Comment on "Anomalous Dielectric Behavior of Nanoconfined Electrolytic Solutions"

In their Letter, Zhu *et al.* [1] use molecular dynamics simulations to calculate the dielectric properties of a salt solution confined in a cylindrical nanopore. The radial and axial components of the spatially varying dielectric tensor, $\epsilon_\perp(r)$ and $\epsilon_\parallel(r)$, respectively, are computed using a linear response formalism. The correct application of this powerful method, however, requires careful consideration of the dielectric boundary conditions [2–4]—a point which unfortunately has been overlooked by Zhu *et al.* As a consequence, they derive an incorrect linear response equation for $\epsilon_\perp(r)$ [Eq. (9) of the Supplemental Material]. This casts serious doubts on their central results given in Figs. 2(b) and 2(d). The proper treatment of dielectric boundary conditions is much more than a technical subtlety: for spherical confinement or planar interfaces, it has dramatic consequences, changing $\epsilon_\perp$ by up to 2 orders of magnitude. We expect similar effects for $\epsilon_\perp(r)$ in the cylindrical geometry of Zhu *et al.*, provided that the linear response formalism is correctly applied.

We now outline the correct derivation in cylindrical coordinates. In contrast to Cartesian coordinates, the dielectric tensor expressed in cylindrical coordinates is diagonal and depends on r only. To be concise, we treat a purely dipolar liquid, noting that for ionic solutions, additional extensions become necessary [5,6]. We consider an infinitely long dielectric cylinder with radius R. A constant "external" line charge with density ρ is placed along the cylinder's axis. The resulting electric and displacement fields in the absence of the dielectric material are purely radial [7]:

$$E^{\text{ext}}(r) = \frac{\rho}{2\pi\epsilon_0 r} \quad \text{and} \quad D(r) = \frac{\rho}{2\pi r}. \quad (1)$$

Upon introducing the dielectric material, an internal (Maxwell) electric field $\Delta E^{\text{int}}(r)$ is created as the sum of the external field plus the field due to the reorientation of the molecular dipoles [8].

The relation between $E^{\text{ext}}(r)$ and $\Delta E^{\text{int}}(r)$ depends on the geometry and in our case can be obtained by considering the displacement field defined in the usual way as $D(r) = \epsilon_0 \epsilon_\perp(r) \Delta E^{\text{int}}(r)$. The displacement field is not modified by the dielectric since the purely radial field is perpendicular to any dielectric boundary [9]. Using Eq. (1) yields

$$\Delta E^{\text{int}}(r) = \frac{E^{\text{ext}}(r)}{\epsilon_\perp(r)}. \quad (2)$$

This relation between ΔE^{int} and E^{ext} is the central point that has been overlooked by Zhu *et al.*: In their attempt to derive $\epsilon_\perp(r)$, they have omitted the fact that the dielectric tensor expressed in Cartesian coordinates is not diagonal and depends on both the radial r and the azimuthal coordinate ϕ. This omission makes it impossible to express correctly the relation between E^{ext} and ΔE^{int}.

To apply linear response theory [10], we write the radial component of the local excess polarization:

$$\Delta P(r) = (\epsilon_\perp(r) - 1)\epsilon_0 \Delta E^{\text{int}}(r) = \frac{(\epsilon_\perp(r) - 1)}{\epsilon_\perp(r)} \frac{\rho}{2\pi r}. \quad (3)$$

Next, the polarization is evaluated as a phase space average [10] denoted by $\langle \ldots \rangle_\rho$ in the presence of the external charge

$$\langle P(r) \rangle_\rho = \frac{\int d\vec{r}^N P(r) e^{-\beta[H + W(\rho)]}}{\int d\vec{r}^N e^{-\beta[H + W(\rho)]}}, \quad (4)$$

where H is the Hamiltonian of the dielectric without the line charge and $W(\rho)$ denotes the energy of the dielectric in the field of the line charge. Linearization for small ρ gives

$$\langle P(r) \rangle_\rho \approx \langle P(r) \rangle_0 - \beta\rho\left(\left\langle P(r)\frac{\partial W}{\partial \rho}\right\rangle_0 - \langle P(r)\rangle_0 \left\langle\frac{\partial W}{\partial \rho}\right\rangle_0\right), \quad (5)$$

where $\langle \ldots \rangle_0$ denote averages in the absence of ρ. The dielectric energy W of a cylinder portion having length L (the simulation box) is given by [10]

$$W = -\int_V P(r) E^{\text{ext}}(r) dV = -\frac{L\rho}{\epsilon_0}\int_0^R P(r) dr. \quad (6)$$

Using Eq. (6) in Eq. (5) and equating $\langle P(r)\rangle_\rho - \langle P(r)\rangle_0$ with $\Delta P(r)$ from Eq. (3) yields the correct linear response formula for a cylindrical geometry

$$\frac{\epsilon_\perp(r) - 1}{\epsilon_\perp(r)} = \frac{2\pi\beta rL}{\epsilon_0}\left(\left\langle P(r)\int_0^R P(r')dr'\right\rangle_0 \right.$$
$$\left. - \langle P(r)\rangle_0\left\langle\int_0^R P(r')dr'\right\rangle_0\right), \quad (7)$$

which should be used instead of Eq. (9) in Ref. [1]. The key feature of this new equation is that it connects the polarization fluctuations with the fraction $(\epsilon_\perp - 1)/\epsilon_\perp$, which is a direct consequence of the aforementioned relation between ΔE^{int} and E^{ext}. In planar geometries, this same relation leads to drastic effects on the local dielectric constant [3,4], thus emphasizing the need for a correct treatment of dielectric boundary conditions.

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[8] In line with Zhu *et al.* we use Δ to emphasize that we require only the excess quantities due to an external field and not the static electric field caused by the intrinsic orientation of the interfacial molecules which is present even without an external field.

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