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Prewetting transition in supercritical argon

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Résumé. — Nous avons obtenu la densité de l'argon au voisinage du point critique à partir de mesures de la constante diélectrique à basse fréquence. Nous avons observé une discontinuité de la densité le long de l'isobare correspondante à 50 atm à une température un peu au-dessus de la température critique. Cette discontinuité suggère une transition de pré-mouillage. Un calcul simple, selon le modèle du champ moyen, réussit à rendre compte de quelques aspects des résultats des mesures.

Abstract. — From the low frequency measurements of the dielectric constant of ultra low impurity liquid argon, we obtain the density of the liquid in the vicinity of the critical point. Along the 50 atm isobar slightly above the critical temperature, we find apparent discontinuity in the density, suggesting proximity to a prewetting transition. A simple mean field theoretical analysis provides a qualitative description of some aspects of this behavior.

1. Introduction.

In the process of measuring the Hall mobility of electrons injected in argon we also measured the low frequency dielectric constant of ultra high purity argon along two supercritical isobars. During these measurements we observed anomalies that suggest the existence of a so called prewetting transition [1, 2]. This is the first example of such a transition in a pure substance. The only previously known example was in a binary fluid system [3].

The fact that the state of an electron emitted from a photocathode into liquid NH₃ might have an energy that is different from what it would have in the bulk of the fluid, was initially suggested by Krohn and Thompson [4] and later experimentally confirmed by Bennet et al. [5]. Such an observation may be interpreted as an indication that the molecules in the immediate vicinity of the photocathode are in a somewhat « ordered » state. Such a state, if it exists, may be produced by the interaction of the dipole moment of the molecule with its image in the metal. Intuitively one might expect that the resulting fluid would then have a larger density near the photocathode.

In the case of rare gas fluids, the individual atoms have no permanent dipole moment but only a dipole moment that fluctuates randomly both in magnitude and direction. The van der Waals interaction between two atoms A and B is normally pictured as the interaction of this random dipole on atom A with the electric dipole it induces on atom B.

In the vicinity of a metal surface, this randomly fluctuating electric dipole moment will interact with its image in the metal. If this interaction is sufficiently large, we may expect that
the fluid density near the metal will be larger than the density in the bulk. In general this
deviation of the density near the surface from the bulk density will have a short range, of the
order of the correlation length. However, as we discuss below, even above the so called
prewetting critical point, remnants of this density deviations may form a macroscopic film.
The remainder of this paper has four sections: the description of the gas purification
procedure, the experimental setup, the experimental results and finally an Ising model
description of the wetting transition which suggests that the experimental result may be a
reflection of the remnants of the density discontinuity associated with the prewetting
transition.

2. Gas purification procedure.

Argon gas whose nominal impurity content was 5 ppm was further purified by initially
condensing it into a vacsorb pump containing 4A molecular sieve [6] that had been activated
in vacuum by heating up to 350 °C. After the liquid argon remained 12 hours in contact with
the molecular sieve the gas was transferred into an all metal system and passed 3 times over Ti
shavings held at \(\approx\) 700 °C, then it was passed two more times over the same Ti shavings
held at room temperature. The system containing the Ti shavings had been previously pumped
and baked so as to reach a pressure \(\approx 10^{-9}\) Torr when the Ti was held at \(\approx 750\) °C and the
remaining system was between 200 °C and 300 °C.

Finally the gas was condensed in a stainless steel sample cell suspended at the end of
a \(\approx 1\) m long 3/4" OD stainless steel tube. The cell and its connecting tube had previously
been baked out so that the limiting pressure before the introduction of the argon was
\(\approx 10^{-10}\) Torr when the system was at room temperature. To maintain the purity of the sample
over the 9 months during which the data reported here as well as other measurements were
taken, non-evaporable getters [7] were in the system near the high pressure valve that isolated
the sample cell from the rest of the vacuum system.

This sample purification procedure was necessary in order to get long electron lifetimes for
a separate experiment in which the Hall mobility measurements were made concurrently with
the present experiment.

The major electron trapping impurity that is normally present in Ar is O\(_2\) with a cross
section \(\approx 10^{-16}\) cm\(^2\) [8]. The other component of air, N\(_2\) has a trapping cross section at least
200 times smaller [8].

The fact that the resulting electron lifetime was \(\approx 10^{-4}\) s, indicates that the oxygen
concentration was in the range of 1 ppb, well below the range estimated by the Ar supplier.
This electron lifetime did not change over a period of 9 months indicating no detectable
change of the impurity content of the fluid.

3. Experimental apparatus.

The sample cell was press fitted into a copper cylinder with 3 mm thick wall and a heater was
wound over it. Inside the cell a 0.13 mm thick copper liner was introduced to further help
maintain a uniform temperature. About 4 cm above the end of the sample cell, a piece of
copper sheet 0.13 mm thick and about 25 cm long was wound around the stainless steel tube
and another heater was wound over it. When the fluid was at the triple point, its level reached
well into this region of the tube. Finally, about 20 cm above the end of the second heater, a
third heater was wound over another smaller piece of copper (about 4 cm wide) and over
about 15 cm of stainless steel tube. The function of this third heater was to assure that there
would be no temperature inversion between the sample cell and the valve held at room
temperature that closed the sample cell. It was also used to adjust the pressure in the system
by changing the position of the liquid vapor boundary (Fig. 1).
Fig. 1. — Sample cell and a small portion of the tube connecting it to the high pressure valve and to the pressure gauge. The electrode assembly pictured in the cut away is suspended in the sample cell. CE is the 3 mm thick wall copper tube into which the sample cell is press fitted. THERM are thermistors used for the temperature control, TC is a thermocouple. HTR are heaters, the top one wound around the copper foil CF that is wrapped around the stainless steel tube supporting the cell. A similar copper foil lines the walls of the sample cell. The capacitor is made out of the electrodes E, E' (platinum on alumina) and the glass spacers F, F'. The remaining electrodes, A, A', D, G, H as well as the spacers B, B', are used in the electrical transport measurements. SS' is the stainless steel wall of the sample cell. The platinum thermometer is located with its axis perpendicular to the plane of the figure, just below B'.
The sample cell and its supporting tube were inserted into another stainless steel tube surrounded by liquid nitrogen. The inside of this second tube was pumped to about $10^{-2}$ Torr so that the energy transfer between the sample cell, its supporting tube and the stainless steel tube immersed into the liquid nitrogen was primarily due to radiation when $T \approx 130$ K.

The function of both the teflon O ring and of the teflon disc at the bottom of figure 1 is to avoid thermal shorts between the sample cell and the walls of the tube containing the heat exchange gas.

The argon pressure was measured with a 16" diameter Bourdon tube gauge (Heise) to an estimated accuracy of $\pm 0.3$ atm. The temperature of the fluid inside the sample cell was measured with a platinum resistor in the 4 wire configuration that was calibrated against a GaAs diode whose calibration could be traced to the NBS. This calibration was checked at the triple point of argon. The current through the platinum resistor was kept at 0.1 ma to assure minimal heat dissipation; near the critical point the power dissipated was $\approx 0.5 \mu$W. The temperature accuracy is estimated at $\pm 0.1$ K.

The dielectric constant was measured by measuring the value of the capacitance of a parallel plate capacitor whose plate separation was $\approx 0.12$ mm and whose area was $1 \text{ cm} \times 5 \text{ cm}$. Such a plate separation is clearly macroscopic so that any measured change of capacity due to condensation of the fluid does not reflect changes taking place over just a few monolayers. This capacitor was located next to the electrodes used for the Hall mobility measurements; these measurements are the subject of a separate publication [9]. The capacitor was made by baking an organic Pt film [10] over 0.6 mm thick alumina plates. In the vicinity of 150 K the thermal conductivity of alumina is $\approx 0.7 \text{ W/cmK}$ [11]. Spacers were made using microscope cover slides. The capacitance was measured using the three wire configuration of a General Radio model 1 615 A transformer ratio bridge. The 1 kHz voltage applied to the bridge was normally kept at 1.3 V r.m.s.; decreasing it 10 times did not have any effect on the measured capacitance. This indicates that the anomaly to be described below, is not caused by the applied electric field. The output of the capacitance bridge was measured using a phase sensitive detector so that the value of the capacitance could be read to $1 \times 10^{-4}$ pF. Random changes of the capacitance associated with vibrations limited the long term reproducibility of the capacitance to about $5 \times 10^{-3}$ pF.

4. Experimental results.

From the measurement of the dielectric constant ($\varepsilon$), the density ($n$) of the fluid can be calculated using Clausius Mossotti relation:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = Mn$$  (1)

$M$ is the Clausius Mossotti constant: $M = 4 \pi \alpha /3$, and $\alpha$ is the polarizability.

In the optical range, the corresponding equation (called the Lorentz Lorentz relation) was used by Teague and Pings [12] who made a detailed study of its applicability in the critical region of argon. An excellent agreement was found between the measured temperature dependence of the difference of the density of the liquid and the density of the gas $(n_L - n_g)$ and the predictions of the theory of critical phenomena. Teague and Pings indicate that the Clausius Mossotti constant changes approximately 1% between the low density gas and the saturated liquid.

Garside et al. [13] made similar measurements in the case of xenon. They find that the constant $M$ varies approximately 4% between the saturated liquid and the low density vapor. They conclude, like Teague and Pings, that $M$ has no anomaly in the critical region.
Thoen and Garland [14] measured the low frequency dielectric constant of xenon near the critical point using a series of capacitors whose plate separation was similar to what was used in the present experiment. Some of these capacitors were above and some were below the liquid vapor separation surface. These authors found no anomaly in the constant $M$ near the critical point.

Initially we measured the dielectric constant of the saturated liquid between the triple point and 147 K. The value of $T_c$ measured by others is between 150.7 K and 150.8 K. Since the value of the density could be independently calculated with the approximate equation of state [15] using as inputs the pressure and temperature of the fluid, the Clausius-Mossotti constant could be calculated. A least-square fit to a series of 98 measurements gave $M = (4.110 \pm 0.001) \times 10^{-3}$ $\text{m}^3/\text{mol}$. This is to be compared with the result of Amey and Cole [16] at the triple point $(4.097 \pm 0.005) \times 10^{-3}$ $\text{m}^3/\text{mol}$, and $(4.106 \pm 0.005) \times 10^{-3}$ $\text{m}^3/\text{mol}$ at the normal boiling point. In the present measurements the deviations between the individual densities calculated from the equation of state and those inferred from the dielectric constant measurements (using the overall fitted value of $M$ quoted above) were under 2%.

Fig. 2. — Projection of portion of the $nPT$ surface of argon in the $nT$ plane. $P_c^{\infty}$ indicates the position of the critical point in the bulk sample. The broken line in it represents the region where the equation of state [12] gives unreliable results. The solid lines terminating on this broken line represent the saturated liquid and saturated vapor lines. The other broken line, starting at the wetting point $T_w$ and terminating at $P_c$, is a speculative representation of the prewetting transition line. Two isobars, corresponding to 50 atm and 55 atm are shown as well. It is not clear from the experimental data whether $P_c$ is above or below the 50 atm isobar. The thicker lines are a representation of the region covered by the measurements discussed in this paper. Not shown is the portion of the saturated liquid line between 140 K and the triple point over which measurements were also taken.
Larger deviations between the densities obtained from the equation of state and those obtained from the measurement of the dielectric constant (≈ 5%) are obtained between 147.0 K and 150.0 K. These deviations were assigned to the acknowledged deficiencies of the equation of state along the saturation line near the critical point [15]. Between 150 K and the critical point these deviations become as large as 30%.

In figure 2 we present a projection of the \(nPT\) surface into the \(nT\) plane. The liquid vapor coexistence curve is shown as well as the 50 atm and the 55 atm isobars. The figure is calculated from the equation of state given in reference [15].

Experimental data do not bear out the expectation that the deviations between the density obtained from the measurement of the dielectric constant and that obtained from the bulk equation of state decrease when moving away from the critical point (Fig. 3). Such a decrease would be expected if the deviations arose either on account of inaccuracies of the equation of state near the critical point or due to the extremely large compressibility of the fluid near \(T_c\).

Fig. 3. — Comparison of the density \(n\) calculated from the equation of state [15] and the density \(n_k\) calculated from the measured dielectric constant along the 50 atm (•) and along the 55 atm (Δ) isobars.

A plot of the temperature dependence of the density obtained from measurements of the dielectric constant along the 50 atm and the 55 atm isobars are given in figure 4. The sharp break observed in the 50 atm data near 152 K is reminiscent of a phase transition.

In figure 5 we plot the temperature dependence of the difference of the density calculated from the measured capacitance and the density calculated from the equation of state [15].

As pointed out before, optical data indicate no anomaly of the Clausius-Mossotti constant. Thus the present observations indicate that the density of the fluid between the capacitor plates is larger than in the bulk of the fluid over a small region of the \(nPT\) surface above the critical isobar. This suggests that the binding energy between an argon atom and the platinum
Fig. 4. — Temperature dependence of the density obtained from the measured dielectric constant along the 50 atm (●) and the 55 atm (△) isobars. Both the full and the broken lines are only a guide to the eye.

Fig. 5. — Temperature dependence of the experimental surface excess density along the 50 atm (●) and the 55 atm (△) isobars.
film that makes up the capacitor plates is sufficiently strong to cause a buildup of the density near the surface.

One must enquire whether the present result may be due either to a thermal inversion or an effect due to gravity. The latter appears unlikely because the detected effect increases when one gets further from the critical point. It is a maximum along the 50 atm isobar about 1.2 K above \( T_c \), while it is a maximum along the 55 atm isobar about 4 K above \( T_c \). A temperature inversion does not seem likely either insofar as the temperature measured by a thermocouple tucked under the copper foil 4 cm above the sample chamber measured a temperature less than about 1 K above that of the platinum thermometer located below all the electrodes used for the Hall mobility measurements. The separation between both sensors was about 20 cm. The data were not taken with either monotonically increasing or monotonically decreasing temperatures. No hysteresis, nor any effects that might be associated with the sample history were detected.

It must also be remarked that, if there would have been a significant temperature inversion, the fluid in the coldest portion of the system would have been denser than in the region where the capacitor was located. Therefore, contrary to observation, since the total quantity of the argon in the system is constant, a density anomaly corresponding to a density lower than the bulk density should have been observed.

Finally, if the present observation would have been associated with a bulk property, some anomaly would have been seen in the measurement of the electron mobility that has a sharp maximum centered at a density near \( 1.28 \times 10^{22} \text{ cm}^{-3} \). This maximum has been seen by several authors [9, 17-19] and appears to be present (at different densities) in several high electron mobility liquids.

Below we suggest a mechanism which would produce the strong interaction necessary for the growth of a macroscopic film.

5. Ising model description.

A realistic calculation of the wetting transition for a fluid is beyond the scope of this work. Instead, assuming that the anomaly observed is indeed caused by prewetting, we consider a simple Ising model description which includes a strong surface interaction and study some of its features associated with prewetting. Our modest aim is to find out if the experimental data indicates that the 50 atm isobar intersects the line of prewetting transitions, whether we can expect the prewetting critical point to be above the bulk critical point for the fluid, and whether one might expect remnants of the wetting transition to appear as anomalies in the temperature dependence of the density in the vicinity of a metal surface.

Although the Ising model oversimplifies the properties of the fluid and its phase diagram has a symmetry that is different from that of a real fluid, it has served well to understand the bulk critical behavior of fluids [20]. In addition, it has been a model that has shed light on several aspects of surface phase transitions [21, 22].

We picture the van der Waals interaction between two atoms A and B by envisaging a randomly fluctuating dipole moment \( p \) on atom A that induces a dipole moment \( p_i = \alpha E \) on atom B; \( \alpha \) is the atomic polarizability. The average energy of \( p_i \) in the field created by \( p \) is

\[
\langle U_{AB} \rangle = -2 \alpha \frac{p^2}{r^6}, \tag{2}
\]

where \( \langle \ldots \rangle \) denotes average over the random angles of \( p \) and \( r \) is the distance between A and B.
In order to calculate the binding of atom A to a metallic surface when A is next to the surface, the induced dipole moment \( p_I \) on B used in obtaining equation (2) must be replaced by the image dipole \( p' \), which is much larger than \( p_I \), at the mirror symmetric position A'. In this case, the average energy is given by

\[
\langle U_{AA'} \rangle = -\frac{4}{3} \frac{p^2}{(2x)^3},
\]

where \( x \) is the distance between A and the metallic surface. If we let \( r = 2x = \sigma \) in equations (2) and (3), where \( \sigma \) is the hard core radius of the atoms, and appropriate values for Ar are substituted, the ratio \( \langle U_{AA'} \rangle / \langle U_{AB} \rangle \) can be as large as 16. It is appropriate to point out, however, that in the solid at 0 K the nearest neighbor distance is 1.11 \( \sigma \). As is seen in figure 2, the density of the fluid is actually near half of the density at the triple point. In any case, \( U_{AA'} \) is always much larger than \( U_{AB} \) independent of the orientation of the dipole moment \( p \) on A. This large surface-atom interaction will be seen below to yield strong surface induced transitions. In addition, higher order induced dipolar interactions decrease by powers of \( \alpha / \sigma^3 \) which is about 0.04 for Ar.

In formulating a lattice-gas Ising model to approximately represent this situation, we truncate both the atom-atom and atom-surface interactions at the nearest neighbor distance \( \sigma \). As in usual lattice-gas models for studying the liquid-gas critical behavior, we partition the space into regular array of cells of size equal to the hard core diameter of the atoms and represent a cell with an atom by an up (+1) Ising spin and one without an atom by a down (−1) spin. Since we must have a surface in the model, we use the semi-infinite simple-cubic lattice. The crudeness of a lattice-gas model is irrelevant for the so-called universal aspects of the bulk critical effects and the approximation is also expected to be useful in giving qualitative descriptions of surface induced phase transitions [22]. Some of the well known defects of this approach are: an atom \( (s = 1) \) and a hole \( (s = −1) \) are treated symmetrically, and pressure is not well represented by the parameters of the model. In addition, a potentially more serious problem is the truncation of the long-range atom-surface interaction [22, 23] this aspect will be pursued further in a subsequent study.

Thus, our initial model Hamiltonian is

\[
H = -J \sum_{\langle \langle i,j \rangle \rangle} n_i n_j - h_B \sum_i n_i + H_S,
\]

where

\[
H_S = -J_1 \sum_{\langle i',j' \rangle} n_{i'} n_{j'} - h_S \sum_{i'} n_{i'} ,
\]

and \( n_i = (s_i + 1)/2 \) is the occupation variable (1 or 0) at site \( i \). The bulk term \( h_B \) represents the chemical potential of the atoms in this grand canonical ensemble. We further approximate this by taking the exchange integral \( J \) in the bulk to correspond to the average energy \( \langle -U_{AB} \rangle \) between neighboring atoms and the surface term \( h_S \) to represent the dipole-image-dipole average energy \( \langle -U_{AA'} \rangle \) for an atom A in the surface layer (next to the metallic surface). This is already a kind of mean field approximation for the fluctuating dipoles, but below we will further use the results of a mean field approximation on the density variable (i.e. the spin variables) in \( H \).

This type of model is well studied theoretically [21, 22] and is known to give surface induced phase transitions called wetting and prewetting transitions for wide range of parameters. In short, a wetting transition occurs on the coexistence curve whereby a macroscopically thick
layer of liquid phase forms on the surface even though the bulk may be in the gas phase — a surface induced phase separation. A series of prewetting transitions can occur slightly off coexistence, leading up to the wetting transition, whereby the surface acquires a high density layer suddenly (the thickness of which varies according to the distance from the wetting transition and other factors). The larger the surface energy $h_s$ the longer the line of prewetting transitions between the wetting point and the so-called prewetting critical point $P_c$.

Now consider a dipole $p$ at $A$ on the surface layer. Then the interaction induced by $p$ between $A$ and another atom in the layer is represented by a surface exchange $J_1$. By considering only two nearest-neighbor sites on the surface layer and identifying the energies of the various combinations of the sites being occupied or empty from the Hamiltonian (4) and those obtained directly from the van der Waals interactions, we obtain

$$J_1 = \langle - U_{AB} \rangle + \langle - U'_{AB} \rangle + \langle - U'_{A'B} \rangle,$$  

(6)

where primes on $A$ and $B$ denote the image locations and those on $U$ the fact that we are only considering interactions arising from the source dipole $p$ on $A$. Note here that we are neglecting all higher order effects, including higher multipoles, higher order induced dipoles such as those through a third atom $C$, and direct further neighbor interactions. We need only to consider one source dipole (together with its image, the moments induced by them, and their images in turn) since interactions between two independent dipoles will always average to zero. We can then write

$$J_1/J = 1 + \Delta,$$  

(7)

where, in principle, $\Delta$ depends on the orientation of the dipole moment $p$. Within the present approximation, however, it is appropriate to evaluate it by using $J$ and $J_1$ obtained by averaging over the orientations of $p$. This parameter $\Delta$ is related to the enhancement factor $g$ discussed, e.g., in reference [21]. Within mean field theory (and for a simple cubic lattice), this relationship is:

$$g = -(J/4 k_B T)(1 - 4 \Delta),$$  

(8)

where $J$ depends on the magnitude of the fluctuating dipole moment $p$ as discussed. Hence, within this theory [22], if $\Delta > \Delta_c = 1/4$ the enhancement is sufficient to extend the prewetting transitions above $T_c$ for small $h_s$.

Strictly within this approximation, it is not difficult to evaluate the value of $\Delta$ for Ar on a metallic surface. As shown in the Appendix, however, the result to the first order in $\alpha/r^3$ is:

$$\Delta \approx -0.045.$$

(9)

Thus there is no net enhancement to this order and we cannot argue on this basis the possibility of $P_c$ being above $T_c$. It remains to be seen whether including long-range effects or otherwise improving the calculations (such as to include second order terms in $\alpha/r^3$) would allow this or not.

From the data in figure 3, it is not clear whether the lack of sharpness of the phase transition is due to intrinsic properties of the prewetting transition, to the possibility that the point $P_c$ may be below the 50 atm isobar or to experimental errors. As is seen comparing either the data corresponding to the 50 atm and the 55 atm isobars, the further away one goes from $T_w$ the smaller is the difference between the density of the film and the density of the bulk fluid. This trend is also illustrated in the model calculation of Nakanishi and Pincus [24] although the measured amount of the density deviations would require surface films of
thicknes much greater than expected in such calculations at a comparable distance from the coexistence curve.

However, broadened and attenuated, remnants of the transition remain at temperatures above that corresponding to $P_c$, e.g. what is seen along the 55 atm isobar. This effect can be demonstrated by calculations based on a simple Ising model described above; an illustration is provided in figure 6. Shown in this figure are the results from the continuum version [22, 24] of the lattice-gas model described earlier. The vertical axis is the surface excess $\Gamma$ per unit area of surface $\Gamma = \int_0^\infty (m - m_{\text{bulk}}) \, dx$ where $m$ is the continuum version of the Ising spin $s$ ($m = 1$ corresponding to the nominal saturation density) and where the unit of length $x$ is the nearest-neighbor distance. The horizontal axis is the reduced temperature $t = (T - T_c)/T_c$. The geometrical parameters chosen for this plot are appropriate for a simple cubic lattice and the surface dimensionless parameters $g$ and $h_1$ (see Refs. [22] and [24] for notation) are arbitrarily chosen to be 1/6, so that the prewetting critical point $P_c$ occurs at about $m = -0.7$, $t = 0.1$, and $h = -0.18$. (The terms $h_1$ and $h$ are essentially like $h_s/2 k_B T$ and $h_B/2 k_B T$.) Since the bulk field parameter for this figure of $h = -0.185$ is slightly less than that for $P_c$, there is no sharp prewetting transition in this figure; yet there is clearly a remnant of the transition in the form of a broad maximum.

Fig. 6. — Temperature dependence of surface excess density theoretically calculated from a continuum Landau theoretical version (see Refs. [22, 24]) of the short-range lattice-gas model described in this paper. The format of this figure is analogous to that of figure 5. The parameters chosen for this plot are described in text. The bulk field value chosen makes this graph not to cross the line of prewetting transitions. Note that the high adsorption occurs on the high temperature side in this calculation in contrast to the experimental case where it should occur at the low temperature side. This difference is attributed to the difference in the theoretical path ($h = \text{constant}$) and the experimental path (pressure = constant) and the defects associated with the forced symmetry of the Ising model.

### 6. Summary.

In conclusion, the experimental data indicates the existence of some sort of phase transition slightly above the critical point that is reminiscent of the theoretical expectations of the prewetting transitions [5]. A plausible mechanism for the enhancement of the interaction
between an argon atom and a metal surface compared with the interaction between two argon atoms in the bulk has been proposed. However, a corresponding plausible mechanism for an enhancement of the interaction between two atoms on the metallic surface does not appear to arise from the short-range, lattice-gas model described here.

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Appendix.

Calculation of $J_1$.

To calculate $\Delta$, first note that on account of symmetry $\langle U'_{AB}\rangle = \langle U'_{A'B}\rangle$. To first order in $\alpha/r^3$, $U'_{A'B}$ is actually the sum of two contributions: the interaction $U_1$ between the image dipole $p'$ at $A'$ and the dipole $(p_1')_h$ induced at $B$ by $p'$, and the interaction $U_2$ between $p'$ and the dipole $p_1$ induced at $B$ directly by $p$. Thus we only need to compute two quantities. We must be careful, however, since not all dipole moments in question are coplanar with each other. That is, while $p$ and $p'$ are coplanar and so are $p'$ and $(p_1')_h$, or $p$ and $p_1$, the planes are not common in general.

Consider a Cartesian coordinate system with the $x$-axis along $A'A$, and the $z$-axis parallel to $BA$. The metal surface is the $yz$-plane. Denote the polar angle of $p$ from the $z$-axis by $\theta$, and by $\phi$ the azimuthal angle made by the projection of $p$ into the $xy$-plane from the $x$-axis (see Fig. 7).

Fig. 7. — System of coordinates used to calculate the additional surface interaction term. The dipole $p$ at $A$ produces an image $p'$ at $A'$ and induces a dipole $p_1 = \alpha E$ at $B$. The image of $p_1$ is $(p_1)'$ at $B'$. The contribution $U_2$ to the term $U'_{A'B}$ is the interaction of $p'$ and $p_1$ (or equivalently that of $p$ and $(p_1')_h$). The contribution $U_1$ to $U'_{A'B}$, on the other hand, is the interaction of $p'$ and its induced dipole $(p_1')_h$ at $B$ (or equivalently that of $p$ and the image of $(p_1')_h$). Both $(p_1')_h$ and its image are left out of the figure for clarity.
In this system, we have
\[
p = p(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta), \quad \text{(A.1)}
\]
\[
p' = p(\sin \theta \cos \phi, -\sin \theta \sin \phi, -\cos \theta), \quad \text{(A.2)}
\]
and
\[
p_1 = (\alpha p/r^3)(-\sin \theta \cos \phi, -\sin \theta \sin \phi, 2\cos \theta). \quad \text{(A.3)}
\]

The first contribution \( U_1 \) is simply
\[
\langle U_1 \rangle = -2\alpha \frac{p^2}{(4x^2 + r^2)^3}, \quad \text{(A.4)}
\]
in analogy to equation (2) for the direct interaction. When \( r = 2x = \sigma \), this gives
\[
\langle U_1 \rangle = (\alpha p^2)/4\sigma^6. \quad \text{(A.5)}
\]
The second term \( \langle U_2 \rangle \) is calculated from
\[
U_2 = (p_1 \cdot p')/R^3 - (3/R^5)(p' \cdot R)(p_1 \cdot R), \quad \text{(A.6)}
\]
where \( R \) is
\[
R = A'B = (2x, 0, -r), \quad \text{(A.7)}
\]
where \( r \) is the nearest neighbor distance \( AB \) and \( 2x \) is \( BB' \). Substituting (A.2), (A.3) and (A.7) into (A.6) and taking angular averages over \( \theta \) and \( \phi \), and further letting \( r = 2x = \sigma \), we obtain
\[
\langle U_2 \rangle \approx 0.295 (\alpha p^2)/\sigma^6. \quad \text{(A.8)}
\]
Therefore, from (2), (7), (A.4) and (A.8), we obtain
\[
\Delta \approx -0.045. \quad \text{(A.9)}
\]

Note that the sign of \( \Delta \) in this approximation is negative, which indicates that there is no net enhancement in \( J_1 \) and rather there is a 4.5% decrease. Thus, this calculation does not allow for the prewetting critical point \( P_c \) to lie above \( T_c \). This effect is largely due to the misalignment on average between the image and the induced dipoles (or equivalently, of the image of the induced dipole relative to the source dipole). Some of the second order terms in \( \alpha/r^3 \) are clearly attractive and may turn this slight decrease into an enhancement. However, it is difficult to imagine an enhancement as large as 25% as required by mean field theory described earlier simply by including higher order terms.

References


[10] Platinum 05x Engelhard Corp, East Newark, NJ 07029.


[25] We may compare this behaviour with the so called capillary condensation. In the latter case, a liquid phase, for example, fills a capillary rather than creating interfaces between the liquid and the undersaturated gas. The capillary condensation in this sense, is the result of a bulk like term in the free energy that competes against surface like terms. Such a description is only appropriate when the plate separation is relatively small (see e.g. EVANS R. and MARCONI U., Phys. Rev. A 32 (1985) 3817). In the present experiment the separation of the plates is of the order of 0.1 mm ; the phenomena are more appropriately described by a semi infinite geometry, and the resulting transition is a prewetting phenomenon. Of course, in a proper treatment of spatially varying density for a finite plate separation, it is expected that the prewetting transition is no longer a true phase transition. In this case, there remains only the shifted (and lower dimensional) bulk phase transition which could be interpreted as a generalized form of capillary condensation (see NAKANISHI H. and FISHER M. E., J. Chem. Phys. 78 (1983) 3279).