Comment on "A spherical cavity model for quadrupolar dielectrics" [J. Chem. Phys. 144, 114502 (2016)]

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Abstract. At the interface between quadrupolar media, the normal displacement field is discontinuous even in the absence of surface charge, because the boundary condition of the quadrupolar Coulomb-Ampère law of electrostatics involves the surface divergence of the surface displacement field. This surface displacement field is proportional to the jump of the quadrupolarization tensor. The term is important for surfaces exposed to a non-homogeneous electric field, and it affects the outcome of the spherical cavity (Onsager) model for quadrupolar dielectrics. With the new correct boundary condition, the predictions of the model are more reasonable; in particular, the reciprocal relationships of Onsager are now valid (cavity field:external field = external dipole:actual dipole, and cavity field gradient:external field gradient = external quadrupole:actual quadrupole).

The displacement field D in a quadrupolar medium involves the divergence of the quadrupolarization tensor $\mathbf{Q}$:

$$D = \varepsilon E - \frac{1}{2}\nabla \cdot \mathbf{Q} , \tag{1}$$

where ε is dielectric permittivity and E is electric field intensity. In order to solve Coulomb's law ($\nabla \cdot D = 0$) for problems involving an interface between two quadrupolar media, a boundary condition is required for D. In Ref. [1], we used the condition for continuity of the normal displacement field (D_r) at the surface of the spherical cavity, eq^18 (we cite the equations from Ref. [1] with superscript 1):

$$D_r(r = R_{cav} - 0) = D_r(r = R_{cav} + 0) , \tag{2}$$

where R_{cav} is the radius of the cavity. This condition is valid only in case that D has no δ-term in its singular expansion at the surface of discontinuity (i.e. if D can be expressed as $D^+\eta^+ - D^-\eta^-$, where $\eta^+ = \eta(r - R_{cav})$, $\eta^- = \eta(R_{cav} - r)$, and D^+ and D^- are continuous functions of the coordinates in the vicinity of $r = R_{cav}$; η and δ are the Heaviside and Dirac functions). However, the quadrupolarization tensor is discontinuous at the interface between the cavity and the medium, i.e. $\mathbf{Q} = \mathbf{Q}^+\eta^+ + \mathbf{Q}^-\eta^-$; from Eq (1) it then follows that D *has* a δ-term:

$$D = D^+\eta^+ + D^-\eta^- + D^S\delta , \tag{3}$$

where the bulk displacements $D^\pm$ stand for

$$D^\pm = \varepsilon^\pm E^\pm - \frac{1}{2}\nabla \cdot \mathbf{Q}^\pm , \tag{4}$$

and the *surface displacement field* D^S is given by

$$D^S = -\frac{1}{2}\mathbf{e}_r \cdot \left(\mathbf{Q}^+ - \mathbf{Q}^-\right) . \tag{5}$$

Here, $\delta \equiv \delta(r - R_{cav})$, $\mathbf{e}_r$ is the unit vector normal to the surface, and we used the relations $\nabla\eta^\pm = \pm\mathbf{e}_r\delta$. The correct boundary condition in the case of non-zero D^S reads[2-4]:

$$D_r(r = R_{cav} - 0) = D_r(r = R_{cav} + 0) + \nabla^S \cdot D^S\big|_{r=R_{cav}} , \tag{6}$$

where ∇^S is the surface nabla operator ($\nabla^S = \nabla - \mathbf{e}_r\partial/\partial r$). The derivations of this equation in Refs. [3,4] were for a flat surface, and D^S in [4] is produced by intrinsic surface polarization. Nevertheless, Eq (6) is valid[2] also for the case we investigate –

spherical surface and D^S induced by the discontinuity of the bulk quadrupolarization, Eq (5) (cf. the supplement). The term $\nabla^S \cdot D^S$ is zero for the problems of quadrupolar electrostatics we solved previously[5-7], since the involved surfaces were homogeneous. However, this is not the case with the four basic problems required by the Onsager model of quadrupolar dielectrics solved in Ref. [1]. The correct expressions follow.

Reaction field of a dipole and a quadrupole. With regard to the problem for a dipole p in the centre of a cavity, the solution for the potential ϕ_{p0} inside the cavity ($r < R_{cav}$) remains formally the same (eq^113), but the one outside the cavity is, instead of eq^114,

$$\phi_p = \frac{p_{ext} \cdot r}{4\pi\varepsilon r^3}\left(1 - \frac{9}{g_p}\frac{L_Q^2}{R_{cav}^2}\frac{r + L_Q}{R_{cav}}e^{-\frac{r-R_{cav}}{L_Q}}\right) . \tag{7}$$

Here L_Q is the quadrupolar length. The *external dipole moment* p_{ext} in Eq (7) is proportional to p:

$$p_{ext} = Y_E p, \tag{8}$$

where Y_E is given by eq^128, $Y_E = 3f_E\varepsilon/(2\varepsilon + f_p\varepsilon_0)$. The quadrupolar factors f_p, g_p and f_E in the formulae above stand for the expressions:

$$f_p = \frac{2 + 8x}{2g_p + 9x^2 + 9x^3} ; \quad f_E = \frac{2g_p}{2g_p + 9x^2 + 9x^3} ;$$

$$g_p = 1 + 4x + 9x^2 + 9x^3 , \tag{9}$$

where $x = L_Q/R_{cav}$; the formula eq^117 for f_p is invalid. The expression eq^115 for the reaction field E_{react} remains formally unchanged, but with the new factor f_p. The calculated limit in eq^118 holds true with the new formulae presented here; note that it is actually incorrect with the old ones, due to an arithmetic mistake. This means that the revised Onsager model following from the new boundary condition (6) leads to the correct continuum single particle limit of the perturbation theory of Milischuk and Matyushov[8], while the old one[1] stemming from Eq (2) does not.

Similar corrections are required in the formulae[1] 20-24 for the reaction field of a quadrupole $\mathbf{q}$ in a cavity. Instead of eq^121, the potential ϕ_q at $r > R_{cav}$ is:

$$\phi_q = \frac{3r \cdot \mathbf{q}_{ext} \cdot r}{8\pi\varepsilon r^5}\left(1 - \frac{18}{g_q}\frac{L_Q^2}{R_{cav}^2}\frac{r^2 + 3L_Q r + 3L_Q^2}{R_{cav}^2}e^{-\frac{r-R_{cav}}{L_Q}}\right) . \tag{10}$$

The *external quadrupole moment* $\mathbf{q}_{\text{ext}}$ is still proportional to $\mathbf{q}$, but instead of $eq^1 23$, the relation is:

$$\mathbf{q}_{\text{ext}} = Y_{\nabla E}\mathbf{q},\tag{11}$$

where $Y_{\nabla E}$ is given by $eq^1 33$, $Y_{\nabla E} = 5f_{\nabla E}\varepsilon/(3\varepsilon + 2f_q\varepsilon_0)$. The quadrupolar factors f_q, $f_{\nabla E}$ and g_q above stand for:

$$f_q = \frac{1 + 6x + 6x^2}{g_q + 12x^2 + 18x^3 + 18x^4}; \quad f_{\nabla E} = \frac{g_q}{g_q + 12x^2 + 18x^3 + 18x^4};$$

$$g_q = 1 + 6x + 24x^2 + 54x^3 + 54x^4.\tag{12}$$

$Eq^1 23$ for the reaction field gradient is valid but with the new f_q-factor.

Cavity field and cavity field gradient. The solution to the problem for a cavity in a quadrupolar continuum polarized by an external field $\boldsymbol{E}_0$, with the new boundary condition (6), also changes compared to $eqs^1 26\text{-}30$. The potential ϕ_E at $r > R_{\text{cav}}$ is:

$$\phi_E = -\boldsymbol{E}\cdot\boldsymbol{r} + \frac{\boldsymbol{p}_{\text{ext},E}\cdot\boldsymbol{r}}{4\pi\varepsilon r^3}\left(1 - \frac{9}{g_p}\frac{L_Q^2}{R_{\text{cav}}^2}\frac{r + L_Q}{R_{\text{cav}}}e^{-\frac{r - R_{\text{cav}}}{L_Q}}\right).\tag{13}$$

The cavity field $\boldsymbol{E}_{\text{cav}}$ is proportional to the external field $\boldsymbol{E}_0$, formally with the same Y_E coefficient, $eq^1 28$, but with the new quadrupolar factors (9). The vector $\boldsymbol{p}_{\text{ext},E}$ in Eq (13) is the excess dipole moment of the cavity induced by the external field, and instead by $eq^1 29$, it is given by:

$$\boldsymbol{p}_{\text{ext},E} = -\frac{4\pi}{3}R_{\text{cav}}^3 Y_E\left(\varepsilon - \varepsilon_0\right)\boldsymbol{E}_0.\tag{14}$$

Finally, let us summarize the solution to the problem for a cavity in quadrupolar medium placed in an external electric field gradient $(\nabla\boldsymbol{E})_0$. The cavity field gradient $(\nabla\boldsymbol{E})_{\text{cav}}$ is proportional to $(\nabla\boldsymbol{E})_0$ with the $Y_{\nabla E}$ coefficient from $eq^1 33$. The potential outside the cavity is:

$$\phi_{\nabla E} = -\frac{1}{2}\boldsymbol{r}\cdot(\nabla\boldsymbol{E})_0\cdot\boldsymbol{r}$$
$$+ \frac{3\boldsymbol{r}\cdot\mathbf{q}_{\text{ext},\nabla E}\cdot\boldsymbol{r}}{8\pi\varepsilon r^5}\left(1 - \frac{18}{G_q}\frac{L_Q^2}{R_{\text{cav}}^2}\frac{r^2 + 3L_Q r + 3L_Q^2}{R_{\text{cav}}^2}e^{-\frac{r - R_{\text{cav}}}{L_Q}}\right).\tag{15}$$

The excess quadrupole moment $\mathbf{q}_{\text{ext},\nabla E}$ of the sphere induced by the external gradient $(\nabla\boldsymbol{E})_0$ is given by the equation:

$$\mathbf{q}_{\text{ext},\nabla E} = -\frac{8\pi}{15}R_{\text{cav}}^5 Y_{\nabla E} A_{\nabla E}\nabla\boldsymbol{E}_0.\tag{16}$$

The quadrupolar factors in these formulae are given by Eqs (12) and the expressions:

$$g_{\nabla E} = 1 + 9x + 39x^2 + 90x^3 + 90x^4;$$

$$A_{\nabla E} = \left(1 + 9x^2\frac{g_{\nabla E}}{2g_q}\right)\varepsilon - \left(1 - 3x^2\frac{1 + 3x + 3x^2}{g_q}\right)\varepsilon_0;$$

$$G_q = \frac{12g_q A_{\nabla E}}{15\left(1 + 6x^2\right)\varepsilon - 10\varepsilon_0}.\tag{17}$$

Reciprocal relationships. Onsager[9] observed that the following reciprocal relation holds for the cavity field and the external dipole in a dipolar medium: $\boldsymbol{E}_{\text{cav}}/\boldsymbol{E}_0 = \boldsymbol{p}_{\text{ext}}/\boldsymbol{p} = 3\varepsilon/(2\varepsilon + \varepsilon_0)$ (his *eq 11*). An important outcome from the revised boundary condition (6) is that such a relation is valid also in a quadrupolar medium:

$$\frac{\boldsymbol{p}_{\text{ext}}}{\boldsymbol{p}} = \frac{\boldsymbol{E}_{\text{cav}}}{\boldsymbol{E}_0} = Y_E.\tag{18}$$

Analogous reciprocal relationship occurs for the external quadrupole and the cavity field gradient:

$$\frac{\boldsymbol{q}_{\text{ext}}}{\boldsymbol{q}} = \frac{(\nabla\boldsymbol{E})_{\text{cav}}}{(\nabla\boldsymbol{E})_0} = Y_{\nabla E}.\tag{19}$$

The old boundary condition (2) leads[1] to results that disagree with Eqs (18)-(19).

The macroscopic polarizability and quadrupolarizability of the medium are obtained in the manner described in Ref. [1]. The result for the polarizability α_P reads:

$$\alpha_P \equiv \varepsilon - \varepsilon_0 = \frac{Y_E}{1 - \alpha_p X_p}\left(\alpha_p + \frac{1}{1 - \alpha_p X_p}\frac{p_0^2}{3k_{\text{B}}T}\right)C.\tag{20}$$

This is the sought generalization of Onsager's[9] formula for ε to quadrupolar medium. The respective equation for the macroscopic quadrupolarizability α_Q of an Onsager fluid is:

$$\alpha_Q \equiv 3\varepsilon L_Q^2 = \frac{Y_{\nabla E}}{1 - \alpha_q X_q}\left(\alpha_q + \frac{1}{1 - \alpha_q X_q}\frac{\mathbf{q}_0 : \mathbf{q}_0}{10k_{\text{B}}T}\right)C.\tag{21}$$

Here, the factors X_p and X_q are given by $eqs^1 15\&22$ and Y_E and $Y_{\nabla E}$ are given by $eqs^1 28\&33$ – but with the new expressions for f_p, f_q, f_E, and $f_{\nabla E}$, Eqs (9)&(12). Eqs (20)-(21) are setting the correct Onsager model for a quadrupolar liquid, instead of $eqs^1 50\&53$. The change is significant enough to affect most of the results presented in Ref. [1]. Qualitatively, the results are similar, with one exception: according to $eqs^1 51\text{-}52$, the quadrupoles have a relatively stronger effect on ε in the case of non-polar liquids; according to Eq (20), the effects are not so different for polar and non-polar fluids. Quantitatively, in most cases, the new term $\nabla^S\cdot\boldsymbol{D}^S$ in Eq (6) leads to a significant change of the final values of α_Q (up to 20%) and cannot be neglected. Correspondingly, $Table^1 1$ and most figures in Ref. [1] are inaccurate – the correct ones follow.

Results. As in the previous paper, we used the following empirical relationship between the cavity radius and the density of the fluid:

$$\frac{m}{\frac{4}{3}\pi R_{\text{cav}}^3} = k_\rho\rho + k_0,\tag{22}$$

where m is the atomic mass. The values of the coefficients k_ρ and k_0 in $Table^1 1$ are incorrect. The correct k_ρ and k_0 are given in Table 1 here; they were determined by regression over the experimental data for ε vs. the theoretical permittivity following from our new Eqs (20),(21)&(22) (solved for the unknown R_{cav}, L_Q and ε). In all cases but water, the analysis of the data for ε suggested that R_{cav} is function of ρ only. For water, as in Ref. [1], statistically significant temperature dependence was evident, and therefore, instead of Eq (22) we used

$$\frac{m}{\frac{4}{3}\pi R_{\text{cav}}^3} = k_\rho\rho - k_T T + k_0.\tag{23}$$

For H_2O, we compared the theoretical permittivities that follow from Eqs (20),(21)&(23) with the data points for ε; the dispersion was minimized with respect to the parameters of Eq (23), leading to best values $k_0 = 2853.7$ kg/m^3, $k_\rho = 0.1195$ and $k_T = 1.057$ kg/m^{3}K (slightly different from those determined in Ref. [1]). The details for the experimental data and the parameter values used in this supplement are described in Ref. [1].

Table 1. Values of the molecular multipole moments & polarizabilities, and the coefficients in dependence (22) of R_{cav} on ρ.

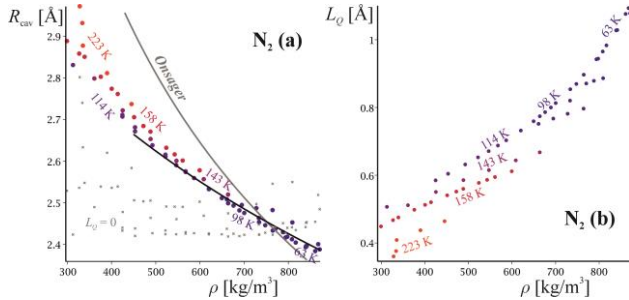|	dipole moment p_0 [Cm]×10³⁰	polarizability $\alpha_p/4\pi\varepsilon_0$ [Å³]	quadrupole moment $(q_0:q_0)^{1/2}$ [Cm²]×10⁴⁰	quadrupolarizability $\alpha_q/4\pi\varepsilon_0$ [Å⁵]	k_0 [kg/m³] in Eq (22)	k_ρ in Eq (22)	$dev_\varepsilon/\varepsilon_0$ of Eq (22) vs. the data for ε
Ar	0	1.639	0	0.454	655.5	0.3134	0.0009
Kr	0	2.488	0	0.913	-	-	-
Xe	0	4.105	0	1.936	-	-	-
CH₄	0	2.597	0	1.681	122.84	0.7019	0.0004
N₂	0	1.737	4.08	1.12	342.2	0.5445	0.0005
CO₂	0	2.98	11.43	2.21	235.64	0.9102	0.0009
CS₂	0	8.215	8.88	11.40	721.2	0.5513	0.0017
C₆H₆	0	10.25	24.87	18.42	695.2	0.3300	0.0019
H₂O	6.204	1.470	8.073	0.496	Eq (23)		0.19
CH₃OH	5.638	3.32	16.436	3.121	1991.3	0.3534	0.7

Fig. 1(a) Cavity radius of N₂ calculated from Eqs (20)&(21) and experimental data for ε and ρ. The colour indicates the temperature. The gray symbols are Böttcher's R_{cav} following from the original theory of Onsager (Eq (20) with $L_Q = 0$). The black line is Eq (22) with $k_\rho = 0.545$ and $k_0 = 342$ kg/m³. **(b)** The quadrupolar length L_Q following from the same model and data. Cf. Ref. [1] for details.
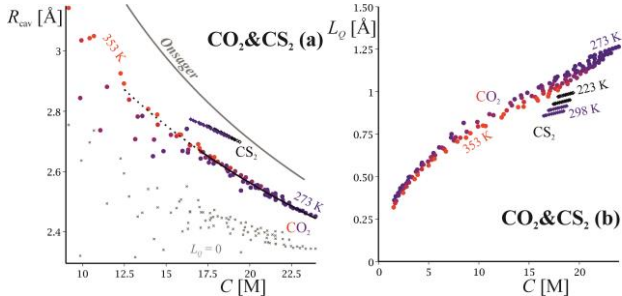

Fig. 2(a) Cavity radius of CO₂ & CS₂ as a function of their concentration C, calculated with Eqs (20)&(21) from experimental data for ε & ρ. The colour indicates the temperature. The gray symbols are Böttcher's R_{cav} following from Onsager's original equation (Eq (20) with $L_Q = 0$). Gray line is Eq (22) with $k_\rho = 1$ and $k_0 = 0$; black line is Eq (22) with $k_\rho = 0.910$ and $k_0 = 236$ kg/m³ for CO₂. **(b)** The quadrupolar length L_Q following from the same model. Cf. Ref. [1] for details.

Fig.[1]*5-9* in Ref. [1] are inaccurate, due to the erroneous *eqs*[1]*50&53*. Fig. 1-5 here show the correct results. For non-polar non-quadrupolar fluids (Ar, Kr, Xe, CH₄), the change is very small, so the respective *Fig.*[1]*3-4* do not need change. For quadrupolar but non-polar molecules (N₂, CO₂, CS₂, C₆H₆), the values of L_Q calculated here at the highest experimental densities are by about 10% smaller than those in Ref. [1] (corresponding to an error in α_Q of about −20%). In Fig. 3, the correct quadrupolar lengths of benzene calculated via Eqs (20)&(21) are compared with those from Ref. [1], to highlight the importance of the term $\nabla^S \cdot D^S$ in Eq (6). For polar species (H₂O, CH₃OH), the new values of L_Q are at most by 5% smaller than those in Ref. [1] (corresponding to α_Q by 10% smaller). The change in the values of R_{cav} compared to those

in Ref. [1] is relatively small (e.g. 1-2%) yet significant in view of the strong dependence of all properties of the quadrupolar liquid on R_{cav}.
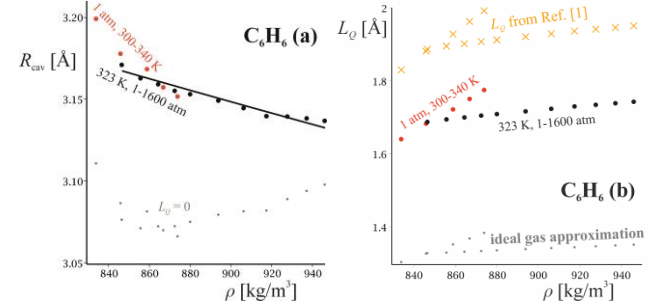

Fig. 3(a) Cavity radius of benzene as a function of ρ, calculated with Eqs (20)&(21) and experimental data for ε & ρ. The red circles correspond to various temperatures (300-340 K) and pressure 1 atm, and the black ones – to various pressures (1-1600 atm) and temperature 323 K. The gray symbols are Böttcher's R_{cav} following from Onsager's equation (Eq (20) with $L_Q = 0$). The black line is Eq (22) with $k_\rho = 0.330$ and $k_0 = 695$ kg/m³. **(b)** The quadrupolar length L_Q following from the same model (circles). Gray dots: α_Q of an ideal gas. Crosses: L_Q calculated1 with the wrong boundary condition (2). Cf. Ref. [1] for details.
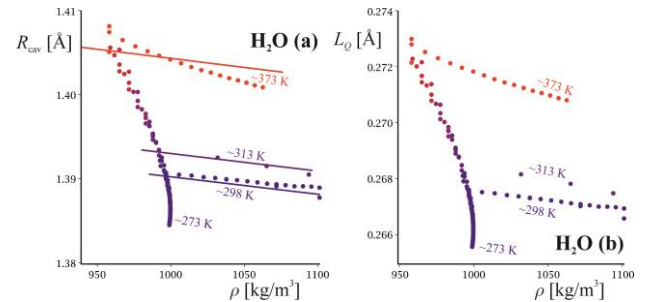

Fig. 4(a) Cavity radius of H₂O calculated with Eqs (20)&(21) and experimental data for ε & ρ. The colour indicates the temperature. The lines are Eq (23) at the indicated temperatures. **(b)** The quadrupolar length L_Q following from the same model. Cf. Ref. [1] for details.

The value of the dipole moment p of a water molecule in liquid environment is larger than the intrinsic dipole p_0 of a molecule in gas phase by a factor of $1/(1-\alpha_p X_p) = 2.17$ (which differs from the value 2.07 calculated previously[1] due to the different f_p factor in the expression for X_p). The quadrupole moment of water increases by a factor of $q/q_0 = 1/(1-\alpha_q X_q) = 1.39$ (instead of[1] 1.36). This suggests that one of the approximations of the Onsager model – for the negligible molecular hyperpolarizabilities – fails even worse for the revised model of Onsager.

An important feature of the quadrupolar Onsager model is that

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it leads to a much smaller field intensity E near the cavity: in the range $r = R_{cav} \dots 3R_{cav}$, using the results for the parameters of water at room temperature, we obtain that the maximal value of E_r varies in the range $3 \times 10^8 \dots 3 \times 10^7$ V/m (2 orders of magnitude smaller than the range obtained previously, due to another error in the calculations). This field is still high and dielectric saturation can still be expected, but not as massive as estimated in Ref. [1]. The dipole moment per each water molecule in the first coordination shell that follows from the Onsager cavity model can be estimated to be of the order of $0.5 \times p_0$. For comparison, the original model[9] of Onsager (with $L_Q = 0$) predicts significantly higher field (up to 8×10^8 V/m at $r = R_{cav}$).
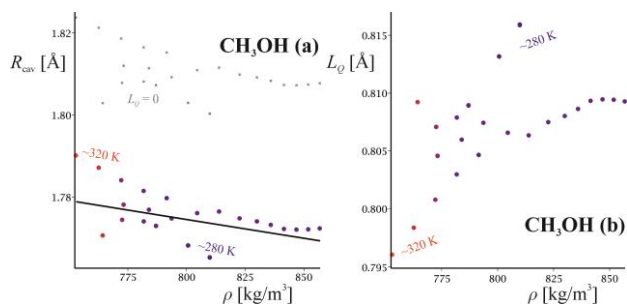

Fig. 5(a) Cavity radius of methanol calculated from Eqs (20)&(21) and experimental data for static permittivity and density. The colour indicates the temperature. The black line is Eq (22) with the coefficients from Table 1. The gray symbols are Böttcher's radii (obtained from Eq (20) with $L_Q = 0$). **(b)** The quadrupolar length L_Q following from the same model. Cf. Ref. [1] for details.

The comparison of the values of the macroscopic quadrupolarizabilities determined by Jeon and Kim[11] from Stokes shift data of coumarin in CO_2 and C_6H_6 ($\alpha_Q = 0.42 \times 10^{-30}$ Fm at $\rho = 800$ kg/m^3 for CO_2 and 2.6×10^{-30} Fm for C_6H_6) with those following from the revised Onsager model at the same conditions ($\alpha_Q = 0.46 \times 10^{-30}$ Fm for CO_2 and 1.9×10^{-30} Fm for C_6H_6) shows very good agreement for CO_2 and acceptable for C_6H_6. The coincidence might be accidental since the Stokes shift formula of Jeon and Kim is based on a set of boundary conditions different from ours[1]. The calculated quadrupole length of methanol varies in the range $L_Q = 0.79\text{-}0.82$ Å, Fig. 5, in satisfactory agreement with the value obtained from the data for the activity coefficient of NaBr in methanol solution[6], $L_Q = 1.1 \pm 0.2$ Å. The difference is most probably due to the neglected hyperpolarizabilities: according to the revised Onsager model, the dipole moment p of methanol is higher than p_0 by a factor of 2.39 (compare to the previous[1] value 2.16), which is too high, and the reaction field is of magnitude 2×10^{10} V/m, large enough for the hyperpolarizabilities to play a role. Another problem with methanol is that its molecule is not spherical, cf. the discussion in Ref. [1].

Clausius-Mossotti-Debye fluid. We would like to use this document to answer a question that we have been asked on several occasions regarding the quadrupolarizability of a liquid, namely: what would a Clausius-Mossotti-Debye-like model give for the properties of a quadrupolar fluid? This model[10] assumes that the local field E_{loc} acting on a molecule in the cavity in the liquid is the sum of the external field E_0 plus the field $E_P = P/3\varepsilon_0$ of a homogeneously polarized medium of polarization P outside the cavity (in contrast, in Onsager's model, the polarization is a function of the coordinates). A similar approach can be applied to a cavity in a homogeneously quadrupolarized medium of constant Q. However, it is easy to show that the potential inside such a cavity is constant, and therefore, the respective electric field gradient $(\nabla E)_Q$ produced by the medium is zero. Consequently, the local electric field gradient is equal to the outer one, i.e. $(\nabla E)_{loc} = (\nabla E)_0$ (compare to the relation eq^143 in an Onsager fluid). Therefore, the quadrupolarizability of a Clausius-Mossotti-Debye liquid is precisely equal to the quadrupolarizability of an ideal gas, eq^11.

Supplementary material

See supplementary material for **(A)** some of the derivations, and **(B)** a sample Maple code for solving Eqs (20)-(21).

Notes and references

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Supplementary information

A. Solving the quadrupolar Coulomb-Ampère law

Let us start with the derivation of Eqs (5)-(6) for a spherical surface. We will first find the divergence of Eq (3); using the relations $\nabla\eta^{\pm} = \pm\mathbf{e}_r\delta$ and $\nabla\delta = \mathbf{e}_r\delta_1(r-R_{cav})$, we obtain:

$$\nabla\cdot\boldsymbol{D} = \eta^+\nabla\cdot\boldsymbol{D}^+ + \eta^-\nabla\cdot\boldsymbol{D}^- + \delta\left(D_r^+ - D_r^- + \nabla\cdot\boldsymbol{D}^S\right) + \delta_1 D_r^S . \quad (24)$$

Next, we use the formula

$$\mathrm{f}(r)\delta_1\left(r - R_{cav}\right) = \mathrm{f}\left(R_{cav}\right)\delta_1 - \left.\frac{\partial\mathrm{f}}{\partial r}\right|_{r=R_{cav}}\delta \quad (25)$$

(where $\mathrm{f}(r)$ is any continuous function) to rearrange Eq (24):

$$\nabla\cdot\boldsymbol{D} = \eta^+\nabla\cdot\boldsymbol{D}^+ + \eta^-\nabla\cdot\boldsymbol{D}^-$$
$$+ \delta\left(D_r^+ - D_r^- + \nabla^S\cdot\boldsymbol{D}^S\right)_{R_{cav}} + \delta_1 D_r^S(R_{cav}) . \quad (26)$$

Coulomb's law requires that $\nabla\cdot\boldsymbol{D} = 0$, and since η, δ and δ_1 are irreducible, the multiplier of δ must be zero, leading to Eq (6). In Eq (26), the surface divergence stands for

$$\nabla^S\cdot\boldsymbol{D}^S = \nabla\cdot\boldsymbol{D}^S - \frac{\partial D_r^S}{\partial r} ,$$

or in spherical coordinates,

$$\nabla^S\cdot\boldsymbol{D}^S = \frac{1}{R_{cav}\sin\theta}\frac{\partial}{\partial\theta}\sin\theta D_\theta^S + \frac{1}{R_{cav}\sin\theta}\frac{\partial D_\varphi^S}{\partial\varphi} . \quad (27)$$

The term $\nabla^S\cdot\boldsymbol{D}^S$ was missing in the boundary condition $eq^1 8$, which makes the results in Ref. [1] incorrect.

All solutions in these errata – Eqs (7)-(17) – were obtained with the new condition (6) following the procedure described in $SI^1 A$, with few changes, as follows. To obtain the general solution, we first consider an auxiliary problem which has radial symmetry, e.g., for the problem for the reaction field of a quadrupole in a cavity, we first consider a quadrupole with the following components:

$$\boldsymbol{q} = -\frac{1}{3}q_{zz}\mathbf{e}_x\mathbf{e}_x - \frac{1}{3}q_{zz}\mathbf{e}_y\mathbf{e}_y + \frac{2}{3}q_{zz}\mathbf{e}_z\mathbf{e}_z . \quad (28)$$

This zero-trace quadrupole creates field that is independent of φ. In this case, $D_\varphi^S = 0$ and

$$D_\theta^S = -\frac{1}{2}Q_{\theta r}^+\Big|_{r=R_{cav}} = -\frac{3}{2}\varepsilon I_Q^2 \left.\frac{\partial E_\theta^+}{\partial r}\right|_{r=R_{cav}} . \quad (29)$$

The solution to the auxiliary problem for the electrostatic potential is obtained via separation of variables $\phi = (z^2 - r^2/3)\varPhi(r)$. The solution for any quadrupole follows easily as described in $SI^1 A$.

B. Sample Maple code for solving Eqs (20)&(21) for L_Q & R_{cav}

The following code for solving Eqs (20)&(21) for methanol at normal conditions can be pasted and executed in Maple:

#1. Equations for LQ and Rcav
```
# Eq 20
eq20:= epsilon-epsilon0=
YE/(1-ap*Xp)*(C*ap+C/(1-ap*Xp)*p0^2/3/kB/T);
# Eq 21
eq21:= 1=YDE/(1-aq*Xq)/3/epsilon*
(C*aq/LQ^2+C/(1-aq*Xq)*q02/10/kB/T/LQ^2);
```

#2. Equations for the quadrupolar factors
```
# Eq[1]28
YE:= 3*fE*epsilon/(2*epsilon+fp*epsilon0);
# Eq[1]15
Xp:=(epsilon-fp*epsilon0)/2/Pi/epsilon0/Rcav^3
/(2*epsilon+fp*epsilon0);
# Eq[1]33
YDE:=5*fDE*epsilon/(3*epsilon+2*fq*epsilon0);
# Eq[1]22
Xq:=9/4/Pi/epsilon0/Rcav^5*
(epsilon-fq*epsilon0)/(3*epsilon+2*fq*epsilon0);
# Eq 9
fp:= (2+8*x)/(2*gp+9*x^2+9*x^3);
fE:= 2*gp/(2*gp+9*x^2+9*x^3);
gp:= 1+4*x+9*x^2+9*x^3;
# Eq 12
fq:= (1+6*x+6*x^2)/(gq+12*x^2+18*x^3+18*x^4);
fDE:= gq/(gq+12*x^2+18*x^3+18*x^4);
gq:= 1+6*x+24*x^2+54*x^3+54*x^4;

x:= LQ/Rcav;
```

#3. Parameter values for methanol
```
with(ScientificConstants):
# molecular dipole moment [Cm], Table 1:
p0:= 5.638e-30;
# molecular quadrupole moment (q0:q0) [C^2m^4]:
q02:=(16.44e-40)^2;
# molecular polarizability αp [Cm^2/V], Table 1:
ap:=3.32*evalf(4*Pi*epsilon0*1e-30);
# molecular quadrupolarizability αq [Cm^4/V]:
aq:=3.12*evalf(4*Pi*epsilon0*1e-50);
# mass of a carbon atom [kg]:
mC:=(GetValue(Element('C',atomicweight))):
# mass of a hydrogen atom [kg]:
mH:=(GetValue(Element('H',atomicweight))):
# mass of an oxygen atom [kg]:
mO:=(GetValue(Element('O',atomicweight))):
# mass of a methanol molecule [kg]:
m:=mC+4*mH+mO;
```

#4. Characteristics of the medium
```
# mass density of liquid methanol [kg]:
rho:=791.32;
# concentration of the molecules [1/m^3]:
C:=rho/m;
# Boltzmann constant [J/K]:
kB:=GetValue(Constant('k')):
# temperature [K]:
T:=298.15;
# dielectric permittivity of vacuum [C/m/V]:
epsilon0:=GetValue(Constant('epsilon[0]')):
# permittivity of liquid methanol [C/m/V]:
epsilon:=32.35*epsilon0;
```

#5. Lower limit of Rcav (from Curie points)
```
# Eq[1]55
Rmin1:=evalf(ap/(4*Pi*epsilon0))^(1/3);
# Eq[1]56
Rmin2:=evalf(3*aq/(4*Pi*epsilon0))^(1/5);
# lower limit of Rcav:
Rmin:= max(Rmin1,Rmin2);
```

#6. Solving the equations
```
sol:=fsolve({eq20,eq21},
{LQ=0..1.3e-10,Rcav=Rmin..3e-10});
# the output is LQ and Rcav in [m].
```