Influence of Ions on the Nucleation Processes in Liquids.

I - Liquids in Stable Thermodynamical Equilibrium.

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Summary. — An attempt is made to study the nucleation of vapour bubbles in liquids, when the contribution of the ions is also taken into account. Some results show substantial differences from those obtained on the basis of the usual theories. The particular case of liquids in stable equilibrium is discussed in some details.

1. — Introduction.

Spontaneous, radioactive and cosmic ray ionization is always present in any liquid. As a consequence of this fact the usual procedure, for studying the nucleation in liquids, where the ionization is neglected, may be considered as an approximation, which in some cases does not allow a good comparison with the experimental results available at present (1).

On the other hand the work of Glaser (2) furnishes definite evidence of the fact that if strong ionization occurs suddenly in a liquid in a metastable state, its equilibrium is so violently perturbed as to give rise to some rupture nuclei.

In the work which is the subject of these papers (3) an attempt has been made to re-examine some aspects of the theory of nucleation of vapour bubbles, in the case in which also the contribution of the ions is taken into account:

(3) In a second paper the case of liquids in metastable state (overheated liquids, liquids under negative pressure) will be treated quantitatively.
the behaviour of some typical quantities describing liquids in various thermodynamical conditions has been studied, and the results have been compared with those given by the usual theory.

2. Contribution of the Electrostatic Terms.

Let us first consider a bubble formed inside the liquid, and let \( N \) be the number of ionized molecules present in the bubble, amongst \((n - N)\) other neutral molecules of vapour. The mean free path of the molecules of vapour is large compared with the size of the bubble (in most cases the radius \( R \) of the bubble does not exceed some hundred Å). On the other hand the mean kinetic energy of the ions in the bubble is of the order of magnitude of \( kT \) and the mean electrostatic energy of the order of \((Ne)^2/R\). Depending upon the values of the temperature of the liquid and the number of ions present in the bubble, we can find a «random» distribution (*) of the ions in the bubble rather than a «shell» distribution, or viceversa.

We want now to determine the value of the electrostatic energy of a system formed by \( h \) charged molecules «captured» into a bubble of radius \( R \). This energy may be expressed as the sum of two terms, the first representing the interaction among the charges themselves inside the bubble (hereafter indicated as space «I») and the second corresponding to the self-energy of the charges placed inside a medium of dielectric constant \( \epsilon \) (space «II»):

\[
U(\epsilon) = \frac{1}{8\pi} \sum_{i \neq k} \int (E_i \times D_k) \, dV + \frac{1}{8\pi} \int (E_i \times D_i) \, dV = \frac{1}{8\pi} \int (E \times D) \, dV + \frac{1}{8\pi} \int (E \times D) \, dV.
\]

The observable energy \( U(N) = U(\epsilon) - U(1) \) is therefore

\[
U(N) = \frac{1}{8\pi} N(N - 1) \int (E \times D) \, dV + \frac{1}{8\pi} N \int (E \times D - D^2) \, dV = \frac{1}{8\pi} N(N - 1) \int (E \times D) \, dV + \frac{1}{8\pi} N \int (D - [E - D]) \, dV.
\]

(*) In this case a «random» distribution may in practice be identified with an «uniform» distribution.