How Multivalency Controls Ionic Criticality

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To understand how multivalency affects criticality in z:1 ionic fluids, we report an ion-cluster association theory embodying ionic solvation and excluded volume for equisized hard-sphere models with $z = 1$–3. In accord with simulation but contradicting integral equation and field theories, the reduced critical temperature *falls* when z increases while the density ρ_c *rises* steeply. These trends can be explained semiquantitatively by noting that 80%–90% of the ions near T_c are bound in neutral or charged clusters, depleting the ionic strength. For $z \neq 1$, predicted interphase Galvani potentials vanish at T_c.

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Multivalent ions play a significant role in condensed-matter, physicochemical, biophysical, and, via the plasma transition, astrophysical contexts [1]. The effects of multivalency are, however, often hard to comprehend. One central issue—relevant to electrolyte solutions, molten salts, liquid metals, and dense plasmas [1]—arises in Coulomb-driven phase separation. The most basic model for such ionic fluids consists of $N = \rho V$ hard-core spherical ions of various species σ in a volume V of uniform dielectric constant D, with $N_\sigma = \rho_\sigma V$ ions of diameter a_σ carrying charges $q_\sigma = z_\sigma q_0$, where q_0 is an elementary charge. In the simple equisized z:1 *charge-asymmetric primitive models* (C_zAPMs), on which we focus here, one has $\sigma = +, -$, $a_+ = a_-$, and $q_+ = zq_0$, $q_- = -q_0$. The basic energy scale and associated reduced temperature and density are then $\varepsilon = zq_0^2/Da$, $T^* = k_BT/\varepsilon$, $\rho^* = \rho a^3$.

Monte Carlo (MC) simulations [2] show that (at least for $z \lesssim 5$) the C_zAPMs exhibit "gas-liquid" phase separation; furthermore, the critical parameters, $T_c^*(z)$ and $\rho_c^*(z)$, are found to reasonable precision: see the open circles in Figs. 1 and 2 and Table I. One observes that $T_c^*(z)$ *falls* with increasing z, while $\rho_c^*(z)$ *rises* sharply. But we ask: How can these trends be understood? Or accounted for semiquantitatively? To address this issue, we review briefly previous work, including a pioneering field-theoretic attack [3], and then report on recent, rather substantial calculations [4] which we believe provide significant insight and a base on which, as we then show, an effective heuristic analysis can be built. This new study [4] extends an earlier analysis **I** [5] for the symmetric $z = 1$ *restricted primitive model* (RPM) that was founded on the original Debye-Hückel (DH) approach but incorporated (i) Bjerrum ion pairs and (ii) their *solvation* in the residual ionic fluid. For $z = 2$ and 3 larger ion clusters, trimers and tetramers, must be included [4]; but then explicit results are also obtained for the *interphase Galvani potential* [6] that appears in any two-phase nonsymmetric ionic system [4,6].

The field-theoretic analysis of Netz and Orland (NO) [3] was designed to address z:1 ionic fluids and colloids ($z \gg 1$) and to include correlations in a systematic manner. The Coulomb interaction, $q_\sigma q_\tau/r$, was transformed to yield a functional integral over an auxiliary potential $\phi(\mathbf{r})$. At the $\langle\phi^2\rangle$ level the DH effective interaction, $v_{\mathrm{DH}} \propto e^{-\kappa r}/r$, is captured with

$$\kappa^2(T;\{\rho_\sigma\}) = 4\pi(q_0^2/Dk_BT)\sum_\sigma z_\sigma^2\rho_\sigma. \tag{1}$$

The reduced free energy density, $\bar{f}(T;\rho) \equiv -F/Vk_BT$, was computed to eighth order in ϕ but a momentum cutoff is essential: NO adopted $|\mathbf{k}_\Lambda| = 2\pi/a$, thereby incorporating the ionic diameter and, for the z:1 case, leading to $\kappa^2a^2 = 4\pi\rho^*/T^*$. Since this treatment of the hard cores is approximate, accurate predictions for $T_c^*(z)$ and $\rho_c^*(z)$ are not expected. Nevertheless, one might anticipate reliable *trends* when z varies in contrast to DH theory, which yields *no dependence* on z with (after **I**)

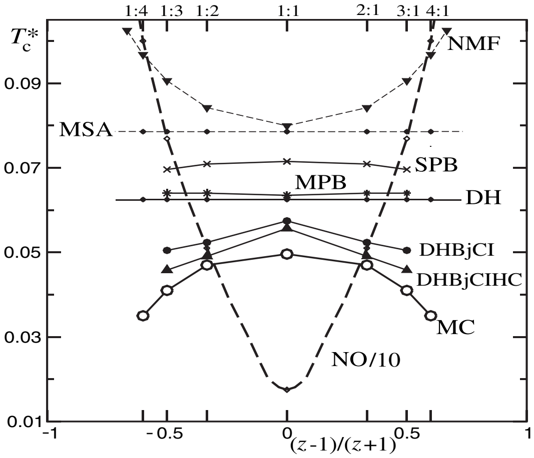

FIG. 1. Reduced critical temperatures for z:1 charge-asymmetric equisized hard-core primitive model electrolytes (C_zAPMs) according to Monte Carlo (MC) simulations [2]; Debye-Hückel (DH) theory; field-theoretic approaches: NO [3] (with a factor $\frac{1}{10}$) and a "new mean-field theory" (NMF) [7]; approximate integral equations: the mean spherical approximation (MSA) [8], and the symmetric (SPB) and modified (MPB) Poisson-Boltzmann theories [9]; and the current solvated ion-cluster theory *with* (DHBjCIHC) and *without* (DHBjCI) hard-core terms [4].

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TABLE I. Monte Carlo (MC) estimates [2] for the reduced critical parameters for z:1 equisized hard-sphere electrolytes; values calculated from the current solvated ion-cluster theory with hard-core terms (CI) [4]; and approximate estimates ($E_{\rm DH}, \dots, E_\kappa$) based on ion-cluster statistics: see text.

	Critical temp.		$10^2 T_c^*(z)$		Critical density		$10^2 \rho_c^*(z)$	
z	MC	CI	$E_{\rm DH}$	$E_{\rm MC}$	MC	CI	E_ρ	E_κ
1	4.93_3	5.56_9	5.45	4.93_5	7.50	2.61_4	2.72	2.37
2	4.70	4.90_7	5.11	4.65	9.3	6.26_1	4.27	3.49
3	4.10	4.33_4	4.85	4.44	12.5	11.90	6.96	5.40

$$\text{DH}: \quad \kappa_c a = 1, \quad T_c^* = 1/16, \quad \rho_c^* = 1/64\pi \simeq 0.005. \tag{2}$$

In fact, as NO report, "the [predicted] deviations from DH theory are pronounced" for $z > 1$: see Figs. 1 and 2.

But evidently the NO results are not merely quantitatively wrong; the *trends* are quite incorrect since T_c^* is asserted to rise rapidly (instead of falling) while ρ_c^* falls sharply for small $z - 1$ (instead of rising) and *then* increases but much too slowly. While one may blame the approximate treatment of the hard cores, we believe this is *not* the primary culprit. Indeed, a recent field-theoretic analysis paid closer attention to the ion-ion repulsions [7]; but the subsequent "new mean-field" (NMF) results still exhibit strong increases in T_c^* and an overly weak variation of ρ_c^*: see the NMF plots in Figs. 1 and 2 [7].

Integral-equation theories are hardly better: see Figs. 1 and 2. The *mean spherical approximation* (MSA), like DH theory, predicts *no variation* of T_c^* and ρ_c^* with z [8]. A *symmetric Poisson-Boltzmann* (SPB) theory [9] *does* predict the correct falling and rising trends for T_c^* and ρ_c^*, but the degree of variation is woefully inadequate. Moreover, the *modified Poisson-Boltzmann* (MPB) approximation, which the same authors [9] argue should be more reliable, yields the *wrong* trend for T_c^*.

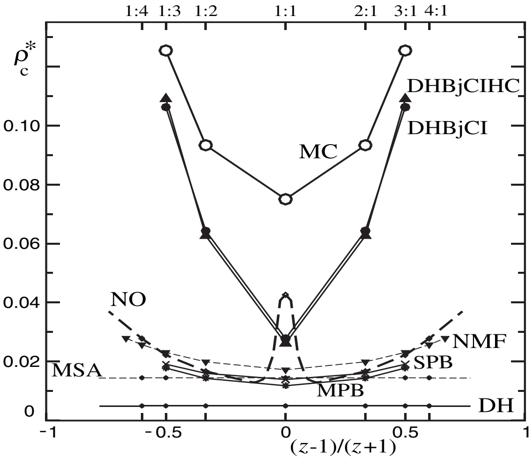

FIG. 2. Reduced critical densities $\rho_c^*(z)$, for the C_zAPM electrolyte as in Fig. 1 (except that the NO plot is not rescaled).

In order to better understand the effects of multivalency we turn to recent calculations [4] based on the *solvated ion-cluster* view [5] of the C_zAPM near criticality that is supported "pictorially" by simulations [2]. In brief, the aim is to construct the free energy density, $\bar{f}(T; \{\rho_\sigma\})$, for ionic species σ consisting of (i) + and − *monomers,* i.e., isolated, $n_+ = n_- = 1$ single, unassociated ions of valency $z_+ = z$ and $z_- = -1$; (ii) a set of associated *primary* clusters, $\sigma = 2, 3, \dots$, dimers, trimers, etc., each consisting of one "central" + ion and $m_\sigma = \sigma - 1$ "satellite" counterions for a total of $n_\sigma = m_\sigma + 1$ ions in a cluster of valency $z_\sigma = z - m_\sigma$; up to (iii), the largest primary cluster, the *neutral* or "molecular" $(z+1)$-mer of one z_+ ion and z negative ions [4].

For each species, $\bar{f}$ contains an ideal-gas term $\bar{f}^{\rm Id}(T, \rho_\sigma)$, and an electrostatic term $\bar{f}_\sigma^{\rm El}(T, \{\rho_\tau\})$, that, following DH, incorporates *cluster solvation* in the partially associated *ionic fluid:* this description is thus dubbed "DHBjCI" [4]. By adding a *hard core* (HC) free-volume term, $\bar{f}^{\rm HC}(\{\rho_\sigma\})$, as in **I**, one may also account for those excluded volume effects not *already* encompassed in the basic solvation and association calculations [4,5], so generating a "DHBjCIHC" theory [4]. (The effective HC virial coefficient $B_\sigma^{\rm bcc} = 4a_\sigma^3/3^{3/2}$ has been adopted [4,5].) Examination of Figs. 1 and 2 reveals that these solvated ion-cluster theories are surprisingly successful. Not only are *both* the downward trend in $T_c^*(z)$ *and* the rapid rise of $\rho_c^*(z)$ well captured, but the *quantitative* agreement with each of the MC estimates is significantly better than achieved by other approaches.

One must recognize that (all) these theories are of mean-field character: thus 5% to 15% overestimates of $T_c^*(z)$ are to be expected. Indeed, neglected fluctuations typically depress T_c by such amounts and also flatten the *coexistence curves* as seen in Fig. 3. Second, note that the hard-core terms have a small effect on $\rho_c^*(z)$ while reducing $T_c^*(z)$ values by only 5%–10%. Nevertheless, Fig. 3 reveals that

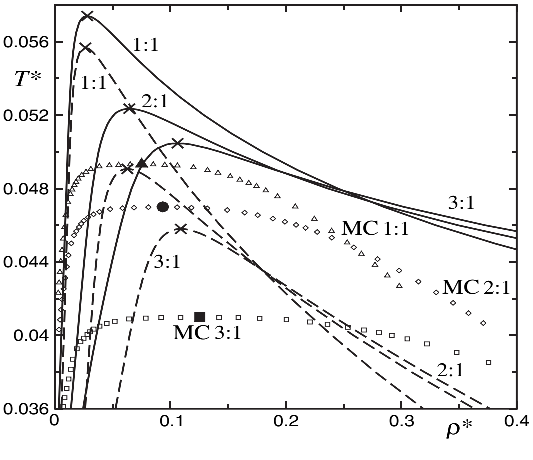

FIG. 3. Coexistence curves predicted for z:1 equisized primitive models by the DHBjCI and DHBjCIHC theories (solid and dashed lines, respectively) together with Monte Carlo estimates based on [10].

the liquid phases, especially for $\rho^* \gtrsim 0.15$, are sensitive to $\bar{f}^{\mathrm{HC}}$: but, recall the discussion in **I**. In fact, the crucial feature of DHBj-type theories—not represented in field-theoretic or standard integral-equation treatments—is the *chemical equilibrium* maintained between the cluster species via the law of mass action:

$$\rho_\sigma = K_{m,z}(T)\rho_+\rho_-^m \exp[\mu_+^{\mathrm{Ex}} + m\mu_-^{\mathrm{Ex}} - \mu_\sigma^{\mathrm{Ex}}], \qquad (3)$$

for $\sigma = m + 1 \geq 2$, with the excess chemical potentials $\mu_\sigma^{\mathrm{Ex}} = -(\partial/\partial\rho_\sigma)[\bar{f}^{\mathrm{HC}} + \sum_\sigma \bar{f}_\sigma^{\mathrm{El}}]$, while *the association constants* are taken as [4,5]

$$K_{m,z}(T;R) = \frac{1}{m!}\prod_{i=1}^{m}\int_a^R d\mathbf{r}_i \exp\left(-\frac{\mathcal{E}_{m,z}(\{\mathbf{r}_i\})}{k_BT}\right), \qquad (4)$$

in which $\mathcal{E}_{m,z}(\{\mathbf{r}_i\})$ is the electrostatic energy of an isolated $(m+1)$-mer with satellite coordinates $\{\mathbf{r}_i\}$. The lower limits a and the condition $\mathcal{E}_{m,z} = +\infty$ for $|\mathbf{r}_i - \mathbf{r}_j| < a$ represent hard cores. Following Bjerrum [5], the necessary cutoff radius R is chosen so that $(\partial K_{m,z}/\partial R)$ is minimal. The resulting threefold $K_{2,z}$ integral is manageable but the sixfold integral for $K_{3,3}$ requires a Padé approximant study of the low-T expansion cross-checked to a part in 10^3 by MC evaluations [4]. It transpires, however, that T_c^* and ρ_c^* are *insensitive* to the $K_{m,z}$ [4].

Lastly, one needs to account for the solvation of *all* the ion species, σ, by the free ions and charged clusters via the electrostatic terms [4,5]

$$\bar{f}_\sigma^{\mathrm{El}}(T;\{\rho_\tau\}) = \frac{4\pi\rho_\sigma}{Dk_BT}\sum_{l=0}^{\infty}\frac{u_{2l}(\kappa a_\sigma)}{a_\sigma^{2l+1}}\sum_{m=-l}^{l}\langle|Q_{lm}^\sigma|^2\rangle, \qquad (5)$$

where the $u_{2l}(x)$ are related to the spherical Bessel functions $k_l(x)$ [4]; the second sum requires the cluster electric multipole moments, $Q_{l,m}^\sigma$, thermally averaged [4] over the ionic configurations that already enter in the $K_{m,z}(T)$.

Finally, a_σ is an *effective cluster diameter,* i.e., the radius of the approximating sphere (centered to minimize $\bar{f}_\sigma^{\mathrm{El}}$) that substitutes for the true, thermally fluctuating, hard-core exclusion domain: see **I** and [4]. One concludes, as in **I**, that a most reasonable choice for a_σ is the average over solid angle of the radial distance to the true exclusion surface of the ground-state cluster: this yields $a_2 = (\frac{3}{4} + \frac{3}{8}\ln 3 \simeq 1.162)a$, $a_3 = 1.250a$, and $a_4 = 1.375a$. For $z = 1$ the values of T_c^* and ρ_c^* vary by less than $\pm 2\%$ over plausible alternatives for a_2 [4]; but the sensitivity to a_3 and a_4 for $z = 2$ and 3 is greater. As a result, this hard-to-avoid approximation contributes significantly to the overall quantitative uncertainties.

From the total free energy $\bar{f}(T,\{\rho_\sigma\})$, all thermodynamic properties follow [4,5]. One may then conclude from Figs. 1 and 2 that the principal defect of the field-theoretic and integral-equation approaches is a failure to account effectively for strong ionic association near criticality. But can the actual *trends* of T_c^* and ρ_c^* with z be demonstrated in a direct, transparent way? To answer, consider the *fractions,* $y_\sigma = n_\sigma N_\sigma/N$, of ions bound in clusters of n_σ ions with $\rho_\sigma = (y_\sigma/n_\sigma)\rho$. The critical point values that result from DHBjCIHC theory [4,11] are displayed in Table II. A significant fact is the rapid decrease in y_+^c, the fraction of unassociated z_+ ions, from 9.1% to 1.3% to 0.3%. But more can be learned.

To understand the variation of $T_c^*(z)$ let us regard the electrolyte in the critical region as a mixture of clusters with fixed mole fractions $x_\sigma = (y_\sigma/n_\sigma)/\sum_\tau(y_\tau/n_\tau)$. A pair (σ,τ) will either mutually repel *or* attract with pairwise binding energies, say, $\varepsilon_{\sigma\tau}$. Thus unlike monomers attract with $\varepsilon_\pm = \varepsilon$. However, a *dimer* attracts only *negative monomers* with $\varepsilon_{2-} = (z - \frac{1}{2})\varepsilon/z$; but repels all $z_+ \geq +2$ ions. Two dimers repel when $z \geq 3$; but one has $\varepsilon_{2,2}/\varepsilon \simeq 0.586$ and 0.345 for $z = 1$ and 2. And so on.

To estimate T_c^* for this mixture we adopt a van der Waals approach as in [10(b)]. Thus, for the overall cluster density $\hat{\rho}\ (= \rho\sum_\sigma y_\sigma/n_\sigma)$, we take $p/\hat{\rho}k_BT \simeq Z(B_0\hat{\rho}) + B_1(T^*)\hat{\rho}$ with $Z(u) = 1 + u + \ldots$ in which the second virial coefficient has been decomposed as $B(T^*) = B_0 + B_1(T^*)$ where B_0 $(= b_0a^3$, say) represents the hard-core repulsions while $B_1(T^*)$ embodies the attractions. Solving $\partial_\rho p = \partial_\rho^2 p = 0$, as usual, yields ρ_c^* and $B_c^* \equiv B_1(T_c^*)/b_0a^3$. At low T, which is relevant here, one has

$$B_1(T^*) \approx -\sum_{\sigma,\tau} b_{\sigma\tau}a^3 x_\sigma x_\tau \exp(\varepsilon_{\sigma\tau}^*/T^*), \qquad (6)$$

where $\varepsilon_{\sigma\tau}^* \equiv \varepsilon_{\sigma\tau}/\varepsilon$, while $b_{\sigma\tau}a^3$ specifies the volume of mutual attractions: this *vanishes* if σ and τ repel.

Now, the x_+x_- term dominates in $B_1(T^*)$ at low T with corrections of relative order $(x_2^2/x_+x_-)e^{-0.414/T^*}$ for $z = 1$ and $2(x_2/x_+)e^{-1/2zT^*}$ for $z \geq 2$. We may then *calibrate* $B_1(T_c^*)/a^3$ by using pure DH theory (2) for which, since association is not considered, $x_+ = x_- = \frac{1}{2}$. Thereby we obtain the E_{DH} estimates

$$T_c^*(z) \simeq 1/[16 + |\ln 4x_+^c(z)x_-^c(z)|], \qquad (7)$$

in which $x_+^c \propto y_+^c$ and $x_-^c \propto y_-^c$ follow from Table II.

The resulting predictions are listed in Table I under E_{DH}. In light of the heuristic nature of the arguments, they reflect the trend of the MC and CI values surprisingly well. Certainly the contention that association is a prime factor is well confirmed. By replacing 16 by 20.27 (or 17.96) in (7), and the factor 4 by $1/x_+^c(1)x_-^c(1)$, one calibrates $B_1(T_c^*)$ on the MC (or CI) values for the RPM. Column E_{MC} in Table I lists the MC-calibrated values: for $z = 2$

TABLE II. Inverse screening length κ and fractions, $y_\sigma = n_\sigma N_\sigma/N$, of ions in clusters of n_σ ions at criticality, as percentages, according to DHBjCIHC theory [4].

z	$\kappa_c a$	y_+^c	y_-^c	y_2^c	y_3^c	y_4^c
1	1.04	9.14	9.14	81.72	$\cdots$	$\cdots$
2	1.37	1.31	10.33	15.43	72.93	$\cdots$
3	1.57	0.34	8.04	3.32	11.13	77.17

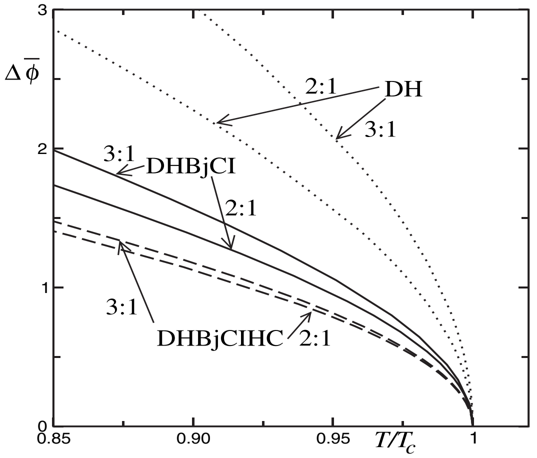

FIG. 4. Reduced Galvani potentials, $\Delta\bar{\phi} = q_0\Delta\phi/k_BT$, vs T/T_c for z:1 electrolytes according to pure DH theory (dotted lines) and DHBjCI(HC) theories: solid (dashed) plots.

and 3 these match the Monte Carlo estimates to within 1% and 8%, respectively.

Now, for the critical density, the significance of ion pairing is already clear in *pure* DHBj theory for the RPM [5]. The heavy depletion of the free ions (which, in DHBj theory, drive the transition *alone*) means that to reach criticality the overall density ρ ($=\rho_+ + \rho_- + 2\rho_2$) must be increased until the DH criterion $\rho_+^* + \rho_-^* = \rho_{\rm DH}^{*c} = 1/64\pi$ is met: see (2). Does the same depletion-by-association mechanism account for the z dependence of $\rho_c^*(z)$?

To progress, rewrite (1) generally as $\kappa^2a^2 = 4\pi\rho^\dagger/T^*$, with the *effective, depleted ionic density*

$$\rho^\dagger \equiv \rho^*\sum_\sigma z_\sigma^2 y_\sigma(T;\{\rho_\sigma\})/zn_\sigma. \tag{8}$$

If one accepts the DH criterion and uses Table II, the estimates E_ρ, in Table I, result. Although these fall short of the Monte Carlo values by 74%, 54%, and 44% for $z = 1$–3, they reproduce the accelerating increase with z (by factors 1.57, 1.63 vs 1.24, 1.34).

An alternative approach adopts the DH value $\kappa_c a = 1$: see (2) but note from Table II that DHBjCIHC theory implies that $\kappa_c a$ rises from 1.04 for the RPM to 1.57 for $z = 3$. Then using the $E_{\rm DH}$ values for T_c^*, in Table I, leads to the E_κ predictions for $\rho_c^*(z)$: these are all rather low but the increases with z, by factors 1.47 and 1.55, again reflect the correct behavior.

Finally, we note that the Galvani potential, $\Delta\phi$, that arises between coexisting phases in charge-asymmetric fluids is readily calculated [4,6]. The predictions from pure DH theory are shown dotted in Fig. 4: one finds $\Delta\phi_{\rm DH} \propto (1 - z^{-1})$. The other plots result from the DHBjCI and DHBjCIHC theories [4]. Surprisingly, the calculations suggest no clear trend with z. It is natural to conjecture that $\Delta\phi$ vanishes as $G_0(T_c - T)^\beta$; moreover, to the extent that the expected mean-field value $\beta = \frac{1}{2}$ is realized, the present results support this.

In conclusion, we have elucidated the mechanisms underlying how multivalency influences critical behavior. Specifically, we have summarized briefly analytical calculations for 3:1, 2:1, and 1:1 equisized charged hard-sphere fluids [4] that, for the first time, reasonably reflect the true variation of critical temperatures and densities, $T_c^*(z)$ and $\rho_c^*(z)$ (as revealed by simulations [2]). On that basis, supported by analysis that correlates $T_c^*(z)$ and $\rho_c^*(z)$ with the increasingly depleted populations of free ions and charged clusters as z increases, it is clear that recognizing ionic association is inescapable for a successful theory. Previous treatments [3,7–9], lacking allowance for ion clusters fail seriously. The ion-cluster solvation theories also yield quantitative results for the interphase Galvani potentials.

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