time leaving the SP charge unaffected, are also quite insightful. As apparent in Fig. 2d, on decreasing the PP charge, both the normal positive B in the megahertz region and the anomalous response in the sub-kilohertz regime decrease, $B(\nu)$ flattening to the value expected on the basis of pure dielectric mismatches. These data unambiguously demonstrate that the low-frequency behaviour is an electrokinetic effect as much as the better understood $B(\nu)$ enhancement at higher frequencies. A similar conclusion is also suggested by the effect of ionic strength: on increasing the electrolyte concentration, the overall amplitude of $B(\nu)$ uniformly decreases without significantly affecting the main features of its frequency dependence.

A quantitative analysis of the data shows that the anomalous effect cannot be explained in terms of electric torque on the rod-like particles. Considering, for example, the data in Fig. 2c and relying on the high-frequency asymptote of B to determine the constant K , we would conclude that the anisotropy of polarizability $\Delta\alpha$ ($\nu = 1$ kHz) = -2.5 and $\Delta\alpha$ ($\nu = 1$ MHz) = 1.1 . Whereas this last value can be easily achieved and is well justified in the high-frequency Maxwell–Wagner regime^{12,13}, the former is impossible. As the polarizability of charged particles in a weakly conducting medium at low frequencies cannot be negative, $\Delta\alpha = -2.5$ implies $\alpha_{\perp} > 2.5$, corresponding to a polarizability much larger than the maximum attainable value. Indeed, given the geometry of the specific PP, and assuming maximum conductive mismatch (conductive particle in an insulator), we obtain $\alpha_{\perp,MAX} \approx 0.8$. Hence, the effects of the SPs cannot be embodied by an effective PP polarizability. This evidence, combined with the lack of $E \rightarrow -E$ symmetry, rules out SP–PP induced dipole interactions. Moreover, the anomaly found in the Kerr regime excludes a contribution to the electric torque higher than $O(E^2)$ —such as those due to $O(E)$ corrections to the local field—to the particle surface charge density or to the particle polarizability.

The frequency dependence of the anomaly is strongly non-Debye and well described by a function for the electric polarizability

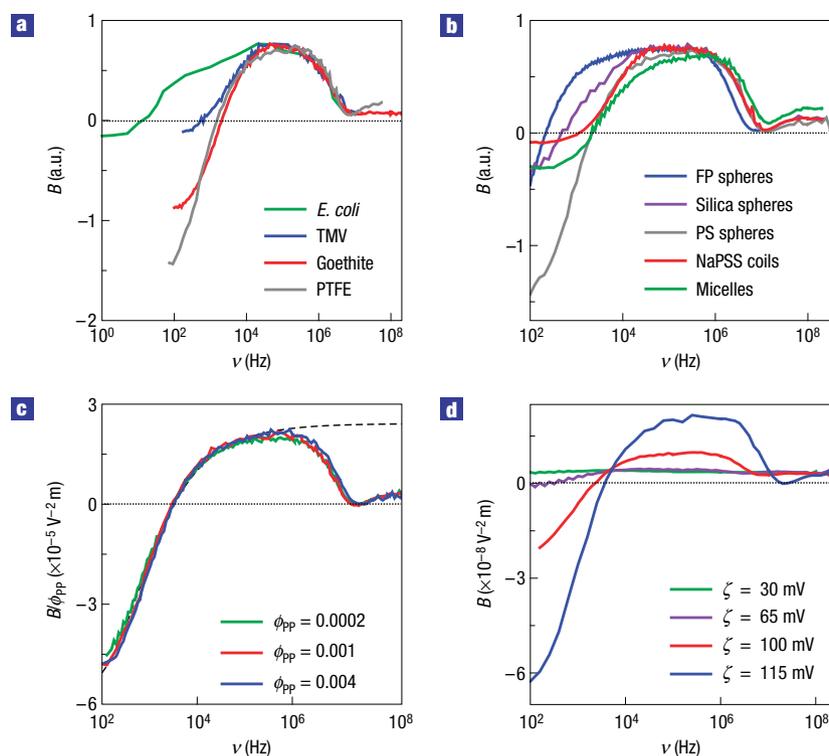


Figure 2 Kerr constant spectra for various mixtures of PPs and SPs. **a**, $B(\nu)$ of mixtures of polystyrene spherical SPs with various PPs. The SPs, here at $\phi_{SP} = 0.01$, are either negatively charged (P18, $R = 18$ nm) or positively charged (P19, $R = 19$ nm). To enable visual comparison between the spectra, data are vertically rescaled. Green line: P18 + *Escherichia coli* (negatively charged, $b = 750$ nm, axial ratio 3, $\phi_{PP} = 0.01$). Blue line: P18 + TMV (negatively charged, $b = 150$ nm, axial ratio 16.6, $\phi_{PP} = 0.005$). Red line: P19 + goethite (iron oxide, positively charged, pH = 5, $b = 625$ nm, axial ratio 10.4, $\phi_{PP} = 0.005$). Grey line: P18 + PTFE (negatively charged, long semiaxis $b = 240$ nm, axial ratio 3, $\phi_{PP} = 0.001$). **b**, $B(\nu)$ of mixtures of PTFE PPs ($\phi_{PP} = 0.001$) with various negatively charged SPs. Blue line: fluoroelastomer spheres ($R = 40$ nm, $\phi_{SP} = 0.01$). Purple line: Ludox silica particles ($R = 20$ nm, $\phi_{SP} = 0.01$). Grey line: polystyrene spheres ($R = 24$ nm, $\phi_{SP} = 0.01$). Red line: sodium polystyrene sulphonate (NaPSS) polyelectrolyte random coils (molecular weight $M_W = 18,000$, $c_{SP} = 10^{-5}$ M). Green line: micelles of sodium dioctyl sulphosuccinate (AOT) ($M_W = 444.6$, $c_{SP} = 4$ mM). An analogous anomaly has been observed with SPs of the same kind but having different radii: 20 nm fluoroelastomer spheres; 18, 30, 32 and 40 nm polystyrene spheres; 15 and 42 nm Ludox particles; and $M_W = 35,000$ and 74,000 NaPSS coils. **c**, Specific Kerr constant $B(\nu)/\phi_{PP}$ of mixtures of PTFE + P18 at fixed $\phi_{SP} = 0.01$ and variable ϕ_{PP} . Green line: $\phi_{PP} = 0.0002$. Red line: $\phi_{PP} = 0.001$. Blue line: $\phi_{PP} = 0.004$. The perfect collapse of the lines makes it hard to distinguish them. Black dashed line: fit of the low-frequency part of the spectrum by the following functional form: $B(\nu) = B(\infty) + (B(0) - B(\infty))(1 + \sqrt{2\pi\nu/\nu_c} + 2\pi\nu/\nu_c)(1 + 2\pi\nu/\nu_c)^{-1}(1 + \sqrt{2\pi\nu/\nu_c})^{-1}$ where ν_c is the characteristic frequency, $B(0)$ and $B(\infty)$ are the asymptotic values. **d**, $B(\nu)$ of mixtures of PTFE PPs ($\phi_{PP} = 0.001$) and Ludox AS30 SPs ($R = 15$ nm, $\phi_{SP} = 0.01$) at different concentration ϕ_T of non-ionic surfactant Triton X100. As ϕ_T controls the PTFE surface charge density¹³, the curves correspond to different ζ -potential of the PPs (the ζ -potential is the electric potential at the shear plane of the particle⁶). Green line: $\phi_T = 10^{-3}$ M, $\zeta = 30$ mV. Purple line: $\phi_T = 10^{-4}$ M, $\zeta = 65$ mV. Red line: $\phi_T = 10^{-6}$ M, $\zeta = 100$ mV. Blue line: $\phi_T = 0$ M, $\zeta = 115$ mV.

of colloidal charged spheres in simple electrolyte solutions given in refs 8,14. In that case the frequency dispersion is related to an accumulation of ions, both positive and negative, on one side of the particle, whereas the mean characteristic frequency ν_c is given by the diffusion time of the ions across the sphere and is typically in the range 10–100 kHz (ref. 8). Here, instead, the values of ν_c we extract by fitting the Fixman function to the anomalous part of the spectrum (as in Fig. 2c, dashed black line) are 10–1,000 times smaller and of the order of the diffusion time of a SP across a PP. These facts suggest an analogy between the asymmetric crowding of ordinary ions in the so-called ‘ α -relaxation’ in the polarization of charged spheres⁸ and the behaviour of SPs in the anomalous part of the EB spectrum, and support the concept that the negative torque is related to the crowding of SPs on one side of the rod. This notion is better explored in Fig. 3a, showing ν_c versus $a + R$ and $b + R$, the short (a) and long (b) semiaxes of the PP incremented by the SP radius (R) to account for the minimal PP–SP separation. Although no regular dependence on the rods’ long axis is found, we observe a power law dependence of ν_c on $a + R$ (with the possible

exception of the very thin tobacco mosaic virus, TMV), suggesting that the relevant phenomenon is the redistribution of the SPs across the PP short axis (as sketched in Fig. 1c). We conjecture that this asymmetric crowding of SPs around each PP is at the origin of an anomalous $O(E^2)$ hydrodynamic torque on the particles. The non-centro-symmetric ion distribution around each PP certainly affects the local counterion distribution in the PP double layer, giving rise, through counterion electromigration, to non-centro-symmetric electro-osmotic flows. These flows, typically symmetric for unperturbed PP double layers, reflect the $O(E)$ asymmetry here, yielding a hydrodynamic torque $O(E^2)$.

A further indication that the anomalous torque is rooted in complex forms of colloidal interactions activated by the presence of external fields is also given by the intriguing dependence of ν_c on the SP concentration (c_{SP}). Although c_{SP} is far too low to significantly affect SP diffusivity and dispersion viscosity, we find a strong dependence of ν_c on c_{SP} . Figure 3b shows such a dependence for PTFE + random coil polyelectrolyte mixtures, the system with the largest, and thus most accurately determined, ν_c (see Fig. 2b).

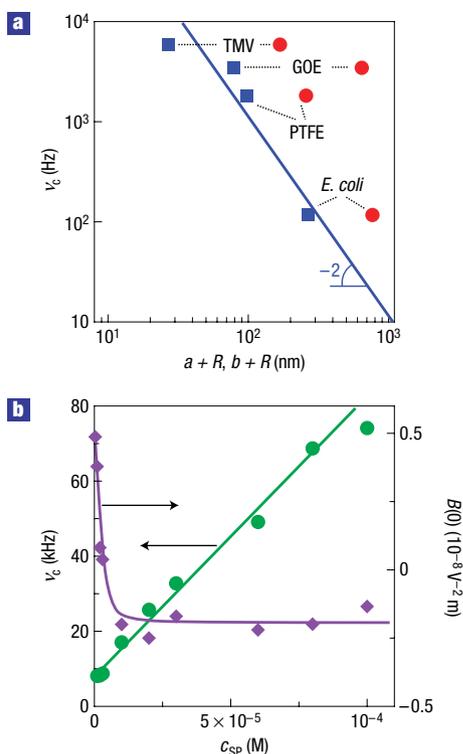


Figure 3 Characteristic frequency ν_c of the anomaly as a function of PP and SP size and concentration. **a**, ν_c as a function of $a + R$ (squares) and $b + R$ (dots), where a and b are the short and long PP semiaxes and R is the SP radius for various mixtures (TMV + P18, PTFE + P18, goethite + P19, *E. coli* + P18). Data are taken at the same conditions and concentrations as in Fig. 2a. The line represents a power law with exponent -2 . **b**, ν_c (green circles, left axis) and low-frequency asymptotic value $B(0)$ of the EB spectrum (purple diamonds, right axis), for mixtures of PTFE + NaPSS polyelectrolytes plotted as a function of NaPSS concentration c_{SP} .

We observe a remarkable increment of ν_c with c_{SP} , linearly growing from a finite low-concentration value. This behaviour indicates the existence of field-induced interactions between the SPs. In the same plot we show the low-frequency asymptote of the EB spectra, showing rapid saturation to a negative value, again in agreement with the notion of interacting SPs, hindering SP crowding at the PP surface. The strong dependence of ν_c on c_{SP} masks the dependence of ν_c on R , which seems, for constant SP volume fraction, as a quite irregular decreasing behaviour. If purely diffusive processes were at play, a $\nu_c \propto 1/R$ scaling would instead be expected.

The physical picture emerging from a combination of the various clues is basically that of a two-step process. First, as scaling and characteristic times indicate, SPs accumulate on one side of the PPs (as sketched in Fig. 1c), and rearrange on the opposite side every time the field sign is changed. This $O(E)$ accumulation is reminiscent of the behaviour of co-ions in ordinary α -relaxation and brings about SP–SP interactions. Second, as a consequence of such asymmetric SP clustering, the $O(E^2)$ electro-osmotic fluxes around the PPs are modified to give negative torque and perpendicular orientation. This is probably because of the interpenetration of SP and PP double layers resulting in a change of the electro-osmotic flow around the PPs. Although the modelling

of these phenomena requires new theoretical tools, experiments have indeed shown that electro-hydrodynamic coupling can be very relevant in the colloidal world^{4,7}. We argue that the anomalous orientation effect is a general phenomenon. The accumulation of smaller particles around larger particles and the presence of non-trivial $O(E^2)$ hydrodynamic fluxes could be ubiquitous in the electric behaviour of polyelectrolytes, although they are generally undetected because they are overshadowed by first-order field effects, such as electrophoretic mobility and electric polarization.

METHODS

The electric birefringence technique⁹ is normally exploited to evaluate the rotational diffusion coefficient of particles, macromolecules and molecular aggregates. The induced birefringence (anisotropy in the refractive index n) $\Delta n = n_{\parallel} - n_{\perp}$ is extracted from the polarization of a laser beam crossing the sample when an electric field is applied. In the absence of internal structure, $\Delta n > 0$ indicates orientation of a rod with the field and $\Delta n < 0$ signifies a perpendicular orientation. In the a.c. variant¹² of the experiment used here, the applied field consists of sine-wave pulses of zero average. We have used electric fields of rather low amplitudes ($E < 10 \text{ V mm}^{-1}$), frequency ν in the range 10 Hz–500 MHz and pulse duration long enough to allow the system to relax into a field-dependent stationary state. The measured Δn has both an oscillatory contribution (of no interest in the present context) and a stationary contribution, $\Delta n_{d.c.}(\nu)$. In low fields, $\Delta n_{d.c.}(\nu)$ is proportional to E^2 ('Kerr regime'), as expected from symmetry arguments⁹. Such proportionality has been observed in all samples and at all frequencies reported in this paper, thus enabling a meaningful extraction of the spectrum of the so-called Kerr constant, $B(\nu) = \Delta n_{d.c.}(\nu)/(\lambda E^2)$, where λ is the laser wavelength. In dilute systems, and apart from possible corrections at low frequencies due to hydrodynamic fluxes, B is proportional to the anisotropy in the particle's electric polarizability $\Delta\alpha$: $B(\nu) = K\Delta\alpha(\nu)$, where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ and K is a constant depending on the optical properties of particle and solvent.

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Competing financial interests

The authors declare that they have no competing financial interests.

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