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THEORY OF NUCLEATION ON CHARGED NUCLEI. 5. CHEMICAL POTENTIAL OF VAPOR ON THRESHOLD OF BARRIERLESS NUCLEATION, AND ASYMMETRY OF CHEMICAL POTENTIAL RELATIVE TO SIGN OF NUCLEAR CHARGE

F. M. Kuni, A. K. Shchëkin, and A. I. Rusanov

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An analytical relationship has been derived for the chemical potential of vapor as a function of the magnitude and sign of the nuclear charge on the threshold of barrierless nucleation.

The presence of charged nuclei in a supersaturated vapor lowers the level of the chemical potential on the threshold of barrierless nucleation. The threshold chemical potential depends on the magnitude of the nuclear charge. A finer effect — especially nonlinear with respect to the field — is the senstivity of the threshold chemical potential to the sign of the charge. The present work has been devoted to a study of the dependence of the threshold chemical potential of vapor on the magnitude and sign of the nuclear charge. The development of this relationship is based on general thermodynamic theory [1] and a procedure of series expansion in the curvature parameter [2, 3] for a drop in the electric field of the nucleus, this drop containing in its surface layer a spontaneous dipole moment.

For the vapor that is in equilibrium with the drops, the dimensionless chemical potential b_ν (expressed in heat units kT and referred to the value for a plane interface in the absence of a field), as a function of the number of molecules of the drop ν, has the following form as given in [3, Eq. (17)]:

$$b_\nu = \frac{2}{3} a\nu^{-1/3}\left[1 - \left(c_1 + \frac{1}{6}c_2\right)\nu^{-1/3} + c_5\nu^{-1}\right]$$
$$-\frac{1}{3}a_q\nu^{-4/3}\left[1 + 2\left(c_1 + \frac{1}{3}c_2 - c_4\right)\nu^{-1/3} - \frac{5}{6}c_3\nu^{-4/3} + 4\left(c_5 - \frac{2}{3}c_6\right)\nu^{-1}\right] \quad (1)$$

where, as in [3, Eq. (10)],

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$$c_1 \equiv (4\pi\rho_\infty^\alpha/3)^{1/3}\lambda_\infty, \quad c_2 \equiv 2\,(4\pi\rho_\infty^\alpha/3)^{2/3}\chi_\infty\gamma_\infty$$
$$c_3 \equiv (4\pi\rho_\infty^\alpha/3)^{4/3}\chi_\infty u_\infty q^2, \quad c_4 \equiv (4\pi\rho_\infty^\alpha/3)^{1/3} k_1/2u_\infty \tag{2}$$
$$c_5 \equiv \frac{4\pi}{3} q \left(\frac{d\mathcal{P}_0}{d\mu}\right)_\infty, \quad c_6 \equiv \frac{2\pi}{3}\frac{\rho_\infty^\alpha k_2 q}{u_\infty}$$

and as in [3, (14) and (15)],

$$a \equiv \frac{4\pi\gamma_\infty}{kT}\left(\frac{3}{4\pi\rho_\infty^\alpha}\right)^{2/3}, \quad a_q \equiv \frac{4\pi u_\infty q^2}{kT}\left(\frac{4\pi\rho_\infty^\alpha}{3}\right)^{1/3}. \tag{3}$$

All of the notation used in [1-3] has been kept intact. The terms with coefficients c_1, .. c_6 in (1) are correction factors. The products of such terms will be neglected, as was done previously.

In accordance with (2) and (3), the following identity given in [3, Eq. (16)] is valid

$$ac_3 = \frac{1}{2} a_q c_2 \quad . \tag{4}$$

When we take into account the results that are already known to us, as given in [2, Eq (33) and (44)], we conclude from (2) that $c_4 \sim c_1$ and $c_6 \sim c_5$ (which signifies in particular that c_6 and c_5 have the same sign), and

$$c_5 = -4\pi\varkappa q\mathcal{P}_{0\infty}/3kT, \ \varkappa \sim 1 \ (\varkappa > 0) \quad . \tag{5}$$

As ean be seen from (2), the coefficients c_5 and c_6 have the feature that they are odd (uneven) with respect to charge. We will break up Eq. (1) into parts that are even and odd with respect to charge. We will use superscripts "+" and "–" for the respective cases $q = |q|$ and $q = -|q|$. Subsequently setting $c_6 = c_5$ for simplicity, we obtain in place of (1)

$$b_\nu^\pm = b_\nu^0 \pm b_\nu^1 \tag{6}$$

where

$$b_\nu^0 \equiv \frac{2}{3} a\nu^{-1/3}\left[1 - \left(c_1 + \frac{1}{6}c_2\right)\nu^{-1/3}\right] - \frac{1}{3}a_q\nu^{-4/3}\left[1 + 2\left(c_1 + \frac{1}{3}c_2 - c_4\right)\nu^{-1/3} - \frac{5}{6}c_3\nu^{-4/3}\right] \tag{7}$$

$$b_\nu^1 \equiv \left(\frac{2}{3}a\nu^{-4/3} - \frac{4}{9}a_q\nu^{-7/3}\right)c_5^+ \quad . \tag{8}$$

Obviously, the multiplier of c_5^+ in (8) vanishes at the point

$$\tilde{\nu} = 2a_q/3a \tag{9}$$

being positive when $\nu > \tilde{\nu}$ and negative when $\nu < \tilde{\nu}$. Now noting that from (6) it follows that

$$b_\nu^+ - b_\nu^- = 2b_\nu^1 \tag{10}$$

we conclude

$$\left.\begin{aligned} b_\nu^+ - b_\nu^- > 0 \text{ when } \nu > \tilde{\nu} \\ b_\nu^+ - b_\nu^- < 0 \text{ when } \nu < \tilde{\nu} \end{aligned}\right\} (c_5^+ > 0) \tag{11}$$

and

$$\left.\begin{aligned} b_\nu^+ - b_\nu^- < 0 \text{ when } \nu > \tilde{\nu} \\ b_\nu^+ - b_\nu^- > 0 \text{ when } \nu < \tilde{\nu} \end{aligned}\right\} (c_5^+ < 0) \quad . \tag{12}$$

Calculating by the use of (7) the value of b_ν^0 at the point $\nu = \tilde{\nu}$, which can be determined by the equality (9), and considering that b_ν^1 vanishes at this point, we obtain from (6), after applying the identity (4),

$$b_{\tilde{\nu}}^\pm = \frac{1}{6} a\left(\frac{2a_q}{3a}\right)^{-1/3}\left[1 - 10\left(c_1 + \frac{19}{240}c_2 - \frac{3}{5}c_4\right)\left(\frac{2a_q}{3a}\right)^{-1/3}\right] \quad . \tag{13}$$

It should be noted that the value of $\tilde{\nu}$ as defined by the equality (9), with $q = \pm q_0$ (q_0 is the elementary charge), lies close to values on the order of 1-10, such that Eqs. (10)-(13) are only approximations.

of b_ν^+ from b_ν^0 in (6) is also odd with respect to q. In higher orders with respect to $c_m\nu_0^{-1/3}$, the difference $\nu^\pm - \nu_0$ may contain terms that are both odd and even with respect to q. Although these terms are outside the framework of the second approximation with respect to curvature, we must keep in view the possibility in principle that they may appear. Summarizing, we write

$$\nu^\pm - \nu_0 = \pm\nu_1 + \nu_2 \tag{23}$$

$$|b_\nu^1/b_\nu^0| \lesssim c_m\nu^{-1/3}, \quad |\nu_1/\nu_0| \lesssim c_m\nu_0^{-1/3}, \quad |\nu_2/\nu_0| \lesssim c_m^2\nu_0^{-2/3} \tag{24}$$

(ν_1 and ν_2 are certain quantities, the explicit values of which are not required).

Expanding $b_{\nu+}^0$ and $b_{\nu-}^0$ in the vicinity of the point ν_0 in Taylor series, and taking (14) and (23)-(24) into account, we obtain for the first term in the right-hand side of (21)

$$b_{\nu+}^0 + b_{\nu-}^0 = 2b_{\nu_0}^0 + \frac{1}{2!}\frac{d^2b_\nu^0}{d\nu^2}\bigg|_{\nu=\nu_0}[(\nu_1+\nu_2)^2 + (\nu_1-\nu_2)^2] + \ldots = 2b_{\nu_0}^0[1 + 0(c_m^2\nu_0^{-2/3})] \tag{25}$$

where it is noted that the differentiation, with respect to ν, of the power function of ν (all of the functions we are considering are just such functions) gives rise to an additional factor of smallness ν^{-1}. This remark will be kept in view in the subsequent calculations. Next, expanding $b_{\nu+}^1$ and $b_{\nu-}^1$ in the vicinity of the point ν_0 in a Taylor series, and taking (23)-(24) into account, we obtain for the second term in the right-hand side of (21)

$$b_{\nu+}^1 - b_{\nu-}^1 = \frac{db_\nu^1}{d\nu}\bigg|_{\nu=\nu_0}\cdot 2\nu_1 + \ldots = b_{\nu_0}^0 0(c_m^2\nu_0^{-2/3}) \quad . \tag{26}$$

From (21), (25), and (26), and also considering the first of the relationships in (20), it follows that

$$b^s = b^0{}_{\nu_0} \tag{27}$$

where the relative error has the order of $c_m^2\nu_0^{-2/3}$, the same as in the entire theory of expansion with respect to the curvature parameter.

Next, again expanding $b_{\nu+}^0$ and $b_{\nu-}^0$ in the vicinity of the point ν_0 in a Taylor series, and taking (14) and (23)-(24) into account, we obtain for the first term in the right-hand side of (22)

$$b_{\nu+}^0 - b_{\nu-}^0 = \frac{1}{2!}\frac{d^2b_\nu^0}{d\nu^2}\bigg|_{\nu=\nu_0}[(\nu_1+\nu_2)^2 - (\nu_1-\nu_2)^2] + \frac{1}{3!}\frac{d^3b_\nu^0}{d\nu^3}\bigg|_{\nu=\nu_0}[(\nu_1+\nu_2)^3 + (\nu_1-\nu_2)^3] + \ldots = b_{\nu_0}^1 0(c_m^2\nu_0^{-2/3}) \quad . \tag{28}$$

Equation (28) shows that ν_2 can make a contribution on the same order of magnitude as ν_1; therefore, we have also brought ν_2 into the analysis. Next, again expanding $b_{\nu+}^1$ and $b_{\nu-}^1$ in the vicinity of the point ν_0 in a Taylor series, and taking into account (23)-(24), we obtain for the second term in the right-hand side of (22)

$$b_{\nu+}^1 + b_{\nu-}^1 = 2b_{\nu_0}^1 + \frac{db_\nu^1}{d\nu}\bigg|_{\nu=\nu_0}\cdot 2\nu_2 + \frac{1}{2!}\frac{d^2b_\nu^1}{d\nu^2}\bigg|_{\nu=\nu_0}[(\nu_1+\nu_2)^2 + (\nu_1-\nu_2)^2] + \ldots = 2b_{\nu_0}^1[1 + 0(c_m^2\nu_0^{-2/3})] \quad . \tag{29}$$

From (22), (28), and (29), and taking into account the second of the relationships in (20), it follows that

$$b^a = 2b_{\nu_0}^1 \tag{30}$$

where the relative error has the previous order of magnitude $c_m^2\nu_0^{-2/3}$. The explicit values of ν_1 and ν_2 did not actually appear in the final results (27) and (30).

The calculation of the right-hand sides of the equalities (27) and (30) is accomplished on the basis of Eqs. (7) and (8) by means of the value of ν_0 defined by the relationship (17) [the correction terms in (7) are already found by means of the formula of first approximation (16) for the value of ν_0]. As a result, we have

$$b^s = \frac{1}{2}a\left(\frac{2a_q}{a}\right)^{-1/3}\left[1 - 2\left(c_1 + \frac{3}{16}c_2 - \frac{1}{3}c_4\right)\left(\frac{2a_q}{a}\right)^{-1/3}\right] \tag{31}$$

where we have taken into account the identity (4); and

$$b^a = \frac{8}{9} a \left(\frac{2a_q}{a}\right)^{-4/3} \left[1 - \frac{15}{4}\left(c_1 + \frac{1}{6}c_2 - \frac{5}{9}c_4\right)\left(\frac{2a_q}{a}\right)^{-1/3}\right] c_5^+ \tag{32}$$

[we have retained in (32) the correction terms, even though the corrections to Eq. (8) itself may be of the same order of magnitude]. Dividing (32) by (31), we also obtain

$$\frac{b^a}{b^s} = \frac{16}{9}\left(\frac{2a_q}{a}\right)^{-1} \left[1 - \frac{7}{4}\left(c_1 + \frac{1}{7}c_2 - \frac{17}{21}c_4\right)\left(\frac{2a_q}{a}\right)^{-1/3}\right] c_5^+ \tag{33}$$

which determines the relation of the fine structure of the doublet of chemical potential values to the center of the doublet. A comparison of Eq. (31) (in which c_5^+ does not appear) with experimental results can provide information on the coefficient c_4 and thereby can serve as a criterion of the consideration of an adsorption nature of the induced surface polarization $\mathcal{P}$, that was used in [2] as a basis for the estimate $c_4 \sim c_1$.

According to (27), (30), and the first of the estimates (24), the ratio $|b^a/b^s|$ does not exceed the order of magnitude of the curvature parameter $c_m \nu_0^{-1/3} \sim c_m(2a_q/a)^{-1/3}$. In the case in which $|c_5^+| \lesssim 1$, it follows directly from (33) that $|b^a/b^s| \lesssim (2a_q/a)^{-1} \sim \nu_0^{-1}$, which gives still smaller value for the ratio $|b^a/b^s|$.

Let us recall now that in the original expression for the chemical potential in terms of the radius of the tension surface r [2, Eq. (43)], it was not the coefficient c_5 that was present in the parameters δ_6, but the coefficient c_6. The appearance of terms with the coefficient c_5 in (1) is due entirely to the change from the independent variable r to the independent ν [3, Eq. (12)]. We can say that the coefficient c_5 (in the parameter δ_5) describes only the shift in reference point for the variable ν. This shift (along with that related to the presence of the nucleus in the drop [3]) does not influence, however, the maximum value of the function $b_\nu^\pm$. From this it is evident that if we had not made the simplifying assumption $c_6 = c_5$ in Eq. (6), then in Eqs. (32) and (33) in place of c_5^+ we would have the coefficient c_6^+. However, since c_6^+ and c_5^+ have the same physical nature and are close in order of magnitude and identical in sign, we will not give any further consideration to this difference.

We will now determine the limitations on the charge $q \equiv zq_0$ ($z = 1, 2, \ldots$) for which Eqs. (14)-(33) are valid. It is obviously necessary that the value of ν_0 determined by the formula of the first approximation (16) must satisfy the conditions we found previously for applicability of the explansion in the curvature parameter ([3, Eq. (32)]*

$$c_m \nu^{-1/3} \ll 1, \quad z^2 (c_3^0/c_m)\nu^{-1} \lesssim 1, \quad |z|(|c_5^0|/c_m)\nu^{-2/3} \lesssim 1 \tag{34}$$

where $c_3^0 \equiv c_3/z^2$, $c_5^0 \equiv c_5/z$ [i.e., c_3^0 and c_5^0 are obtained from the coefficients c_3 and c_5 determined from Eqs. (2) and (5) by replacing q by q_0, so that these quantities do not depend on z].

Here also, actually, the correction to ν_0 itself that is given by the formula of the second approximation (17) and the additional correction ν_1 (and all the more ν_2) for the root $\nu^\pm$ in (23), will not be relatively small, such that in the end, the conditions (34) will be observed for $\nu = \nu^\pm$ as well (which, strictly speaking, should not be required). Thus, we substitute into (34) in place of ν the value of ν_0 determined from Eq. (16). Considering the equality $a_q = z^2 a_{q_0}$ that ensues from (3) (a_{q_0} does not depend on z), and also using the identity (4), we obtain

$$\frac{c_m}{|z|^{2/3}}\left(\frac{2a_{q_0}}{a}\right)^{-1/3} \ll 1, \quad \frac{c_2}{4c_m} \lesssim 1, \quad \frac{|c_5^0|}{|z|^{1/3} c_m}\left(\frac{2a_{q_0}}{a}\right)^{-2/3} \lesssim 1. \tag{35}$$

The second of the conditions (35) is not related to the charge, and it is always fulfilled. The first and third of the conditions (35) impose a lower limit on $|z|$. This limit will be less restrictive for larger values of $2a_{q_0}/a$ (of course, we should still remember the limitation $|z| \geqslant 1$ due to the existence of the elementary charge).

Considering c_m and $2a_{q_0}/a$ as assigned, we will determine what values of c_5^0 and z will give a maximum in the ratio $|b^a/b^s|$ within the limits of applicability of the theory, and will also determine the order of magnitude of this maximum. Segregating in (33) the dependence on z and limiting ourselves to the first approximation (for which we can be sure), we have

*In accordance with what was said in [3], we have replaced c_1 by c_m in (34), where c_m is the greater of the values c_1 and c_2.

$$|b^a/b^s| = \frac{16}{9}\,[(|c_5^0|/|z|)\,(2a_{q_0}/a)^{-1}]\,. \tag{36}$$

As the maximum allowable value of the curvature parameter $c_m \nu_0^{-1/3}$ appearing in the left-hand side of the first of the inequalities (35) we can take $\sim 1/5$. Obviously, the left-hand sides of the first and third of the inequalities (35) reach their maximum values of $\sim 1/5$ and ~ 1 simultaneously, with

$$|c_5^0| \sim 5^{1/4} c_m^{3/2} (2a_{q_0}/a)^{1/2},\quad |z| \sim 5^{3/2} c_m^{3/2} (2a_{q_0}/a)^{-1/2} \tag{37}$$

Here, the product of the left-hand sides of these inequalities also reaches its maximum value $\sim 1/5$. The value of $|b^a/b^s|$, according to (36), is equal to this particular product, to within a factor of 16/9. We can see that the relationships (37) determine the optimal values of c_5° and z (within the limits of applicability of the theory) at which $|b^a/b^s|$ has a maximum. This is equal to

$$|b^a/b^s|_{\max} \sim 16/45 \simeq 0.36 \tag{38}$$

and hence is completely independent of c_m and $2a_{q_0}/a$. Since $|z|$ actually assume only integral values 1, 2, 3, ..., the realization of the maximum still requires that the right-hand side of the second of the relationships (37) must lie close to one of such values. It is actually necessary for it to be considerably less than unity. If this condition is not fulfilled with given values of c_m and $2a_{q_0}/a$, then the corresponding substance cannot manifest any significant sign asymmetry of the thresholds of barrierless nucleation, whatever may really be the values of $|c_5^\circ|$ and $|z|$ compatible with the third of the inequalities (35).

Just as close to the optimal values of c_5° and z that are required by the relationships (37) do we find reinforcement of the process of forming water drops on singly charged ions ($z = \pm 1$) at a temperature $\sim 0°C$. Using the available data for water, we have in accordance with (2), (3), and (5): $c_1 \simeq c_4 \simeq 0.5$, $c_2 \simeq 0.36$, $c_5^\circ \simeq 1.4\varkappa$, $a \simeq 9.9$, and $a_{q_0} \simeq 160$ (for water, $\mathcal{P}_{0\infty} < 0$* and $4\pi q_0 \mathcal{P}_{0\infty}/kT \simeq -4.2$ [4-7]). Next (with $z = \pm 1$, i.e., $q = \pm q_0$), we find from (9) and (13): $\tilde{\nu} \simeq 11$ and $b_{\tilde{\nu}}^{\pm} = 0.016$. Since along with $c_5^\circ > 0$, the condition $c_5^+ > 0$ is also fulfilled, it then follows from (11) that $b_\nu^+ - b_\nu^- > 0$ when $\nu \gtrsim 11$. Now we have $2a_{q_0}/a \simeq 32$, and, according to (17), $\nu_0 \simeq 43$. By means of (31) and (33) we find $b^s \simeq 1.2$ and $b^a/b^s \simeq 0.075\varkappa$. The value of b^s is close to that observed experimentally [8, 9]. This provides support for the estimate $c_4 \sim c_1$ (adsorption nature of $\mathcal{P}_e$). As regards the ratio b^a/b^s, according to [8] and [9], this ratio is +0.19 and +0.11, respectively, where we have particularly emphasized that in either case the value is positive. This means that the experiment requires that the values of $\varkappa$ are positive. We came to the same conclusion in [2] by means of two theoretical arguments that provide mutual support for each other. The agreement with experiment will be not only qualitative but also quantitative if we set $\varkappa \simeq +2.5$ (i.e., $c_5^\circ \simeq 3.5$) and $\varkappa \simeq +1.5$ (i.e., $c_5^\circ \simeq 2.1$) on the basis of data from [8] and [9], respectively. This is also in agreement with a theoretical prediction [2] of the order of magnitude of $\varkappa$. With the value of $\varkappa$ found from experiment, the left-hand side of the last of the inequalities of (35) is no greater than 0.7, which is adequate for fulfillment of this inequality with some reserve. The left-hand side of the first of the inequalities of (35) is equal to approximately 0.16, such that this inequality also (a strong inequality) can be considered to be fulfilled for practical purposes. The fact that the experimentally observed value of b^a/b^s is somewhat smaller than that allowed by the estimate (38) is explained by the deviation of the actual values $|c_5^\circ| \sim 2.1$-3.5 and $|z| = 1$ from the optimal values $|c_5^\circ| \sim 4$ and $|z| \sim 0.7$ that are required by the relationships of (37) (with $c_m \simeq 0.5$ and $2a_{q_0}/a \simeq 32$).

When we speak of a comparison with experiment, we should keep in view that rapid generation of drops as the chemical potential of the vapor is increased† may begin, owing to an increase of fluctuations, slightly before the threshold of barrierless nucleation.

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*The directions starting from the center of the drop are positive.

†In the experiments in [8, 9], the vapor was expanded adiabatically, which also led to an increase in the dimensionless chemical potential that we used (expressed in units of kT and referred to the value at a plane interface in the absence of a field).

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