

Contribution of vaporization and boiling to thermal-spike sputtering by ions or laser pulses

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Here we consider what, in our terminology, we designate as normal vaporization, normal boiling, and phase explosion. In the case of vaporization, one is dealing with the emission of particles (atoms or molecules) from the extreme outer surface of either a solid or liquid for any temperature exceeding 0 K. In the case of boiling, one is (at least ideally) dealing with *heterogeneously* nucleated bubbles which diffuse to the outer surface of a liquid or solid and then escape, the latter being possible for temperatures equal to or exceeding the boiling temperature (T_b). In the case of phase explosion one is dealing with the consequences of what happens when a liquid approaches the thermodynamic critical temperature (T_c or T_c), and massive *homogeneous* nucleation takes place. Although these three mechanisms have been reviewed in reasonable detail in recent work, we will here present evidence, apparently not previously considered, that boiling, whether the distance scale is atomically small (5–15 nm, as for laser-pulse impact on a metal in the absence of thermal diffusion) or much larger, has a prohibitive kinetic obstacle because it requires *bubble diffusion* if the bubbles are formed other than at the outer surface. That is to say, boiling will never be a significant process whether with ion or laser-pulse impact. This leaves vaporization and phase explosion as the only possible thermal-spike processes capable of expelling material from an ion- or laser-pulse bombarded surface in a significant quantity. But even with vaporization it can be shown that a kinetic obstacle, although not as severe as for boiling, will enter. The final result is that only phase explosion will normally be relevant for sufficiently short time scales. [S1063-651X(99)06209-1]

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I. INTRODUCTION

We have already adequately reviewed the ensemble of mechanisms which arise when ion beams, electron beams, or laser pulses interact with solid or liquid surfaces. Each type of incident particle or radiation leads to a variety of observable phenomena. For example, with ions or electrons, one can expect sputtering, mixing, or composition change, each of which will have varieties such as ballistic, thermal-spike, residual-defect-induced, electronic, or exfoliational. See Table 1 of Ref. [1]. We here use the term “thermal spike,” rather than simply “thermal,” to emphasize that we are dealing with very short-lived effects.

The situation with laser-pulse impact is slightly different. Considering just the primary interactions, one has the same family of observable phenomena (Table I of Ref. [1]). The emphasis is not the same, however: there is a marked importance of thermal-spike processes with laser pulses and a minimal importance with ions. We associate this difference both with the volume of disturbance (very small for ions) and with the time scale (always short for ions and sometimes short for laser pulses). Both ions and the very shortest laser pulses (<100 ps) do not provide enough time for either boiling or vaporization, whereas the converse is partly true for laser pulses having durations of 10–100 ns. See, for example, Table 4 of Ref. [1]. Also, one must not forget that even with longer laser pulses (10–100 ns) it is unclear whether boiling is ever significant. This is perhaps the most important point that will be made in the work presented here

(Sec. II and Table I in particular).

What we seek to do here is settle, hopefully in a definitive way, the relevance of (normal) vaporization and (normal) boiling. Why this is a problem arises, in our opinion, from a widespread misreading of thermodynamic tables combined with a lack of understanding of bubble diffusion. One would be surprised at how frequent is the use of the term “vaporization” to include all possible processes leading to a liquid-to-vapor transition, as well as the assertion that this transition begins abruptly (and rapidly) at T_b , the boiling temperature.

II. GENERAL COMMENTS ON MATERIAL REMOVAL BY VAPOR FORMATION

We will show in Tables II, III, IV, and V why there might be confusion in quantities relevant to vapor formation. Table II serves to emphasize that T_m , the melting temperature, is well defined. By contrast, T_b , the boiling temperature, varies widely depending on the ambient gas pressure. Table III serves to emphasize that normal vaporization is sometimes able to account for significant material loss. At least this is so if the temperature is high enough and the time scale is long enough. For example, 100 ns is sometimes sufficient, but 1 ns is nearly always too little.

Older data suggest, if the time scale is moderately short (<1 ns), that even phase explosion may possibly be unimportant [2–5]. If this were so, then a liquid-to-vapor transition would be in general excluded, and the only possibilities left would be electronic processes. There is some indication, however, that the criterion “<1 ns” is not realistic (Sec. II C and Tables IV and V).

A. Normal boiling

Here we deal with a process, namely normal boiling, that is already adequately discussed (Sec. 5.3.2 of Refs. [6,7])

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TABLE I. Bubble diffusion distances in liquids according to the volume-diffusion mechanism. D_b^{vol} , the volume-diffusion coefficient for a bubble, was evaluated with Eq. (9). In so doing r was taken as 20, i.e., 20λ . The various substances are listed in order of increasing T_m .

Substance	T_m (K)	T for calculation (K)	$10^5 D_{\text{vol}}$ (cm^2/s)	$(D_b^{\text{vol}} t)^{1/2}$ for 1 ns (nm)	$(D_b^{\text{vol}} t)^{1/2}$ for 100 ns (nm)	Refs.
C ₂ H ₅ OH	159	296	1.31	0.009	0.089	[10]
Hg	234	234	1.01	0.008	0.078	[29,30]
		468	3.25	0.014	0.14	
H ₂ O	273	293	0.91	0.009	0.087	[10]
In	430	430	2.87	0.013	0.13	[31,32]
		860	8.94	0.023	0.23	
Sn	505	505	1.54	0.0096	0.096	[33,34]
		1010	9.67	0.024	0.24	
Ag	1234	1234	3.3	0.014	0.14	[35,36]
		2468	13	0.028	0.28	
Cu	1356	1356	3.6	0.015	0.15	[34,37]
		2712	24	0.038	0.38	
Fe	1809	1809	4.5	0.016	0.16	[38,39]
		3618	22	0.036	0.36	

except for two aspects. These relate to establishing whether *heterogeneous* nuclei can form at all in particular locations and whether, once formed, the time scale is adequate to permit the bubbles to diffuse to the outer surface. Here we use the term “normal boiling” to establish a contrast with both vaporization and “explosive boiling,” the latter being an alternative term for “phase explosion” (Sec. 5.3.3 of [6,7]).

Normal boiling involves *heterogeneous* nucleation. These are vapor bubbles which, in the case of liquids, initiate heterogeneously from a variety of disturbances such as gas or solid impurities, or defects, or an underlying solid surface, or an enclosing solid surface. In the early stages such bubbles are sometimes termed “embryos,” being typically $\ll 50$ – 100 nm in diameter and growing rapidly ($\propto t$) [8,9]. The embryos finally either disappear (“collapse”) or grow up to and then

beyond a critical size given by

$$R = \lambda_{\text{probe}} \sqrt{2\pi n} \approx 50\text{--}100 \text{ nm.}$$

The growth is then slower ($\propto t^{1/2}$). Here λ_{probe} is the wavelength of a laser used to infer the presence of bubbles, and n is the refractive index of the target (which was either water or CH₃OH in Ref. [8]). We will term such entities “bubbles.” Once formed, bubbles tend to diffuse and may, given enough time together with the inequality $T > T_b$, escape from the outer surface of the liquid. Bubbles may form either in solids (as in nuclear fuel) or in liquids, but given the problem of mobility only liquids need to be considered for the short-time-scale processes that are considered here.

We see in Table II that T_m is a relatively well-defined

TABLE II. Here we give a typical tabulation of T_m , the melting temperature, and T_b , the boiling temperature. T_m is a relatively well-defined quantity, characterized by both positive and negative changes with temperature which are, however, almost always numerically small [10]. T_b , by contrast, shows a marked variation [14,15]. In all cases the units of pressure are similar or identical to atm. For example, information from Ref. [14] was expressed in atm, whereas that from Ref. [15] was in 0.1 MPa.

Substance	T_m (K) for $p \approx 0$	T_m (K) for $p \approx 1000$	T_m (K) for $p \approx 10\,000$	T_b (K) for $p_b \approx 0.01^{\text{a}}$	T_b (K) for $p_b \approx 1$	T_b (K) for $p_b \approx 100^{\text{b}}$
Na	371	379	440	802	1156	2270
Ag	1234	1251	1361	1783	2436	3950
Zn	693	698	739	852	1180	1980
Cd	594	600	646	746	1040	1780
Ga	303	301	281	1816	2478	3940
In	430	435	478	1694	2346	3790
Sn	505	508	530	2097	2876	4530
Pb	600	608	671	1413	2023	3680
Sb	904	903	897	1220	1860	4020
Bi	544	541	502	1326	1837	3270

^a p_b is the partial pressure of *nonvapor* permanently present in the ambient.

^bReference [15], which expressed the pressures in terms of our Eq. (1), was used for $p_b \approx 100$.

TABLE III. Atom layers (λ) removed by normal vaporization at temperatures straddling T_b for various substances listed in order of T_m . Unless otherwise indicated, we give information in each case appropriate to metal(l) \rightarrow metal(g), where l refers to liquid and g refers to gas. The evaluations were made with Eq. (2c), into which vapor pressures (p_{atm}^{sv}) from Refs. [14,15,40,41] were introduced.

Substance	T (K)	Atom layers in 1 ns	Atom layers in 100 ns	T_b (K)	T (K)	Atom layers in 1 ns	Atom layers in 100 ns
Na	1000	0.020	2.0	1156	1500	0.78	78
Bi ^a	1000	0.000	0.000	1837	2000	0.058	5.80
Sb ^b	1000	0.000	0.002	1860	2000	0.047	4.7
Ag	2000	0.002	0.24	2435	3000	0.31	30.5
U	4000	0.005	0.48	4404	5000	0.069	6.9
Nb	4500	0.003	0.27	5017	5500	0.069	6.9
Mo	4000	0.001	0.092	4912	5000	0.028	2.8
W	5000	0.000	0.041	5828	6000	0.010	1.04

^aThe sum of two processes, involving Bi(g) and Bi₂(g), was considered.

^bThe sum of three processes, involving Sb(g), Sb₂(g), and Sb₄(g) was considered.

quantity up to roughly $p=1000$ atm (p. 63 of Ref. [10]). Moreover, melting is very rapid, ~ 0.3 ps (Sec. 4.3 of Ref. [11]). By contrast, T_b , the onset temperature for boiling, shows a remarkable variation if the ambient pressure is increased or decreased by even a factor of 100. To understand this one must realize that T_b is the temperature at which the equilibrium (equivalent to *saturated*) vapor pressure, p_{sv} , equals (the usual definition) or *exceeds* (a correct but sometimes overlooked definition [8]) the boiling pressure, p_b , i.e., the partial pressure of *nonvapor* permanently present in the ambient. If this condition is met, whether as an equality or inequality, then heterogeneously nucleated bubbles, *provided* that they are able to diffuse to the outer surface, will escape. Obviously there would be *no* kinetic problem for bubbles

nucleated near the outer surface, but such ‘‘bubbles’’ will be argued below [heading (1)] not to constitute true bubbles. In addition, as will be discussed in Sec. III and as seen in Table I, the values of $(D_b^{vol}t)^{1/2}$ appropriate to boiling by the volume-diffusion mechanism are extremely small even for a nm distance scale, and even with $t=100$ ns and $T=2T_m$ being insufficient. [The extreme slowness of bubble diffusion is a well known (but qualitative) observation when water is induced to boil on a stove.]

Historically, bubble diffusion became scientifically important with the development of nuclear reactors, since the two fission products Kr and Xe together account for $\sim 12\%$ of all fission products [12]. Since, furthermore, they are not soluble (whether in Pu, U, UC, or UO₂) they precipitate into

TABLE IV. Experimental estimates of τ_{hm} , the time constant for homogeneous nucleation, and thus for phase explosion. All values are based on either laser experiments or laser simulations. τ_{hm} is assumed to be given by τ_{hm} less than or equal to the pulse duration unless other effects (as with item 4) intervene. The older theory used by Martynyuk [2–5] is not considered, as it leads to unacceptably high time constants, 1–100 ns.

Number	Target	Pulse energy (i.e., fluence) (J/cm ²)	Pulse duration	Pulse wavelength (nm)	Expt. or simul. ^a	Phase explosion?
1	YBa ₂ Cu ₃ O _{7-x} (‘‘YBCO’’)	6.6	30 ns	248	expt.	yes
2	Ni	various	26 ns	248	expt.	5.2–9.0 J/cm ²
3	Ni	2.5–5.9	26 ns	248	expt.	2.5–5.9 J/cm ²
4	organic ^b	various ^b	300 ps (15 ps)	337 (337)	simul. (simul.)	>0.20 eV/molecule (no) ^b
5	organic ^c	various	150 ps	337	simul.	>0.0040 J/cm ²
6	cr-Al ₂ O ₃	~ 10	30 ps	266	expt.	>20 pulses
7	organic ^c	various	15 ps	337	simul.	>0.17 eV/molecule ^c
8	cr-Al ₂ O ₃	4.3	2.8 ps	800	expt.	>30 pulses
		4.0	0.2 ps	800	expt.	>30 pulses

^aExpt., experimental. Simul., simulation.

^bThe target was atypical, namely, a sphere with a 100-nm diameter. Also, the pulse energy (fluence) had unusual units, eV/molecule, which is equivalent to much less than 1 J/cm². The phase explosion occurred only for a 300-ps pulse, since in this case there was no pressure build up (see Table V).

^cThe target in this case was of normal macroscopic form. With item 7, the pulse energy (fluence) again had the unusual unit of eV/molecule.

TABLE V. Continuation of Table IV, in which we indicate the evidence for phase explosion and the references.

Number	Target	Evidence	Ref.
1	YBa ₂ Cu ₃ O _{7-x} (“YBCO”)	(a) Upper limit to time for phase explosion, namely, 30 ns ^c . (b) Clear evidence for both vapor (i.e., plume) and particulates.	[20]
2	Ni	(a) Upper limit to time for phase explosion, namely, 26 ns ^c . (b) Surface temperature constant for 5.2–9.0 J/cm ² , as if $T \approx T_{tc}$. (c) Inferred evidence for both vapor and liquid droplets.	[21]
3	Ni	(a) Upper limit to time for phase explosion, namely, 26 ns ^c . (b) Explicit optical evidence for 130-nm particulates which were ejected directly from the target surface and had time-invariant size.	[22]
4	organic ^a	(a) (300 ps) Very little pressure buildup, yet finally the target evolved to monomers plus liquid droplets. (b) (15 ps) Pressure buildup, and thus mechanical breaking apart.	[42]
5	organic ^b	(a) A much faster etch rate above fluence threshold. (b) Monomers plus liquid droplets.	[43]
6	cr-Al ₂ O ₃	(a) A much faster etch rate for >20 pulses. (b) Extreme roughness of the target surface.	[44]
7	organic ^c	(a) A factor of 2 increase in the etch rate above the fluence threshold. (b) Monomers plus liquid droplets.	[45]
8	cr-Al ₂ O ₃	(a) Rapid increase in the etch rate and in the ion yield for >30 pulses. (b) Monomers plus liquid droplets, the latter seen on the target surface around the crater rims.	[19]

^aFootnote b from Table IV.

^bFootnote c from Table IV.

^cWe indicate these times as being upper limits. In fact, 26 and 30 ns are the pulse durations rather than the *minimum* times necessary for phase explosion.

bubbles and then, given that a nuclear fuel maintains a high temperature for long periods of time, diffuse slowly whether the fuel is solid or liquid. This leads to swelling of the fuel and possibly even rupture of the cladding.

It is interesting to note that T_b is often confused as describing the onset of the liquid→vapor transition, just as T_m is correctly taken as describing the solid→liquid transition. We suspect that this error is due mainly to a misreading of thermodynamic tables, such as the excellent tables of Kubaschewski and Alcock [13].

We have already defined p_b as the boiling pressure, i.e., the partial pressure of *nonvapor* permanently present in the ambient. The evaluation of T_b up to and including $p_b = 1 \text{ atm} \approx 0.1 \text{ MPa}$ can be accomplished very simply with the information given by Hultgren *et al.* [14]. For higher values of p_b the information of Ref. [15] is useful, as we here find expressions of the type

$$\ln(p_{sv}) = e \times 10^3 \times T^{-1} + f \ln(T) + g, \quad (1)$$

where p_{sv} is the equilibrium vapor pressure in units of 0.1 MPa, and e , f , and g are constants listed in Ref. [15].

As seen in Figs. 1 and 2, embryos, and thus bubbles, may form variously at the outer surface of the liquid, in the bulk of the liquid, and at an underlying or enclosing solid surface.

(1) Consider first outer-surface bubbles [Fig. 2(a)]. Whether the dimensions of the depth of disturbance are large or small, it follows that the bubbles will tend to have a form that is approximately that of a half sphere. Such objects are, in fact, not true bubbles but just an uneven surface, and it is easily shown that, if R is the width of the disturbance, then the surface area evolves from R^2 to $\sim (\pi/2)R^2$. This leads to an increase in normal vaporization, but of negligible extent, and at the same time there is no boiling at all in the sense of a process involving bubble diffusion to the outer surface.

(2) Consider next bubbles formed in the bulk of the liquid [Fig. 2(b)]. Fucke and Seydel [16] quote examples, all relating to liquids, with which the density of bulk heterogeneous nuclei is suggested to be of order 10^3 g^{-1} , i.e., negligibly

BASIS OF NORMAL BOILING

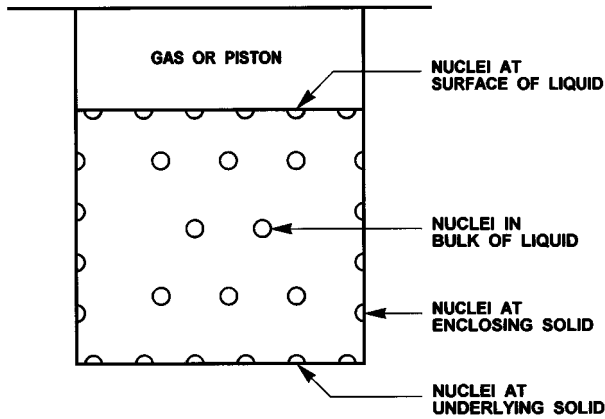


FIG. 1. Schematic representation of the three basic locations where heterogeneous bubbles may form, namely, at the outer surface of the liquid, in the bulk of the liquid, or at an underlying or enclosing solid surface. These three possibilities are discussed in Sec. II A, where it is recognized that in all three cases bubble formation will not permit boiling. At least this is true in the case of ion or laser-pulse bombardment. This is because the bubbles serve variously either to roughen the outer surface of the liquid, are largely nonexistent (bulk of the liquid), or are largely immobile (liquid-solid interface).

small. For a typical substance with density $\rho = 10 \text{ g/cm}^3$, a disturbed area of $1 \times 1 \text{ cm}^2$, and a disturbed depth of either $5\text{--}15 \text{ nm}$ or $\geq 5\text{--}15 \text{ nm}$, one would expect no nuclei, and thus no bubbles, at all.

(3) Consider finally bubbles formed at an underlying or enclosing solid surface [Fig. 2(c)]. The situation is now rather different, as neither of the problems brought up in (1) or (2) enter. We will suppose that even embryos, which have radii similar to the smaller estimated depth of disturbance ($5\text{--}15 \text{ nm}$), are able to diffuse. Alternatively, the depth of disturbance may greatly exceed $5\text{--}15 \text{ nm}$, as is possible not only with semiconductors and insulators but also when $(\kappa t)^{1/2}$ plays a role. Here κ is the thermal diffusivity (cm^2/s). Both embryos and true bubbles are now relevant. In either case, however, the classical problem of "bubble diffusion" [17] would exist and, as will be treated in Sec. III, would lead to negligible distances of transport.

Anticipating the final result we find that the diffusive motion of either embryos or bubbles is far too slow to have any physical significance for a short time scale ($< 1 \mu\text{s}$). In effect, normal boiling is totally prohibited for a short time scale no matter where the bubbles form and no matter what is the depth of disturbance.

B. Normal vaporization

One must next ask whether, if normal boiling can be excluded because of being exceedingly slow, would normal vaporization ever be important? By *vaporization* we refer to the passage from a condensed phase (solid or liquid) to vapor by virtue of the emission of particles (atoms or molecules) from the extreme outer surface under conditions of electron-phonon coupling. Obviously "vaporization," as we use the term, includes "sublimation" and "evaporation." In Table

MODES OF HETEROGENEOUS NUCLEATION

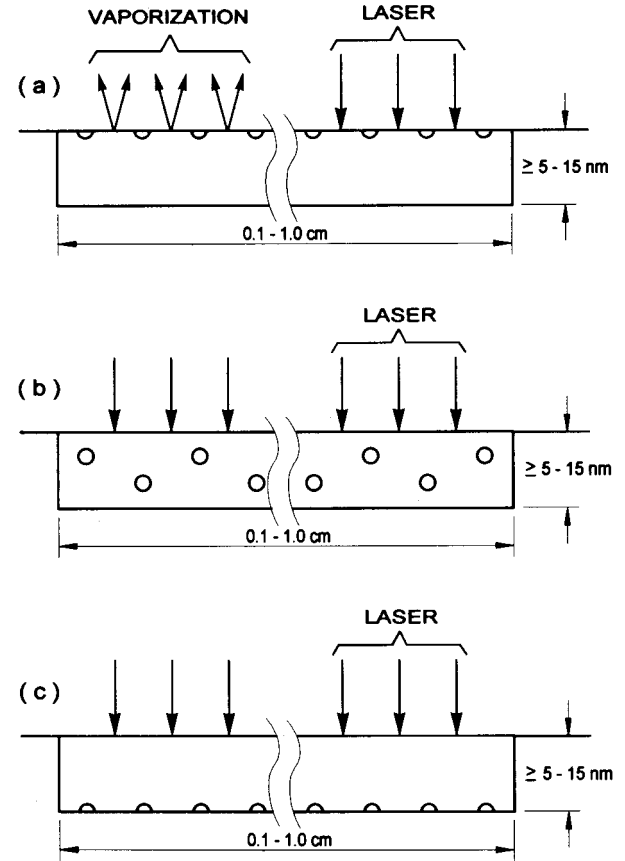


FIG. 2. As in Fig. 1, we represent schematically, but in greater detail, the three basic locations where bubbles may form under the assumption that laser-pulse bombardment is involved. We consider three cases, wherein the bubbles form (a) at the outer surface of the liquid, (b) in the bulk of the liquid, or (c) at an underlying or enclosing solid surface. The bubbles are shown in their earliest state of existence, when they are termed embryos, and have dimensions that may in principle be smaller than the depth of disturbance. As the embryos grow the final results are as follows. Case (a) leads only to a roughening of the liquid surface, and thus to a very slight enhancement of normal vaporization. Case (b) is in no case correct, whether for embryos or fully grown bubbles, as the density of heterogeneous nuclei is believed to be negligibly small [16]. Case (c) is rather different, as neither of the problems associated with (a) and (b) enter. However, the classical problem of "bubble diffusion" [17] would exist and, as shown in Table I, would lead to negligible distances of transport.

III, therefore, we give values of atom layers vaporized for either 1 or 100 ns and for temperatures straddling T_b . These values were obtained with the Hertz-Knudsen equation, which can be written

$$\text{flux} = \alpha p_{s,v} (2\pi m k_B T)^{-1/2} \text{ particles/m}^2 \text{ s.} \quad (2a)$$

Here α is the condensation (or vaporization) coefficient, $p_{s,v}$ is again the equilibrium vapor pressure but this time in units of Pa, and m is the particle mass (kg). The form of Eq. (2a) assumes that the partial pressure of *vapor* permanently present in the ambient is zero.

Normal vaporization can be expected to occur transiently with both insulators and metals at any laser fluence and pulse length, i.e., there is no temperature threshold. (Both normal boiling and, to some extent, phase explosion have a threshold.) It will, however, not be important for low fluences (i.e., low temperatures) or very short pulses (Table III). The flux (particles/m² s) is governed by Eq. (2a), which if multiplied by m/ρ (equivalent to λ^3 , ρ being the target mass density and $\lambda \approx 0.25$ nm being the mean atomic spacing of the target) gives the velocity of surface recession in a one-dimensional situation:

$$(\partial x/\partial t)|_{x=0} = \alpha p_{sv} (2\pi m k_B T)^{-1/2} \lambda^3 \quad \text{m/s} \quad (2b)$$

$$= \alpha p_{\text{atm}}^{sv} \left(\frac{1000}{T} \times \frac{100}{M} \right)^{1/2} \times 5.28 \\ \times 10^7 \quad \text{monolayer/s.} \quad (2c)$$

Here p_{atm}^{sv} is p_{sv} in units of atmosphere (~ 0.1 MPa). Since the vapor pressure is nonzero at all temperatures exceeding 0 K, it follows that for normal vaporization the surface temperature is *not* fixed. Claims to the contrary, that is that a ‘‘vaporization temperature’’ (T_v) exists, are therefore wrong.

It is found (Table III) that vaporization will be important (i.e., lead to loss of rather more than λ , the mean atomic spacing) if the time and temperature are sufficient. Specifically, for temperatures exceeding T_b , 100 ns is often sufficient, 1 ns is nearly always too little, and a ps time scale will definitely exclude all possibility of vaporization. One concludes that there will be no vaporization for time scales of < 1 ns, and thus for neither ion impact nor for ps laser pulses.

C. Phase explosion

We finally ask whether phase explosion has kinetic limits. The non-laser data of Martynyuk [2–5] suggest a time scale of about 1 ns. Thus, it was argued that the necessary *homogeneous* nucleation was governed by

$$I \approx 1.5 \times 10^{32} \exp(\Delta G_n/k_B T) \exp(-\tau_{hn}/t) \quad \text{cm}^{-3} \text{s}^{-1}, \quad (3)$$

where ΔG_n is the free energy for formation of a stable homogeneous nucleus (i.e., a sphere of vapor within the liquid) and τ_{hn} is the relevant time constant. What is important is the value of τ_{hn} , calculated values due to Martynyuk [2–5] ranging from 1 to 100 ns and suggesting that phase explosion is possibly irrelevant for ps laser pulses. This conclusion was tentatively accepted in earlier work by the authors [18], but since then important experimental examples of phase explosion have appeared with time scales ranging from 15 to 300 ps (Tables IV and V) and, more recently, even in the interval 0.2–3 ps [19]. For this reason, we must discount the calculations of Martynyuk.

We would note, in addition, that contemporary experiments using relatively long laser pulses [20–22] confirm phase explosion at ~ 30 ns (Tables IV and V). This does not, however, constitute the definition of a lower time limit but simply a typical pulse duration which led to phase explosion.

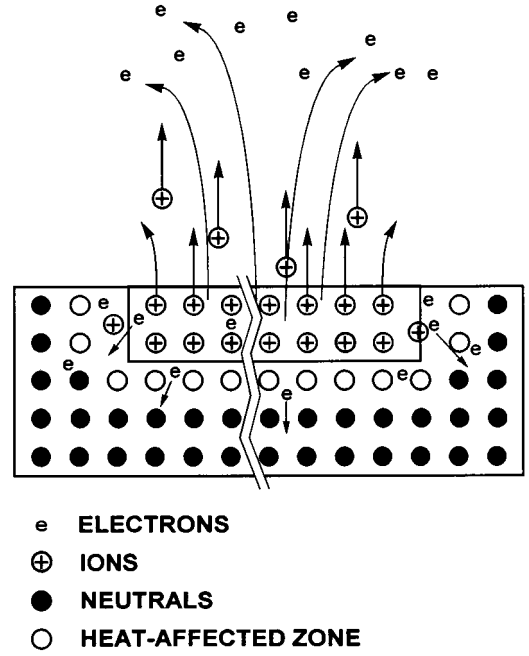


FIG. 3. Schematic view of a planar Coulomb-explosion mechanism as is appropriate for a material bombarded with laser pulses. We note that a spatial separation between electrons and ions is assumed to develop *parallel* to the target surface, with the result that the system in principle ‘‘explodes’’ outwards. The basic symmetry is therefore different from the Coulomb explosion assumed to be associated with very high-energy particles such as fission fragments, where the electron-ion separation should be parallel to the particle track [25], and the corresponding explosion should be perpendicular to the track. Unfortunately, the mechanism is in both cases somewhat speculative.

The question that we must address is, therefore, this: what is the relevant sputtering (i.e., material-loss) mechanism for very short laser pulses? That there *is* material loss for pulse durations between 0.1 and 5 ps is not in question for such materials as Al₂O₃ [19], CaF₂ [23], or SiO₂ [24]. We do not intend to pursue the problem in detail, but we still have a general point to make. There are, indeed, three short-time-scale alternatives to normal vaporization and normal boiling.

(1) Phase explosion, notwithstanding the unfavorable time scale (1–100 ns) that was advocated by Martynyuk [2–5].

(2) Coulomb explosion, a process pioneered many years ago by Fleischer, Price, and Walker [25] in the context of fission-track formation, but more recently applied also to ps laser bombardment [19]. We recognize, of course, that in both Refs. [25] and [19] the mechanism is somewhat speculative.

(3) Other electronic processes (Sec. 5.2 of Refs. [6,7]).

Interestingly, Stoian *et al.* [19] found significant material loss from Al₂O₃ with 0.2–3 ps laser pulses, and proposed that for fewer than ~ 20 –30 pulses Coulomb explosion was occurring. This is the process in which a spatial separation between electrons and ions is assumed to develop parallel to the target surface (Fig. 7 of Ref. [19]; see also the present Fig. 3), with the result that the system ‘‘explodes’’ outwards. The argument developed in Ref. [25] concerned the tracks (normally amorphous) created in solids by very high-energy particles such as fission fragments. It was suggested that the tracks owed their origin to Coulomb explosion but with a

geometry different from that applicable to laser pulses (Fig. 3). Thus the spatial separation between electrons and ions was assumed to develop parallel to the particle track rather than parallel to the surface. To complete the argument, it will, of course, be necessary to evaluate the relevant time scales, namely, that for electron separation and that for the positive ions to move apart violently.

For more than ~ 20 – 30 pulses, Stoian *et al.* [19] pointed out that the evidence favored *phase explosion* rather than *Coulomb explosion*. The argument was based on scanning electron microscopy (SEM) of the target surface, as well as on time-of-flight spectra, and forms the basis of our claim that phase explosion can occur for 0.2–3 ps (Tables IV and V). We are unable to conclude whether phase explosion is, or is not, possible with ion bombardment at low to medium energies.

III. MECHANISMS OF BUBBLE DIFFUSION

A. General comments

Historically bubble diffusion became important with the development of nuclear reactors. (Here and thenceforth we will refer only to “bubbles,” but do not exclude the fact that “embryos” are probably also relevant.) Why bubble diffusion was important in this context is that the gases Kr and Xe are the dominant fission products. Because of the high temperature of the fuel and the very long time scale (weeks to months), the bubbles are able to diffuse in spite of the fuel being solid. Three diffusion mechanisms are relevant which are of fundamental interest in the present context because precisely these mechanisms will also serve to transport bubbles in the process of *normal* boiling. We emphasize *normal* here because it is not clear whether phase explosion (“explosive boiling”), which involves homogeneous (rather than heterogeneous) nuclei, requires formal bubble transport. In fact, we suspect that phase explosion involves such a high density of nuclei that the affected region of the liquid simply disintegrates without any kinetic obstacle.

B. Surface-diffusion mechanism

The surface-diffusion mechanism of bubble motion is based on an in-surface atom which leaves the liquid surface surrounding a bubble, diffuses along the surface inside the bubble, and finally returns to the liquid surface when an appropriate sink is encountered. In some cases the motion will be simply from ledge to ledge. A schematized example is shown in Fig. 4, while the applicability to a bubble is shown in Fig. 5.

We will now summarize the derivation of D_b^s , the bubble *surface-diffusion* coefficient, but we hasten to add that we cannot evaluate the result because of the lack of information on D_s , the surface-diffusion coefficient for liquid metals. In Sec. III C we will evaluate D_b^{vol} , the bubble *volume-diffusion* coefficient, and will obtain the striking result that boiling is simply *not possible* on a short time scale. (This result is, of course, obvious “in hindsight” to any person who has brought water to the boiling point on a stove.) Nevertheless, an immense number of publications on laser-surface interaction strongly advocate the claim that boiling plays a role when the temperature exceeds T_b . Worse still, T_b is nor-

NORMAL SURFACE DIFFUSION

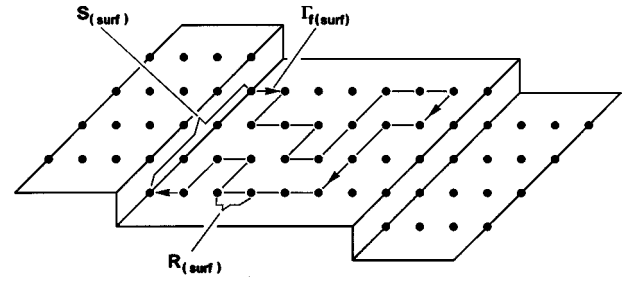


FIG. 4. Schematized example of surface diffusion, in which an atom leaves a liquid or solid surface, diffuses along the surface, and finally returns to the surface when an appropriate sink is encountered. In the example shown, the motion is shown to be from ledge to ledge, but there are other possibilities. Also shown are two possible definitions of the jump distance, namely, the individual surface jump distance ($R_{(\text{surf})} \equiv R_s$), and the distance between formation and condensation of a surface defect ($S_{(\text{surf})} \equiv S_s$).

mally taken as involving a fixed temperature and a short time scale on the basis of T_m being characterized in this way (Table II).

Let us now summarize the mechanism of bubble motion by surface diffusion as developed in Ref. [17]. For any three-dimensional random motion, the diffusion coefficient is given by

$$D \approx (1/6)\Gamma R^2 \lambda^2, \quad (4)$$

where Γ is the jump frequency (s^{-1}), λ is the mean atomic spacing (~ 0.25 nm), and R (in units of λ) is the individual root mean square jump distance. For a bubble moving by surface diffusion we seek $\Gamma_b^{(\text{surf})} \equiv \Gamma_b^s$, which could, if desired, be related to the frequency $\Gamma_{(\text{surf})} \equiv \Gamma_s$, per area λ^2 of surface of individual surface jumps. The result is straightforward:

$$\Gamma_b^s = \Gamma_s (4\pi r^2),$$

SURFACE DIFFUSION

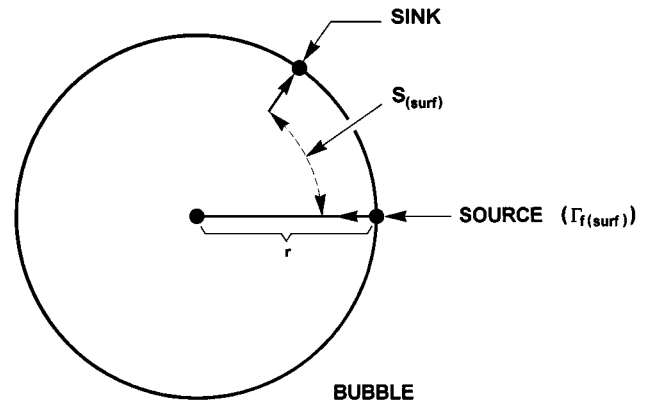


FIG. 5. More precise schematization of the surface-diffusion mechanism for bubble motion. We recognize the source of the surface defect (the formation rate is $\Gamma_{f(\text{surf})} \equiv \Gamma_{fs}$), the quantity $S_{(\text{surf})} \equiv S_s$ (already introduced in Fig. 4), and the sink or, equivalently, the point of condensation.

r (in units of λ) being the bubble radius (Fig. 5). Γ_s can, in turn, be obtained by rearranging the general expression for the surface diffusion coefficient

$$D_s = (1/4)\Gamma_s R_s^2 \lambda^2, \quad (5)$$

with the result

$$\Gamma_b^s = (4D_s/R_s^2 \lambda^2)(4\pi r^2).$$

Here $R_{(\text{surf})} \equiv R_s$ (in units of λ) is the individual surface jump distance (Fig. 4).

As an alternative, one could write D_s in terms of $\Gamma_{f(\text{surf})} \equiv \Gamma_{f_s}$ [16]. Γ_{f_s} is the frequency per area λ^2 of surface of surface-defect formation, being shown explicitly in both Figs. 4 and 5. The same figures also clarify $S_{(\text{surf})} \equiv S_s$ (in units of λ), the rms distance between formation and condensation of a surface defect. The general expression for D_s now becomes

$$D_s = (1/4)\Gamma_{f_s} S_s^2 \lambda^2$$

and for Γ_b^{fs} becomes

$$\Gamma_b^{fs} = (4D_s/S_s^2 \lambda^2)(4\pi r^2).$$

The rms bubble jump distance, R_b^s or S_b^s , will be related to R_s or S_s according to

$$R_b^s = R_s(3/4\pi r^3)$$

or

$$S_b^s = S_s(3/4\pi r^3),$$

so that, as the final result, we obtain

$$D_b^s = (1/6)\Gamma_b^s (R_b^s)^2 \lambda^2 = (1/6)\Gamma_b^{fs} (S_b^s)^2 \lambda^2 = (3/2\pi r^4)D_s. \quad (6)$$

The final result is, as it must be, independent of whether R_s or S_s is used.

As already stated above, however, we cannot evaluate Eq. (6) because of the lack of information on D_s for liquid metals. This is, however, not a problem as the volume-diffusion mechanism (Sec. III C) is easily quantified. Unfortunately, the argument is not as transparent as that for the surface-diffusion mechanism.

C. Volume-diffusion mechanism

The basic transport process in the volume-diffusion mechanism of bubble motion might be described as particle motion from one position on the bubble surface to another by diffusion in the surrounding liquid [17]. Unlike the surface-diffusion mechanism, there is no problem related to the lack of information on the relevant diffusion coefficients. Note that we use subscript or superscript ‘‘def’’ to refer to mobile defects in the liquid, but ‘‘vol’’ to refer to volume diffusion. The nature of the mobile defects is discussed in Ref. [26] on the basis of Swalin’s theory [27]. Whether the defects are, or are not, understood, however, is immaterial because we ultimately make recourse to experimental transport data.

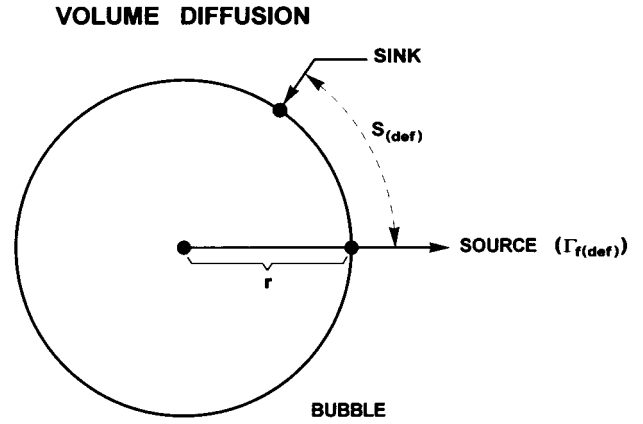


FIG. 6. Schematization of the volume-diffusion mechanism for bubble motion. We recognize the source of the defect (the formation rate is $\Gamma_{f(\text{def})}$), the quantity $S_{(\text{def})}$ (the volume analog of S_s), and the sink or, equivalently, the point of condensation. The volume-diffusion mechanism is actually more complicated than implied by Fig. 6, because two classes of event can occur. These relate to defects which return to the original bubble (as shown in Fig. 6) and defects which escape to another bubble but are replaced by a like number coming from random sources (not shown in Fig. 6).

We begin, as before [Eq. (4)], with the general relation for three-dimensional random diffusion:

$$D \approx (1/6)\Gamma R^2 \lambda^2.$$

Figure 6 schematizes the problem, where we recognize a bubble (radius r in units of λ) which introduces a defect into the surrounding liquid. The defect diffuses and finally either returns to the original bubble or else escapes to another bubble. In the latter case it will be replaced by a like number of defects coming from random sources. (This is a major complication for quantifying the volume-diffusion mechanism.) The first step is similar to that of the surface-diffusion mechanism, namely, recognizing that Γ_b^{vol} is related to the frequency $\Gamma_{f(\text{def})}$ per area λ^2 of surface of individual defect-formation jumps:

$$\Gamma_b^{\text{vol}} = \Gamma_{f(\text{def})}(4\pi r^2).$$

$\Gamma_{f(\text{def})}$ is developed in a slightly different manner than Γ_s . In particular a relation analogous to Eq. (5),

$$\Gamma_{f(\text{def})} = (6D_{\text{vol}}/S_{(\text{def})}^2 \lambda^2),$$

is probably *not* correct. Our justification (which is basically qualitative) for this claim is that the defect-formation jump is unidirectional (hence no ‘‘6’’) and has a length similar to λ rather than $S_{(\text{def})}\lambda$. Here $S_{(\text{def})}$, in units of λ , is the volume analog, as in Fig. 6, of S_s , as in Fig. 5. Rather, we have previously suggested [17] the use of

$$\Gamma_{f(\text{def})} \approx D_{(\text{def})} C_{(\text{def})} \alpha \lambda \approx D_{\text{vol}} \alpha / \lambda^2, \quad (7)$$

where $C_{(\text{def})}$ is the defect concentration in the liquid and α is the defect condensation efficiency at the bubble surface. Equation (7) describes the situation in which defects leaving the bubble surface are balanced by defects returning from the liquid.

The rms bubble jump distance, R_b^{vol} , can be expressed as

$$R_b^{\text{vol}} = S_{(\text{def})} (3/4 \pi r^3).$$

We will not attempt to derive the somewhat complicated quantity $S_{(\text{def})}$ but rather refer to Ref. [17]:

$$S_{(\text{def})}^2 \approx 4r/\alpha. \quad (8)$$

The difficulty in deriving the result seen in Eq. (8) is, as already indicated at the beginning of Sec. III C, that two classes of event can occur. These relate to defects which return to the original bubble and defects which escape to another bubble but are replaced by a like number coming from random sources. The latter defects take up a random position at rms distance $2^{1/2}r$ from their point of origin. The final result follows as

$$D_b^{\text{vol}} \approx \frac{1}{6} \left\{ \frac{D_{\text{vol}} \alpha}{\lambda^2} \times 4 \pi r^2 \right\} \left\{ S_{(\text{def})} \times \frac{3}{4 \pi r^3} \right\}^2 \lambda^2 \\ \approx (3/2 \pi r^3) D_{\text{vol}}, \quad (9)$$

an expression which is conveniently independent of α . When evaluating Eq. (9) it is important to recognize that r is in units of λ rather than being a true length. Also, we have reason to believe, Ref. [17] notwithstanding, that it is not correct to introduce the correlation factor (f) [28] in Eqs. (7)–(9).

The crucial details relevant to the volume-diffusion mechanism are given in Table I. We here give values of D_{vol} for various liquids and then [using Eq. (9)] deduce the corresponding values of D_b^{vol} as well as the values of the mean diffusion distance for 1 and 100 ns, i.e., time scales appropriate to ns laser-pulse bombardment but much greater than those appropriate to either ion or ps laser-pulse bombardment. r was taken as 20λ .

The striking aspect of the information in Table I is that it follows, very simply, that normal boiling is impossible on a short time scale. This includes not only the ns-laser time scale, but also all possible bombardment processes involving shorter timescales.

D. Vaporization-condensation mechanism

A third mechanism, based on vaporization-condensation and represented schematically in Fig. 7, is also possible. We will not discuss it here but note that a derivation is given in Ref. [17] and that the final result scales as

$$D_b^{\text{vap}} \propto r^{-2}. \quad (10)$$

VAPORIZATION - CONDENSATION

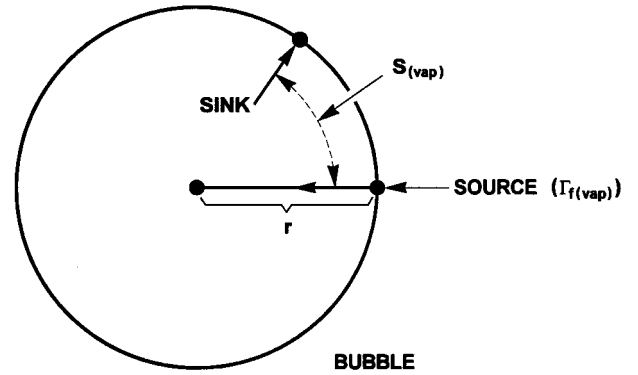


FIG. 7. Schematization of the vaporization-condensation mechanism for bubble motion. We recognize the source of the gaseous species (the formation rate being $\Gamma_{f(\text{vap})}$), the quantity $S_{(\text{vap})}$ (the vapor analog of S_s or $S_{(\text{def})}$), and the sink or, equivalently, the point of condensation.

IV. CONCLUSIONS

We argued in Sec. II A (supported by Table II) that melting (governed by T_m) is a relatively well-defined phenomenon up to at least $p \approx 1000$ atm (p. 63 of Ref. [10]). Moreover, the act of melting involves a very short time scale (of order ~ 0.3 ps [11]). By contrast, boiling (governed by T_b) depends explicitly on p_b , the partial pressure of *nonvapor* permanently present in the ambient, and is, therefore, subject to great variability.

In addition, boiling is subject to major obstacles in the process of bubble formation. Although we have not discussed ion impact, it can be shown that the disturbed volume is normally (≤ 50 keV) insufficient for even one bubble to form. With laser-pulse bombardment there are three possibilities. As discussed in Sec. II A, the first is that heterogeneous bubbles form at the liquid surface, bubbles which however serve mainly only to roughen this surface, thereby leading to a minimal enhancement of normal vaporization. But, as seen in Table III, vaporization is in any case not important for the shortest time scales (< 1 ns). The second possibility is that heterogeneous bubbles form in the bulk of the liquid. Interestingly, this process is probably highly unfavorable due to a lack of nuclei [16]. The third possibility is that bubbles form at an underlying or enclosing solid surface. Such bubbles will be quite numerous, but will be subject to a major kinetic obstacle: they must diffuse to the surface and such motion is sufficiently slow that it will simply not occur for $t < 100$ ns. This is because the value of D_b^{vol} as in Eq. (9) leads to values of $(D_b^{\text{vol}} t)^{1/2}$ which are atomically small (Table I). This is true both for 1 ns and 100 ns, and both for $T = T_m$ and $T = 2T_m$.

These points are not surprising. What is surprising is the fact that many persons do not recognize the details outlined in this work. Moreover, there is a completely inexcusable tendency to believe that, just as T_m does indeed describe the solid \rightarrow liquid transition, so also T_b describes the onset of the liquid \rightarrow vapor transition. In fact, vaporization occurs at all temperatures exceeding $T = 0$ K.

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