Investigations of condensation phenomena of electron-hole drops in pure Ge

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We have performed electron-hole drop (EHD) luminescence threshold experiments in conditions where an optical hysteresis can be observed. The characteristics of the thresholds are investigated and support the idea of supersaturation to create EHD. A simple model of the growth time of embryos shows that this requirement can explain the discrepancy between the spectroscopic and thermodynamic values of the exciton work function. From our calculations we deduce for the EHD surface energy a value in range of 1.8–2.6 erg/m^2.

I. INTRODUCTION

The condensation of gaseous free excitons (FE) into electron-hole drops[1] (EHD) is characterized by a threshold which reveals the occurrence of a phase transition and has been studied by various techniques: cyclotron resonance,[2] luminescence, and p-n junction experiments.[3,4] An interpretation of the temperature dependence of the threshold obtained above 2 K in these experiments leads to a thermodynamic value of the FE work function ($\phi_{th} \sim 17-18$ K), which differs from the spectroscopic value[5] ($\phi_s \sim 23$ K). This intriguing discrepancy has motivated further investigations.

Here we report luminescence threshold measurements between 4.2 and 1.4 K. In particular experimental conditions an optical hysteresis effect first reported by Lo *et al.*,[4] can be observed.[6] This strongly suggests that, by analogy with water-vapor condensation, for example, supersaturation is needed to develop EHD at a sufficient rate. This necessity has also been demonstrated by Silver.[7] We will show that calculations of the growth time of EHD embryos can account for the discrepancy between ϕ_{th} and ϕ_s.[8] Using a simple model, we deduce from our results that the EHD surface energy σ is with our choice of parameters in the range 1.8–2.6 erg/m^2. This is higher than previous theoretical estimations obtained by variational methods[9] (0.8–1.4 erg/m^2) and lower than the recent results of Vashista *et al.*[10] (3.5–4 erg/m^2). The agreement with previous experimental[11] determinations is reasonable. We discuss the reasons why we cannot at the present time expect a more accurate value of σ from a nucleation theory.

II. EXPERIMENTAL TECHNIQUES

In our experiments a sample of pure Ge ($N_A - N_D \sim 2\times10^{10}$ cm^{-3}) which is fixed on a large copper block and immersed in pumped liquid helium, is excited by a mercury or an halogen lamp. Typical size of the sample is $15\times4\times3$ mm^3. The temperature of the bath, which is very close to that of the sample because of the small excitations used (less than 1 mW/cm^2), is measured with a very sensitive Allen-Bradley carbon resistor. The excitation and the luminescence light intensities are measured by a photoelectric cell and a PbS cell, respectively, at dry ice temperature. Luminescence is analyzed with a grating spectrometer and the output signals are sent into lock-in amplifiers followed by an X-Y recorder. The excitation light intensity can be continuously varied using a diaphragm monitored by a stepping motor.

III. EXPERIMENTAL RESULTS

Whereas the FE luminescence can be observed at any excitation J, the EHD luminescence line at 709 meV appears (when the excitation is increased from zero) only at a certain threshold J_{th}^A which is strongly temperature dependent. If the modulator (usually at 75 cps) required for lock-in amplification is placed between the light source and the sample, the same threshold is obtained when the excitation intensity is decreased down to zero. This is obvious because in this case all the carriers are destroyed at each modulation and the memory of the sense of variation of the light power is lost. On the contrary, when the chopper is placed between the Ge crystal and the spectrometer, the sample is thus continuously illuminated and the threshold J_{th}^B obtained when the excitation is decreased can eventually be different from J_{th}^A. This is the case below ~ 2.25 K. The thresholds obtained between 4.2 and 1.4 K are presented in Fig. 1. The ratio between both thresholds increases very rapidly below 2.2 K up to $J_{th}^A/J_{th}^B = 4$ for 1.8 K, and then tends to decrease.

The EHD luminescence signal I at a given excitation J greater than J_{th}^B depends on the excitation history (sense of variation, speed of variation, maximum excitation) used to reach J. Figure 2 displays some results obtained at 1.9 K. Branch A is obtained when the excitation is regularly increased; branch B when it is decreased from some maximum value $J_{max} \sim 10\, J_{th}^A$, the whole run being done in two minutes. If we had

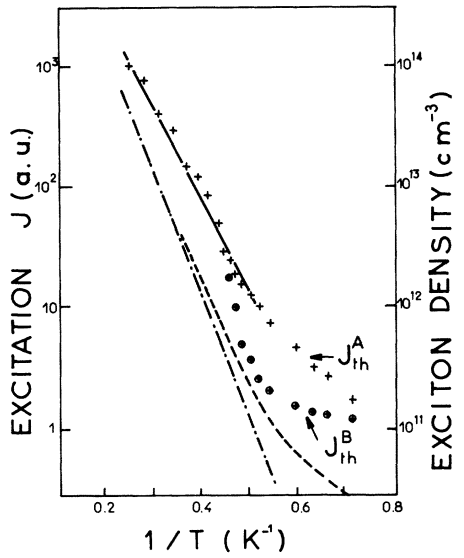

FIG. 1. Temperature dependence of the luminescence thresholds J^A_{th} and J^B_{th} of the 709-meV line owing to the recombination of condensed pairs in EHD with emission of an LA phonon. Crosses are the experimental points for the nucleation threshold J^A_{th} whereas the circled crosses represent those for the destruction threshold J^B_{th} when it is different from J^A_{th}. Threshold is defined as the point at which the signal comes out of the noise level. Solid line is the theoretical variation of the threshold J^A_{th} between 4.2 and 2.0 K calculated with $\sigma = 2.4$ erg/m^2, $A = 3.8\times10^{10}$ sec^{-1}K^{-2} and $x_m = 10$ pairs. Its slope is 17.4 K. Dashed line represents the variation of $n_{ex}(r^*)$ for the same set of parameters. Dashed-dotted line gives the variation of $n_{ex,0}$; its slope is the exciton work function. Value of the exciton density is obtained from by Eq. (1) with the indicated values of the parameters.

stopped at J_1, J_2, J_3, ..., the corresponding descending branches would be B_1, B_2, B_3, ... The important observation is the following: as soon as EHD have been created ($J > J^A_{th}$), the luminescence signal will go to zero only at J^B_{th}, whatever the way of variation of J between J^A_{th} and J^B_{th} has been. Another interesting and intriguing observation is a slow variation of the luminescence signal. For instance, at a given excitation J, points C and D drift, respectively, to C' and D' (see Fig. 2). This evolution is not strictly exponential at the beginning but can be then characterized by a time constant of ~400 sec below 2 K. Note that, in our experiments, points C' and D' never coincide. Above the λ point of helium the time constant of the drift is much smaller, certainly because of fluctuations owing to bubbles in evaporating normal helium. We have also observed that the threshold J^A_{th} is independent of the chopping frequencies we have used (up to 1000 cps) to modulate the excitation light. This means that at J^A_{th} the drop formation time is less than 1 msec.

IV. DISCUSSION

A. Equilibrium model

Our attempt to interpret the preceding data is based in this paper on the following approximations: (i) we consider the equilibrium between the FE gas and individual drops, ignoring interactions (like collisions for example) between them; (ii) we neglect the gradient in the FE density owing to the strongly absorbed light excitation; (iii) we suppose that the FE density is kept constant when EHD are formed or destroyed. With these limits, calculations are considerably simplified and we think that these assumptions are justified in the excitation region close to thresholds, because the FE diffusion length ($L \sim 1$ mm) is large and the EHD density is small throughout the excited region.

It is well known[12] that the combined effects of the EHD surface energy σ and lifetime τ give the following relation between the EHD radius r in equilibrium with an FE gas of density n_{ex}:

$$n_{ex}(r) = \alpha\, r + n_{ex,0}\, e^{2\sigma/r\, n_0 kT} \qquad (1)$$

where

$$\alpha = 4\, n_0/3\, v_{ex}\, \tau \quad \text{and} \quad n_{ex,0} = g(2\pi m^* kT/h^2)^{3/2} e^{-\phi/kT},$$

v_{ex} is the FE thermal velocity, ϕ the FE work function, m^* is the FE translation mass, g is the FE ground-state degeneracy, and n_0 is the EHD bulk density. We use[1] $\tau = 40$ μsec, $n_0 = 2.4\times10^{17}$ cm^{-3}, $g = 16$, and $m^* = 0.33\, m_0$.

The smallest stable radius r^* at a given temperature corresponds to the minimum density

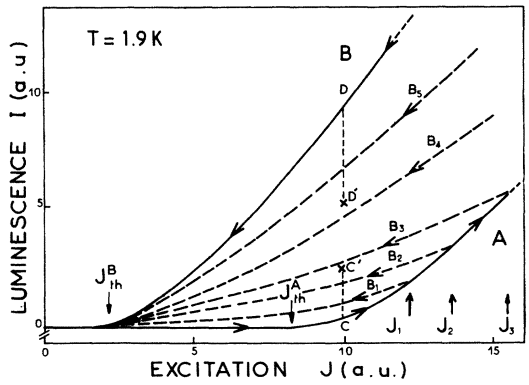

FIG. 2. Variation of the peak luminescence intensity I of the 709-meV line as a function of the excitation power J. When the excitation light increases from zero, the luminescence follows branch A. When it decreases from $J_{max} \sim 10\, J^A_{th}$ it follows branch B. If we stop at J_1, J_2, J_3, ..., the corresponding descending branches are B_1, B_2, B_3, ... All the branches converge at J^B_{th}. If we wait a long time at the excitation corresponding to points C and D there is a continuous shift towards points C' and D'.

n_{ex} (r^*) in equilibrium with a drop and it is given by

$$r^* = \beta(A\sigma\tau)^{1/2} e^{-\phi/2kT} e^{\sigma/r^* n_0 kT},$$

where

$$\beta^2 = \frac{2(3/4\pi)^{1/3}}{k n_0^{4/3}} \quad \text{and} \quad A = \frac{(3\pi^2/4n_0)^{2/3} 8m^* g k^2}{h^3},$$

A is the Dushman-Richardson constant and is equal to 3.2×10^{10} $\text{sec}^{-1}\,\text{K}^{-2}$. Above this minimum density, there is an equilibrium[6] corresponding to two EHD radii; it is unstable for the smaller radius and stable for the greater one.

As we have already reported[6] using a very sensitive differential method, we have been able to measure the ratio σ/r at different excitations close to the thresholds on both branches A and B of the hysteresis between 2.2 and 1.5 K. We have interpreted the value of this ratio at the threshold J_{th}^B to be σ/r^*. We obtained an excellent agreement between our measurements and the model, provided we used for the FE work function ϕ the value ϕ_s and not ϕ_{th}. We could also deduce that $A/\sigma = 1.6\times10^{10}$ $\text{sec}^{-1}\,\text{K}^{-2}$ $\text{erg}^{-1}\,\text{m}^2$ with $\phi = 23$ K. Hence $\sigma = 2$ erg/m^2 if we keep the theoretical value of A.

With the same method we have also measured the ratio σ/r on branch A of the optical hysteresis and we have checked[13] that at a given excitation, the drops have larger radii and are less numerous than on branch B. According to the preceding equilibrium model, this observation supports the idea that some supersaturation is required to allow the formation of EHD. When some of them have grown and when the excitation is then decreased, their size can diminish to a value smaller than that at J_{th}^A and they can reach a radius very close to r^* at J_{th}^B. In fact when the radius is slightly above r^*, the mean destruction time of the EHD due to fluctuations processes can be short, so that the drop cannot reach exactly the minimum stable size. This effect will be considered later in this section and the results will show that it is nearly negligible in the whole temperature range considered here.

Hence we should expect from these size measurements that the threshold J_{th}^B would be proportional to the FE density n_{ex} (r^*). However, as can be seen in Fig. 1, the temperature dependence of J_{th}^B is complicated. In particular the rapid decrease of the optical hysteresis above 2 K and its disappearance above ~2.25 K cannot be explained by the simple equilibrium model given by Eq. (1). We think that an interpretation of this phenomenon would take into account the motion of EHD. On the contrary, below 1.7 K, the variation of this threshold with temperature is very slow, and it is not accounted for by the variation of n_{ex} (r^*). As shown later the correction due to the destruction time of EHD is even smaller on the FE density than on the radius and cannot exceed some per cent. Thus it seems that the interpretation of this threshold J_{th}^B cannot be done within the approximations that we have presented at the beginning of this section.

The temperature dependence of J_{th}^A is simpler. We have to calculate the critical rate of the supersaturation that allows an embryo to grow and reach its equilibrium size in a short enough time. This formation time will appear to be dramatically dependent on the FE gas density. Usual condensation theories[14] cannot be directly applied because of the finite lifetime τ of the condensed pairs.[15] We shall use a method based on probabilistic considerations because it gives a concrete sight of the growth process. This method can be applied to the calculation of the destruction time as well.

B. Stochastic model

Let us consider a drop surrounded by the FE gas. As pointed out by Silver,[12] the different mechanisms of loss and gain of an electron-hole pair by this EHD are stochastic events and this drop will have a continuously fluctuating size. Having x pairs at time t, it will be a small time h later either in state x, $x-1$, or $x+1$ with the following respective probabilities:

$$\begin{aligned} P(x, x-1) &= e(x)h, \\ P(x, x+1) &= c(x)h, \\ P(x, x) &= 1 - [e(x) + c(x)]h, \end{aligned} \tag{2}$$

where h is chosen independent of x and small enough so that the higher-order processes are negligible.

When x is not too small $c(x)$ and $e(x)$ are given by:

$$\begin{aligned} c(x) &= v_{ex} n_{ex} \pi r^2 = AT^2 S x^{2/3} e^{-\phi/kT} \\ e(x) &= x/\tau + AT^2 x^{2/3} e^{-\phi/kT} e^{2\sigma/rn_0kT}, \end{aligned} \tag{3}$$

with $x = \frac{4}{3}\pi n_0 r^3$. Here $S = n_{ex}/n_{ex,0}$ is the supersaturation rate and will act upon the EHD formation through the term $c(x)$. The larger this quantity, the faster the growth of the embryos.

When x is small, the expressions given by Eqs. (3) are certainly not appropriate. The collecting process at the very beginning will be the attractive interaction between the excitons or from a possible nucleation center. Furthermore, statistical mechanics should be used to describe small embryos and in the framework of our drop model, parameters like n_0, σ, and τ have certainly different values. But to our knowledge cor-

rect expressions for $e(x)$ and $c(x)$ have not yet been calculated.

The independence of the probabilities given by Eq. (2) with respect to t is typical of Markoffian processes and very general results can be obtained.[16] Because of the finite lifetime τ, the Markoffian process in the case of EHD is irreducible and recurrent. This means that starting from a state x the probability P_x^y that the embryo will reach another state y at a certain time later is always equal to one. This is why there is an equilibrium distribution $n_e(x)$. It is obtained readily from the detailed balance principle and has been studied by Silver.[12] For any x we have the following relation:

$$c(x)\, n_e(x) = e(x+1)\, n_e(x+1). \tag{4}$$

Here $n_e(x)$ is the density of embryos in state x.

When τ is infinite, as in the case of classical vapors, the Markoffian process is transient. The equilibrium distribution cannot be maintained by the system, because the probability P_x^y tends to zero when y is small with respect to x. But the system can reach a steady-state nonequilibrium distribution[14] $n_f(x)$, corresponding to a nonzero flux F, independent of the size x and the time. This flux is the number of embryos formed per unit volume and time and is given by

$$F = c(x)\, n_f(x) - e(x+1)\, n_f(x+1).$$

The distribution $n_f(x)$, being a decreasing function of x, is usually cut at a maximum value x_{max} for which $n_f(x_{max}) = 0$. The value[17] of F is then

$$F = n_{ex}\left\{c(1)\Big/\left[1 + \sum_{j=2}^{x_{max}}\left(\prod_{n=2}^{j}\frac{e(x)}{c(x)}\right)\right]\right\}. \tag{5}$$

When x_{max} is chosen larger than about twice the unstable equilibrium size x_i, F is remarkably insensitive to the choice of x_{max}. In the case of EHD this is only true when x_i and the stable equilibrium size x_s are well separated. But even then, if x_{max} is chosen larger than x_s, F now tends to zero. This is clearly owing to the fact that the embryos cannot grow indefinitely and that there is an equilibrium distribution.

Having created in our crystal a supersaturated vapor of FE, we can divide within the framework of our approximations the condensation process into three main phases, at least when x_i and x_s are not too close. First there is an induction period where the first embryos form and have to pass beyond the point x_i. Then, when there is enough embryos for the distribution $n_f(x)$ to be accommodated, the condensation occurs at a constant flux F obtained from Eq. (5) with x_{max} between x_i and x_s. Finally, when nearly all the embryos have been formed the flux F decreases to zero and the distribution tends to $n_e(x)$. This whole study would be helpful to understand the excitation dependence of the number of EHD but, here, we will restrict our attention to the threshold of condensation only.

A complete mathematical treatment of the relaxation of the initial distribution towards $n_e(x)$ is at the present time beyond our scope. But, using the fact that the probability P_x^y to reach any final state y from any initial state x is always equal to one in our case, we can calculate the mean time T_f that an embryo needs to grow from $x = 1$ to the stable equilibrium state x_s at a fixed supersaturation S. It will be a simple way to study the possibility of the beginning of the condensation process.

For this purpose we have to consider the random walk of the embryo in the state space. It can be easily deduced from Eqs. (2) that an embryo will stay in state x for time τ_x, which has an exponential distribution law, the mean time $\bar{\tau}_x$ being

$$\bar{\tau}_x = [e(x) + c(x)]^{-1}. \tag{6}$$

Then, when the transition occurs, the embryo will either gain a pair with the probability P_x^+ or lose one with the probability P_x^-:

$$P_x^+ = \frac{c(x)}{e(x)+c(x)}, \quad P_x^- = \frac{e(x)}{e(x)+c(x)} \tag{7}$$

and, from the reached state, the process will start again, and so forth indefinitely. Let us call $t(x)$ the mean time to reach the stable equilibrium state x_s starting from x, smaller than x_s. Obviously $t(x_s) = 0$. We can obtain the following relation which is easily interpreted:

$$t(x) = \bar{\tau}_x + P_x^+\, t(x+1) + P_x^-\, t(x-1). \tag{8}$$

Then, introducing the quantity $\Delta(x) = t(x) - t(x+1)$, we get the following recurrent relation:

$$\Delta(x) = 1/c(x) + [e(x)/c(x)]\,\Delta(x-1)$$

and the time we are looking for is finally:

$$T_f = t(1) = \sum_{x=1}^{x_s-1} \Delta(x)\ . \tag{9}$$

The destruction time can be calculated in a similar way. We introduce $t'(x)$ the mean time required to reach the state 1 starting from a state x and $\Delta'(x) = t'(x) - t'(x-1)$. We obtain the following relations:

$$t'(x) = \bar{\tau}_x + P_x^+\, t'(x+1) + P_x^-\, t'(x-1), \tag{10}$$

and

$$\Delta'(x) = 1/e(x) + [c(x)/e(x)]\,\Delta'(x+1).$$

Unfortunately Eq. (10) now has an infinite number of solutions but it can be shown[16] than the one we are looking for is the smallest and corre-

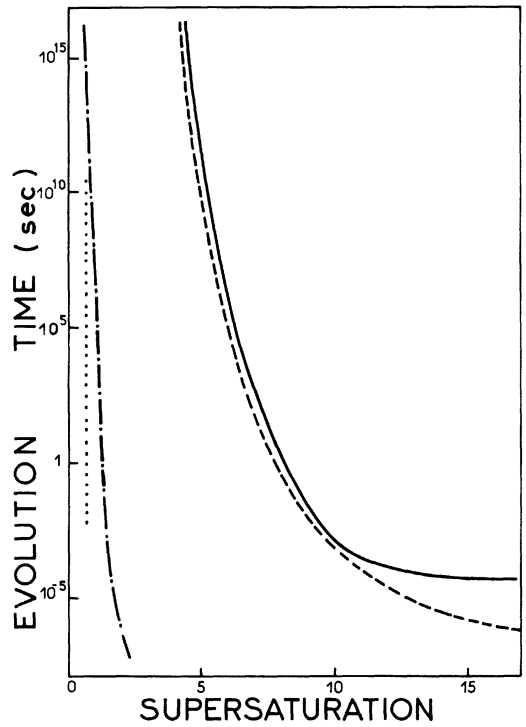

FIG. 3. Variation of the evolution time of a drop as a function of the absolute supersaturation rate $S_1 = n_{ex}/n_{ex,0}$. Solid line gives the formation time T_f at 2.0 K. It can be compared to the time to go only to the unstable equilibrium point which is given by the dashed line. Destruction time T_d at the same temperature corresponds to the dotted line. Dashed-dotted line gives the formation time T_f at 4.0 K.

sponds to

$$\Delta'(x_s) = \frac{1}{e(x_s)}\left[1 + \sum_{j=x_s}^{\infty}\left(\prod_{i=x_s}^{j}\frac{c(x_i)}{e(x_{i+1})}\right)\right] .$$

This series is convergent because the lifetime τ is finite; and the time of destruction is finally

$$T_d = t'(x_s) = \sum_{x=2}^{x_s} \Delta'(x) . \qquad (11)$$

This time T_d depends clearly on all the quantities $c(x)$ and $e(x)$, whereas T_f depends only on these quantities for x smaller than x_s. As already pointed out, the values of $e(x)$ and $c(x)$ are not known for small systems and even their order of magnitude is questionable. This uncertainty is not so important for T_d because at the supersaturation rates at which this time is not too large, the size x_i is not too small. It is the contrary for the time T_f and we do not know whether the formation time of small embryos is long because they have a large probability to be destroyed before collecting new pairs, or whether it is short because, for example, a nucleation center may have a large cross section to capture excitons. We have attempted to test this in a very crude manner. We supposed that the formation of a small embryo can be neglected up to a minimum size x_m and we tried successively $x_m = 3$, 5, 10, 15, 20, and 25. The larger x_m, the easier the formation of the embryos. From the state x_m, we still used Eqs. (3) to get $c(x)$ and $e(x)$, essentially because they have the limit behavior $e(x)/c(x) \to \infty$ when $x \to 0$, which is a way to express the difficulty of building these embryos.

C. Numerical results

We have performed calculations at various temperatures for different values of A and σ keeping their ratio constant and equal to our experimental result,[6] i.e., 1.6×10^{10} sec^{-1} K^{-2} erg^{-1} m^2.

Let us first discuss the destruction time T_d. The possibility of destruction of a drop by stochastic fluctuations will be realized in a short time only when x_i and x_s are not too different, and this is the case near the critical size. We find such a strong dependence of T_d on the supersaturation that this effect is completely negligible above 2 K. The results obtained at 2 K as a function of the supersaturation are presented in Fig. 3. With a small change of the supersaturation we change from $T_d = 10^{-2}$ sec to $T_d = 10^{10}$ sec. The lower the temperature, the less rapid this variation. Table I shows the results obtained between 2 and 1.25 K for $T_d = 1$ sec, which is the lock-in time constant we used in our experiments. At the lowest temperature in the differential experiment (1.5 K), the correction on the radius is ~20% which is of the order of the experimental error, so that we can consider that the interpretation of the data given in Ref. 6 to get A/σ was correct. We see that the corrections on the threshold are very small and cannot explain J_{th}^{B}

TABLE I. Minimum drop sizes obtained in different models as a function of temperature. The radius r^* is the minimum stable drop size corresponding to the equilibrium model given by Eq. (1). In the stochastic model it appears that drops having a size slightly above this limit can be destroyed by fluctuations far much faster than they can form again. The radius τ corresponds to a destruction time T_d of 1 sec, Δ is the relative difference between r and r^*, and S_2 is the relative supersaturation $n_{ex}(r)/n_{ex}(r^*)$. The numerical values are obtained with $\sigma = 2.5$ erg/m^2 and $A = 4$ sec^{-1} K^{-2}. Above 2 K the difference between r and r^* is negligible.

T (K)	2.00	1.82	1.67	1.54	1.43	1.33	1.25
r^* (Å)	2560	1550	1000	700	520	410	340
r (Å)	2760	1740	1140	840	640	550	480
Δ (%)	8	12	16	20	25	34	42
S_2	1.00	1.01	1.01	1.03	1.05	1.12	1.19

TABLE II. Slopes and supersaturations as a function of surface tension σ and embryo size parameter x_m. The main figure is the slope in degree Kelvin obtained between 4.2 and 2.0 K for the temperature variation of the nucleation threshold J_{th}^A in the usual coordinate scheme (ln $J_{th}^A T^{-3/2}$ vs $1/T$). The formation time has been chosen to be $T_f = 0.5$ msec and we present the results when the slope is between 15.9 and 18.1 K. The figures in parentheses are the relative supersaturation rates $S_2 = n_{ex}/n_{ex}(r^*)$ at 2.0 K for the corresponding values of σ and x_m.

σ (erg/m^2)	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2
$x_m = 3$	18.1 (3.8)	17.6 (4.7)	17.0 (6.0)	16.4 (7.7)	15.9 (9.8)				
$x_m = 5$		18.0 (4.0)	17.6 (5.0)	17.2 (6.2)	16.6 (8.0)	15.7 (9.2)			
$x_m = 10$			18.3 (4.0)	17.9 (4.7)	17.4 (5.7)	17.0 (7.0)	16.5 (8.7)	16.0 (10.1)	
$x_m = 15$				18.3 (4.1)	17.9 (5)	17.5 (5.7)	17.0 (7.2)	16.4 (8.9)	15.9 (10.5)
$x_m = 20$					18.2 (4.2)	17.9 (5.0)	17.5 (6.0)	17.1 (7.5)	16.5 (9.1)
$x_m = 25$						18.1 (4.6)	17.8 (5.5)	17.4 (6.4)	17.2 (7.6)

below 2 K. This point remains unclear. Let us now consider the formation time T_f. We have calculated the critical supersaturation at which it has a value of 0.5 msec, for example. Plotting our results in the usual coordinate system (ln $n_{ex} T^{-3/2}$ vs $1/T$), we obtain a linear variation between 4.2 and 2 K and a less rapid variation below. Although this behavior is analogous to the experimental one, we have no confidence in the results obtained when the unstable equilibrium size is very small and too close to the minimum size x_m. This is the case below 2 K and we think that it is more reasonable to restrict our attention to higher temperatures to fit the experimental data. Neglecting the EHD surface energy σ would give a slope of ln $n_{ex} T^{-3/2}$ vs $1/T$ equal to the FE work function. When σ is taken into account, the critical supersaturation being larger at lower temperature, the slope is smaller. Our results are presented in Table II. As we could have expected, the slope increases with x_m at a given σ: when the formation of the first embryos is more rapid, the effect of σ is less important because this quantity acts to enhance the evaporation in small embryos. In the same way, the slope decreases when σ is larger at a given x_m because the unequilibrium state is larger and then more difficult to overstep.

These variations of σ and x_m will also modify the critical supersaturation at a given temperature. In Table II we have also indicated the relative supersaturation $n_{ex}/n_{ex}(r^*)$ at 2 K to get a given slope. This supersaturation increases with x_m. We can compare it with the experimental ratio of the thresholds, i.e., $J_{th}^A/J_{th}^B = 3.6$ at this temperature. We have pointed out previously that the temperature dependence of J_{th}^B cannot be simply explained, and then there is no reason that both the ratio J_{th}^A/J_{th}^B and n_{ex}/n_{ex} (r^*) should be equal. The latter is certainly larger than the former but it seems reasonable to assume that the difference will not be too important. Therefore we think that the results obtained with x_m larger than 15 are not acceptable. On the other hand, we cannot trust calculations performed with x_m smaller than five pairs, which corresponds to an embryo radius of 170 Å (when n_0 is kept constant). Therefore we conclude that starting from an FE work function of 23 K to reach a slope of 17–18 K leads to an EHD surface energy in the range of 1.8–2.6 erg/m^2. A fit is presented in Fig. 1. We display in Table III the critical values for both the absolute and relative supersaturation rate, i.e., $S_1 = n_{ex}/n_{ex,0}$ and $S_2 = n_{ex}/n_{ex}$ (r^*) at different temperatures for the

TABLE III. Variation of the absolute and relative supersaturation rates, i.e., $S_1 = n_{ex}/n_{ex,0}$ and $S_2 = n_{ex}/n_{ex}(r^*)$, as a function of temperature for the choice $\sigma = 2.4$ erg/m^2 and $x_m = 10$ to have a formation time T_f of 0.5 msec.

T (K)	4.00	3.33	2.86	2.50	2.22	2.00
$1/T$ (K^{-1})	0.25	0.30	0.35	0.40	0.45	0.50
S_1	2.5	3.2	4.1	5.4	7.3	10.1
S_2	2.5	3.1	3.8	4.7	5.4	5.7

choice $\sigma = 2.4$ erg/m^2 and $x_m = 10$.

As we have already emphasized, the EHD formation time is very strongly dependent on the supersaturation rate and this can be seen in Fig. 3. This phenomenon has the same origin as in the case of classical vapors and can be easily understood by inspecting Eqs. (7). Up to the unstable equilibrium point x_i, the destruction process of the embryos is quite favorable with respect to the formation process because $e(x) > c(x)$. It is the reverse between both equilibrium points x_i and x_s, but for two reasons this does not lead to a negligible growth time between them. First, an embryo always has a certain probability to decrease again below x_i before reaching x_s. Second, the number of pairs to gain is quite important. We find in our calculations at 2 K that down to $T_f \sim 5\times10^{-4}$ sec, both the time to grow from x_m to x_i and then from x_i to x_s are nearly equal. At higher supersaturation, the second part becomes larger so that the total time is nearly constant and equal to $\sim 5\times10^{-5}$ sec. We have also checked in a simple way that the decrease in supersaturation owing to the simultaneous formation of a reasonable density of drops will not modify the growth time too much. Each growth step is less rapid but x_s becomes smaller.

V. CONCLUSION

We want to point out that in the case of classical vapors the surface energy is obtained from accurate experiments which are different from the measurements reported here. The nucleation theory is then used to be a test for itself. The description of the formation of small embryos can lead to very different results. No nucleation theory at all can avoid this difficult problem.

Here the reverse procedure has been used because σ has not yet been obtained independently of other parameters. Such an experiment would be very useful to study the nature of the nucleation process. Nevertheless, we believe that the study reported here gives an approximate value of of the EHD surface energy and provides a simple explanation of the discrepancy between ϕ_s and ϕ_{th}.

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