

Electric-field-induced condensation: An extension of the Kelvin equationHans-Jürgen Butt,* Maria B. Untch, Ali Golriz, Sascha A. Pihan, and Rüdiger Berger
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The Kelvin equation relates the vapor pressure of a volatile liquid to the curvature of the liquid surface. It describes phenomena such as capillary condensation, capillary adhesion, nucleation, and the adsorption of vapors into porous media. Here we propose an extension of the Kelvin equation, which takes into account changes of the vapor pressure due to electric fields. The presence of electric fields reduces the saturation vapor pressure and leads to field-induced condensation. Field-induced condensation can explain the presence of water bridges in scanning probe nanolithographic methods such as anodic oxidation.

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I. INTRODUCTION

Since the invention of the scanning tunneling microscope (STM) [1] and the atomic force microscope (AFM) [2], different methods of nanolithography have been developed. In many of these methods a high electric potential is applied between the tip of the STM [3–5] or AFM [6–11] and the sample. One prominent example is anodic oxidation, also called field-enhanced oxidation [4,9,10]. In anodic oxidation a potential difference of typically 4–10 V is applied between a conducting substrate and the conducting tip, the tip being negative. Electrochemical reactions are supposed to lead to a local oxidation of the substrate surface [5,12,13]. With anodic oxidation structures as small as a few tens of nanometers in width have been written into silicon [4,6–8,12], titanium [5,9,12], and GaAs [14].

Anodic oxidation is applied in air. For electrochemistry to work, water needs to be present. Indeed, the nanostructures formed and the voltage required to form the nanostructures depend on humidity [15]. It is generally accepted that an aqueous bridge is formed between the substrate and the tip from adsorbed water and by capillary condensation [13]. Indications for the existence of a water bridge are the observation that anodic oxidation takes place even when tip and substrate are not in contact but are separated by few nanometers [16] and an increased adhesion at high humidity [14]. Water in the form of an adsorbed film or a capillary bridge also plays a decisive role in the STM imaging of DNA on insulating substrates such as mica [17,18] and in the etching of pits into highly oriented pyrolytic graphite (HOPG) [19,20].

That water menisci form between two surfaces in close proximity or even in contact is well established (for review see [21]). A prerequisite is that the surfaces are hydrophilic and that the contact angle with respect to water is much below 90°. Recently, 20–25-nm-thick poly(methylmethacrylate) films on gold [22] and 70–90-nm-thick polystyrene and poly(*N*-vinyl carbazole) films on silicon wafers [23] have been modified by applying voltage pulses of 7–18 and 40 V, respectively, to the tip of an AFM. Again, humidity had a strong influence on the resulting structures. In this case the formation of a water bridge is hindered by the fact that the polymer surface is hydrophobic.

These observations motivated us to further analyze the fundamentals of capillary condensation in the presence of high electric fields. Thermodynamic theory [24] and computer simulations [25–28] show that the presence of strong electric fields increases the boiling point of a liquid [29]. It is also well established that the presence of free ions reduces the energy barrier for nucleation (see [30–32] and references therein). Ion-mediated nucleation is the basis for the function of cloud chambers and is relevant in atmospheric aerosol nucleation [33]. In scanning-probe-based nanolithographic methods the applied electric field can induce capillary condensation. Such an effect was already described by Gómez-Monivas *et al.* [34]. They showed that the formation of a water bridge between a hydrophilic sphere and a plate is enhanced by the electric field. We extend this approach and derive a generalized Kelvin equation, which relates the field strength to a change in the saturation vapor pressure. The Kelvin equation relates the vapor pressure of a volatile liquid to the curvature of the liquid surface. It describes phenomena such as capillary condensation, capillary adhesion, nucleation, and the adsorption of vapors into porous media.

II. THEORY

Derivation of the modified Kelvin equation. The energy density (energy per unit volume) of an electric field is [35]

$$u = \frac{\epsilon\epsilon_0}{2} E^2. \quad (1)$$

Here, ϵ_0 is the vacuum permittivity and E is the field strength. The energy density depends on the relative dielectric permittivity of the intervening medium ϵ . As a consequence, material with a high relative permittivity is drawn into an electric field.

Let us consider a system which is in contact with a reservoir of vapor at constant temperature and vapor pressure P (Fig. 1). Let P_0 be the saturation vapor pressure of the liquid with a planar surface and in the absence of an electric field. We assume that the actual vapor pressure is below the saturation vapor pressure P_0 ($P < P_0$) so that the vapor does not condense. In a small region of the system we apply an electric field. In that region condensation is favored because an energy given by Eq. (1) is gained by condensation. As a result the saturation vapor pressure at which condensation sets in is lowered from P_0 to P_0^E .

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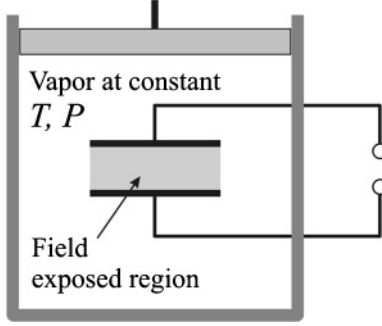


FIG. 1. Schematic of the system considered.

The molar Gibbs energy changes when the liquid is exposed to an electric field. The change of the Gibbs energy per mole of liquid is

$$\Delta G_m = -\frac{(\varepsilon - 1)\varepsilon_0}{2} V_m E^2. \quad (2)$$

Here, V_m is the molar volume of the liquid.

If we assume that the system is in equilibrium, the molar Gibbs energy of the vapor is equal to the molar Gibbs energy of the liquid. The molar Gibbs energy of the vapor depends on the vapor pressure. For a vapor in equilibrium with the liquid in the absence of electric fields it is [36]

$$G_m = G_m^0 + RT \ln P_0. \quad (3)$$

Here, R is the gas constant and T the temperature. For simplicity we assumed that the vapor behaves like an ideal gas. Inside the electric field the Gibbs energy per mole of vapor is

$$G_m^E = G_m^0 + RT \ln P_0^E. \quad (4)$$

In equilibrium the change in molar Gibbs energy in the vapor,

$$\Delta G_m = G_m^E - G_m = RT \ln \frac{P_0^E}{P_0}, \quad (5)$$

is equal to the change in molar Gibbs energy of the liquid Eq. (1). This leads to

$$\ln \frac{P_0^E}{P_0} = -\frac{V_m(\varepsilon - 1)\varepsilon_0 E^2}{2RT}. \quad (6)$$

As for any condensed material $\varepsilon > 1$, the right-hand side is negative, and the saturation vapor pressure is decreased by the presence of an electric field: $P_0^E < P_0$.

This treatment is valid for planar liquid surfaces. To include the effect of curvature we add a term $\gamma V_m C$ to the right-hand side of Eq. (6) [37]. Here, C is the curvature of the surface described by the two principle radii of curvature r_1 and r_2 by $C = 1/r_1 + 1/r_2$. A concave shape towards the condensed phase is counted positive, a convex shape is negative. This leads to a change in the vapor pressure:

$$\ln \frac{P_0^E}{P_0} = -\frac{V_m}{RT} [(\varepsilon - 1)\varepsilon_0 E^2/2 - \gamma C]. \quad (7)$$

Equation (7) is an extended Kelvin equation, which takes the effect of an electric field into account.

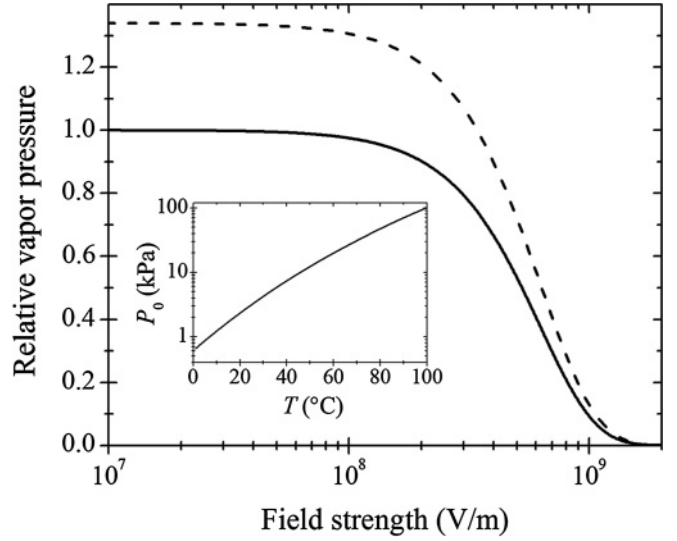


FIG. 2. Relative saturation vapor pressure versus electric field strength for water at 25 °C (solid line). The dashed line shows the relative vapor pressure at which condensation sets in if the exposed region has a temperature of 30 °C. The dielectric permittivity was assumed to be constant. Inset: Saturation vapor pressure of water versus temperature.

III. DISCUSSION

Consequences for scanning probe microscopy. The change in relative vapor pressure versus field strength is plotted in Fig. 2 for water at 25 °C ($\varepsilon = 78.5$, $V_m = 18.0 \times 10^{-6} \text{ m}^3/\text{mol}$). For normal field strengths experienced in daily life or most technical applications the change in saturation vapor pressure is negligible. For example, for $E = 10^8 \text{ V/m}$ the vapor pressure is only reduced by 2.5%. Thus water would condense at a vapor pressure of $P_0^E = 3091 \text{ Pa}$ rather than $P_0 = 3169 \text{ Pa}$. In typical imaging conditions for STM experiments the electric fields are much stronger. Typically the tip is 1 nm away from the substrate surfaces. At a potential of 0.5 V the field reaches $5 \times 10^8 \text{ V/m}$. This already leads to a condensation at 54% relative humidity. In anodic oxidation with the AFM, typical separations between the conducting part of the substrate and the tip are 10 nm and 10 V, leading to $E = 10^9 \text{ V/m}$ [7]. Then water condenses at a humidity of 8%. Thus, the electric fields used in scanning probe microscopy are strong enough to enhance condensation.

The field strength at which field-induced condensation takes place depends on the material properties of the liquid, namely its permittivity and molar volume. It is instructive to define a critical field strength at which the relative saturation vapor pressure has decreased to $1/e$. According to Eq. (6) for a planar liquid surface it is given by

$$e_C = \sqrt{\frac{2RT}{V_m(\varepsilon - 1)\varepsilon_0}}. \quad (8)$$

For polar liquids a typical critical field strength is $6 \times 10^8 \text{ V/m}$, assuming that ε is constant (Table I). Nonpolar liquids condense around $2 \times 10^9 \text{ V/m}$. To be precise one should take into account that the dielectric permittivity depends on the field strength. For water it remains constant within 10% up

TABLE I. Critical field strength E_C for common liquids with a planar surface calculated with Eq. (8) at 20 °C together with the relative permittivity ϵ , the surface tension γ , and the molar volume V_m (liquid), and assuming that ϵ is constant. In addition, the relative saturation vapor pressure for a radius of curvature of 1 nm in the absence (P/P_0) and presence (P^E/P_0) of an electric field of 5×10^8 V/m was calculated with Eq. (7).

	V_m (mL/mol)	ϵ	γ (mN/m)	E_C (10^8 V/m)	P/P_0	P_0^E/P_0
Water	18.05	80.1	72.8	6.2	0.58	0.30
Toluene	106.29	2.4	28.4	19.2	0.29	0.27
Chloroform	80.17	4.81	27.5	13.4	0.40	0.35
Pentane	115.22	1.84	16.0	23.9	0.47	0.45
Hexane	130.97	1.89	18.4	21.7	0.35	0.35
Octane	162.72	1.95	21.6	18.9	0.24	0.24
Benzene	89.12	2.28	28.9	22.0	0.35	0.33
Methanol	40.45	33	22.5	6.5	0.69	0.38
Ethanol	58.37	25.3	22.1	6.2	0.59	0.31
1-Propanol	74.80	20.8	23.7	6.1	0.48	0.25
1-Butanol	91.53	17.84	25.4	6.0	0.39	0.19
1-Pentanol	108.24	14.2	25.8	6.2	0.32	0.17
1-Hexanol	125.59	13.03	26.2	6.0	0.26	0.13
Acetone	73.52	21.01	24.0	6.1	0.48	0.25
Decaline (isomeric mixture)	157.10	2.2	31.5	17.1	0.13	0.12

to 10^9 V/m, then starts to decrease proportionally to E^2 , and finally saturates [38–41].

Equation (7) shows that curvature *and* electric field both affect the relative vapor pressure in an additive way. As one example we consider a curvature of $C = -10^9$ m⁻¹. This example represents a lyophilic AFM tip at a distance of 2 nm above a solid surface. The tip itself is assumed not to be sharp so that its radius of curvature is much larger than 1 nm. In that case $C = -10^9$ m⁻¹ corresponds to a liquid meniscus with $r_1 = 1$ nm (counted negative) and r_2 is very large. The example also represents the condensation of liquid in cylindrical pores of 2 nm radius ($r_1 = r_2 = 2$ nm). In the absence of an electric field water vapor would condense at a reduced pressure of 58% of the saturation vapor pressure of a planar liquid surface (Table I). In absolute values, the saturation vapor pressure with respect to a planar surface is 2339 Pa. Condensation in the gap of 2 nm separation would already occur at 1364 Pa. When in addition applying an electric field of 5×10^8 V/m the vapor pressure would further be reduced to 30% or 713 Pa. Table I shows that the influence of curvature is particularly strong for molecules with a low surface tension. The electric field affects mainly polar molecules. Both effects are more pronounced for small molecules. Please note that we used the values of the surface tension for a planar surface at zero electric field. As a first approximation we assumed that the surface tension does not change for a curved surface and when applying a field. At the high curvatures and at the high electric fields considered this may not be a good approximation.

In practical applications condensation is often counterbalanced by a local increase in temperature. If, for example, an electric current is flowing, Joule heating will increase the local temperature. When the temperature in the field-exposed region is higher than in the reservoir, condensation is hindered because the vapor pressure increases with temperature. For water the temperature dependence of the saturation vapor pressure can be described by [42]

$$\ln\left(\frac{P_0}{P_C}\right) = \frac{T_C}{T} (A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^{3.5} + A_5\tau^4 + A_6\tau^{7.5}) \quad \text{with } \tau = \frac{T_C - T}{T_C}. \quad (9)$$

$T_C = 647.096$ K and $P_C = 22\,064$ kPa are the critical temperature and pressure of water. The empirical constants are $A_1 = -7.859\,517\,83$, $A_2 = 1.844\,082\,59$, $A_3 = -11.786\,649\,7$, $A_4 = 22.680\,741\,1$, $A_5 = -15.961\,871\,9$, and $A_6 = 1.801\,225\,02$.

As one example the effect of a local increase of temperature by 5 K is shown as a dashed line in Fig. 2. When the local temperature is 30 °C, rather than 25 °C, an oversaturation of $P/P_0 > 1.34$ would be necessary in the reservoir to initiate condensation in the hot region. As a result water would not condense in the hot region but in the reservoir. Only at field strengths above 3.5×10^8 V/m is condensation favored in the field-exposed region.

Usually capillary condensation is only possible if the contact angles of the liquid and the solid surfaces are significantly below 90°. Otherwise the curvature of the liquid meniscus would be concave with respect to the liquid, leading to an increased vapor pressure. Equation (7) shows that in the presence of a localized electric field capillary condensation can occur even between surfaces which form a contact angle around or above 90°. An additional effect is the change in contact angle when applying an electric field. This effect is called electrowetting (for review see [43]) and it might further enhance capillary condensation.

For applications in scanning probe microscopy two more effects might change the effect of capillary condensation: First, the presence of a liquid meniscus changes the electric field and leads to a modified field distribution [14]. Vice versa, the electric field can modify the shape of the liquid meniscus. Second, we assumed the surface tension of the liquid to be

constant and not to depend on the electric field. Strong fields may, however, change the surface tension of the liquid [44].

Phase separation in mixtures. This treatment is not only applicable to liquid-vapor phase transitions but also to the phase separation between two liquids. Field-induced phase separations have been observed near the critical point in liquid mixtures and polymer solutions (for review see [45]). Therefore, we consider a mixture of a liquid A with B. Let us further assume that for very low molar fraction, B mixes with A. At some molar concentration c_0^B the mixture phase-separates into an A-rich phase and a B-rich phase. If the two phases have different dielectric constants, ϵ_A and ϵ_B , an applied electric field favors or hinders phase separation. The concentration at which phase separation occurs is shifted to

$$\ln \frac{c_0^{BE}}{c_0^B} = -\frac{V_m^B}{RT}[(\epsilon_B - \epsilon_A)\epsilon_0 E^2/2 - \gamma_{AB}C]. \quad (10)$$

Here, c_0^{BE} is the concentration of B at which the two phases separate in the presence of an electric field and a possible curvature of the interface. Since only the ratio of c_0^{BE} and c_0^B enters Eq. (10), the unit, e.g., mol/liter, molar ratio, or volume

percent, is irrelevant. V_m^B is the molar volume of B in the A-rich phase and γ_{AB} is the interfacial tension. The curvature is counted positive if the B-rich phase is concave.

IV. CONCLUSIONS

An extended Kelvin equation has been derived to relate the field strength to the reduction in the vapor pressure at which condensation sets in. The critical field strength is given by the dielectric permittivity and the molar volume of the liquid phase. To induce capillary condensation the electric field needs to be of the order of 10^9 V/m. In scanning tunneling microscopy and in several nanolithographic methods using the AFM such strong fields are applied and capillary condensation has to be taken into account.

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