Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information to:

Dielectric response of confined water films from a classical density functional theory perspective

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Unless specified, references to equations and figures correspond to those of the text.

I. LINEAR RESPONSE EXPRESSION OF $\epsilon_\perp(z)$, EQS. 9-12

For small perturbing fields such that the linearisation in eq. 5 applies, the minimisation of the polarisation functional in eq. 8 for a fixed $n(z)$ yields

$$\int dz_2\, \chi_0^{-1}(z_1, z_2)\, P(z_2) = \alpha_d E_0(z_1) \tag{1}$$

with

$$\chi_0^{-1}(z_1, z_2) = \frac{1}{n(z_1)}\delta(z_{12}) - \frac{1}{3}c_L(z_{12}) \tag{2}$$

which gives by inversion the linear response formula 9 relating the polarisation to the external field. Classically, after decomposition of the susceptibility in a self and distinct contribution as in eq. 11, writing

$$\int dz_3\, \chi_0^{-1}(z_1, z_3)\chi_0(z_3, z_2) = \delta(z_{12}) \tag{3}$$

is equivalent to solving the following inhomogeneous Ornstein-Zernike-like integral equation for h_L knowing c_L[1]

$$h_L(z_1, z_2) = c_L(z_{12}) + \frac{1}{3}\int dz_3\, c_L(z_{13})n(z_3)h_L(z_3, z_2) \tag{4}$$

The dependence of the ideal part of χ_0^{-1} in the local density $n(z_1)$ makes that both χ_0 and h_L depend on z_1 and z_2 rather than just z_{12}.

A few remarks are worth mentioning here:

1) Even though the c-function $c_L(z_{12}$ appearing above in the inverse susceptibility is that of the bulk, the pair distribution $h_L(z_1, z_2)$ that follows from the OZ inversion is not the bulk one; it depends on both z_1 and z_2, not on z_{12} only. The fact that the presence of boundaries modifies the fluid response function with respect to the bulk and makes it depend on the two bodies positions rather than only on their relative distance is familiar to inhomogeneous OZ approaches. This fact was also brought up by David Chandler using a Gaussian field theory of fluids with excluded volumes[2], and his findings were further interpreted in a classical DFT framework[3]. Using the bulk $h_L(z_{12})$ may turn out to be a reasonable approximation, especially with a smooth, coarse-grained $n(z)$ as input as done in Ref.[4]. It relates to the inverse dielectric approximation proposed by Vorotyntsev *et al.*[7].

2) The inhomogeneous fluid density $n(z)$ does enter in eq. 12 at two places; the first one indicates that the local response function should be zero where there is no particle, $n(z) = 0$. The second one excludes the nonlocal contribution to the polarisation response coming from region where the density

is zero, $n(z_2) = 0$. This nonlocal cut-off effect on the polarisation response near the boundaries was pointed out recently by Olivieri *et al.*[5]. It is contained in the field theoretical approach of Monet *et al.*[4].

3) Following the behaviour of $c_L(z_{12})$ that is short-ranged (see Fig. 1), $h_L(z_1, z_2)$ is also short-ranged, and the influence of the walls is expected to be short-ranged too. The bulk value of $f(z)$ and $\epsilon_\perp(z)$ should thus be reached after only a few particle diameters from the walls.

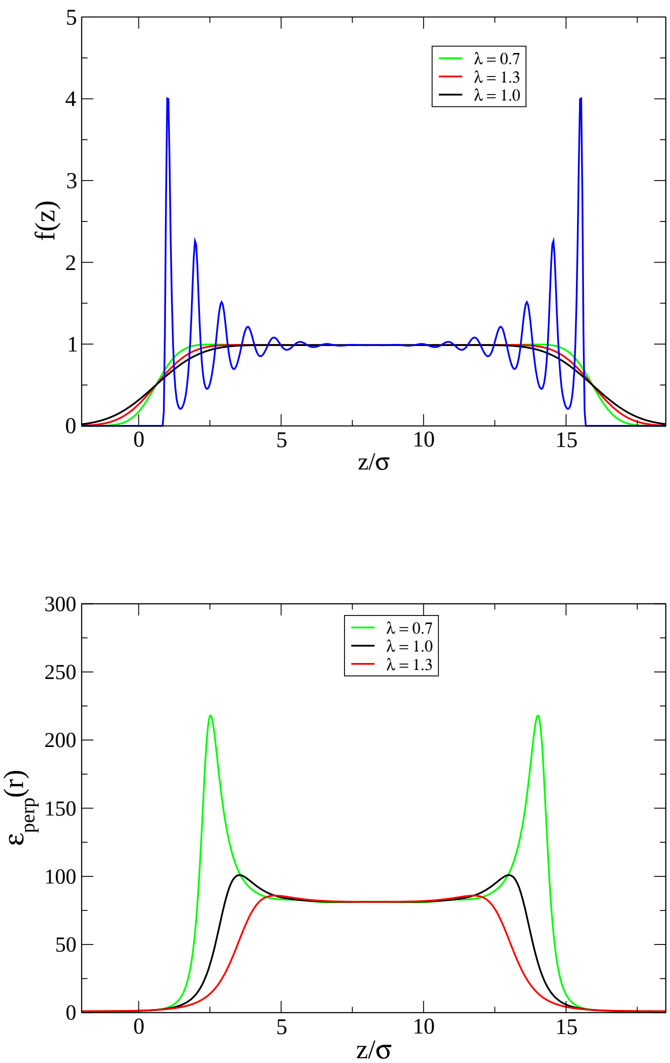

Figure 1. Top: Microscopic polarisation of the Stockmayer fluid in a slab of width $h = 50\,\text{Å}$ (in terms of the response function $f(z) = 4\pi P(z)/E_0$) (blue curve) and its coarse-grained equivalents obtained with different coarse-graining lengths $\sigma_P = 0.7, 1.0, 1.3\,\text{Å}$ (green, black and red curves, respectively). Bottom: Same for the coarse-grained dielectric constant $\tilde{\epsilon}_\perp(z)$.

II. INFLUENCE OF THE COARSE-GRAINING LENGTH σ_P

As noted in the text when introducing the coarse-grained polarisation $\tilde{P}(z)$, the coarse-graining length σ_P should not be considered as fundamental quantity, but rather as an observation length scale. To keep a microscopic character in our analysis, we suggest to take σ_P large enough to smooth the spurious behaviour of $\epsilon(z)$, but small enough keep its overall behaviour unchanged in particular the value at which the bulk value is reached. The influence of parameter $\lambda = \sigma_P/\sigma_{LJ}$ is illustrated in Fig. 1 of this SI for the Stockmayer fluid in a 50 Å slab. Both the coarse-grained polarisation (in terms of the coarse-grained response function $\tilde{f}(z) = 4\pi\tilde{P}(z)/E_0$) and the coarse-grained dielectric constant $\tilde{\epsilon}_\perp(z)$ are plotted for various values of λ. It is seen that one should have typically $\lambda \lesssim 1$ to minimise the propagation of $\tilde{f}(z)$ into the walls and to remain at a microscopic level. Besides we find that the condition of positivity of $\tilde{\epsilon}_\perp(z)$ is realised only for $\lambda \gtrsim 0.6$. The choice of $\lambda = 0.7$ in the text is a compromise between those two requirements. It insures in particular that the near equality in eq. 16 is realised.

We note that the two peaks appearing for the $\tilde{\epsilon}_\perp(z)$-curves in the interfacial regions for $\lambda \lesssim 1$ are unimportant when looked from the point of view of the dielectric response, indeed the fundamental quantity to be considered. If the results presented here were to guide the modelling of an effective, coarse-grained dielectric constant, one should rather focus on the coarse-grained dielectric response that can be well approximated with two inverted sigmoid-like curves in the form $\tilde{f}(z) = S(z-z_0)S(h-z+z_0)$, yielding smooth curves when converted to $\tilde{\epsilon}_\perp(z)$. The choice $\lambda = 0.7$ remains relevant in that context. Choosing a larger value, such as $\lambda = 1$, implies a further smoothing of the dielectric boundaries. The best modelling strategy is left to applications.

III. INFLUENCE OF THE UNCERTAINTY ON THE SLAB THICKNESS. CONNECTION TO THE DIELECTRIC CONTINUUM THEORY

Here we adopt some notations compatible with Ref.[8]. Let us call w the slab thickness defined as in the text as the distance between the center of the surface atoms of each plates, $d/2$ the width of the depletion layer due to wall-solvent repulsion that can be inferred from, *e.g.*, in Fig. 1 ($d/2 \sim 2$ Å). Now we call h the experimental definition/measure of the device thickness, typically $h = w + \delta$ (δ positive or negative); our convention up to now was to take $h = w$. The effective dielectric constant of the slab can be defined as

$$\frac{1}{4\pi}\left(1 - \frac{1}{\bar{\epsilon}_\perp}\right) E_0 = M/V = \mu/h \tag{5}$$

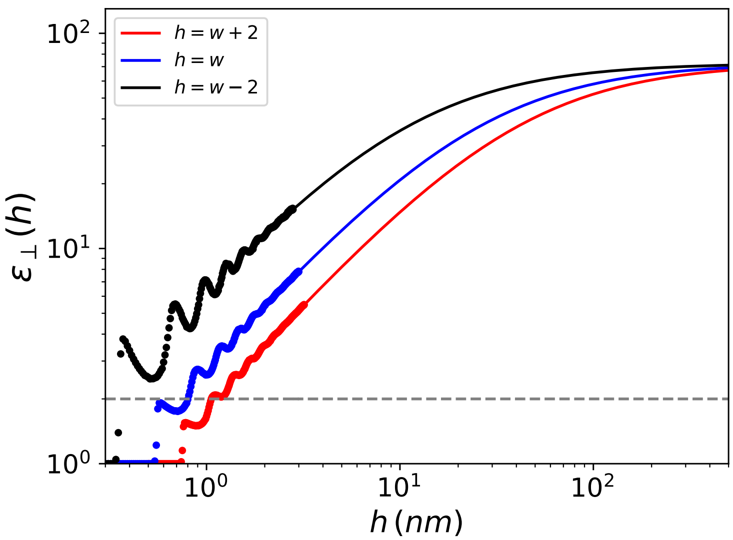

Figure 2. Effective dielectric constant computed using cDFT for the model Stockmayer fluid embedded in a slab of width h as function of h. We compare the previous result of Fig. 6 obtained for $h = w$ (blue curve) to those obtained with $h = w - 2$ (black) or $h = w + 2$ (red).

where M is the total dipole of the device, $V = h\mathcal{A}$ its volume, $\mu = M/\mathcal{A}$ its dipole per unit area, *i.e.*,

$$\mu = \int_0^w P(z) = \int_{\delta/2}^{w-\delta/2} P(z)$$

The second equality applies for any $\delta < d$, since $P(z) = 0$ for $z < d/2$ and $z > w - d/2$. Thus within this limit, the total dipole of the device does not depend on the choice of the boundaries whereas the polarisation does through the definition of the device thickness $h = w \pm \delta$. This is illustrated in the Fig. 2 of this SI where we plot $\bar{\epsilon}_\perp(h)$ versus h and compare our natural, previous choice $h = w$ to $h = w \pm 2\,\text{Å}$, the typical range presented in Ref.[8]. We recover indeed a similar influence of the parameter δ (or h), monitoring the uncertainty in the definition of the "confining volume", on the location of the curves.

REFERENCES

[1] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids: With Applications to Soft Matter*, Academic Press, Amstersdam, 4th edn, 2013.

[2] D. Chandler, *Physical Review E*, 1993, **48**, 2898–2905.

[3] V. Sergiievskyi, M. Levesque, B. Rotenberg and D. Borgis, *Condens. Matter Phys.*, 2017, **20**, 1–14.

[4] G. Monet, H. Berthoumieux, F. Bresme and A. Kornyshev, *Phys. Rev. Lett.*, 2021, **126**, 216001.

[5] J. F. Olivieri, J. T. Hynes and D. Laage, *J. Phys. Chem. Lett.*, 2021, **12**, 4319–4326.

[6]P. A. Bopp, A. A. Kornyshev and G. Sutmann, *Phys. Rev. Lett.*, 1996, **76**, 1280–1283.

[7]M. A. Vorotyntsev and A. A. Rubashkin, *Chem. Phys.*, 2019, **521**, 14–24.

[8]S. J. Cox and P. L. Geissler, *Chem. Sci.*, 2022, **13**, 9102–9111.