

A microscopic mechanism for shock-wave generation in pulsed-laser-heated colloidal suspensions

Hartmut Löwen^{a)} and Paul A. Madden^{b)}

Laboratoire de Physique,^{c)} Ecole Normale Supérieure de Lyon, 69364 Lyon Cedex 07, France

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The kinetics of the heat and mass transport involved in vapor bubble formation around a colloidal particle which has been heated rapidly to high temperatures are examined with a theoretical model. It is argued that the likely mechanism of bubble formation on the nanosecond time scale is a spinodal decomposition of the liquid at the particle surface to the low density (vapor) phase. This process is shown to give rise to extremely rapid changes in the density and pressure fields of the fluid. The existence of such rapid events has been invoked to explain experimental observations of acoustic shocks generated in laser-pulse-heated colloidal suspensions.

I. INTRODUCTION

Recent nonlinear optics experiments¹ on dilute suspensions of colloidal particles which are capable of absorbing the laser radiation have provided evidence that, under appropriate conditions, the heated particles drive the pressure field of the suspending fluid on a very short time scale (i.e., "explosively"). The time scale of the impulse is considerably shorter than the laser pulse duration. The resulting change in the refractive index of the fluid provides an efficient mechanism for phase conjugation.

In this paper, we examine a novel mechanism for this phenomenon. We study the growth of vapor bubbles in the vicinity of the colloidal particles. Our attention is focused on the kinetics of this phenomenon and the kinetic equations are derived by analogy with those which have recently been applied successfully to crystal growth.²⁻⁴ These equations contain a thermodynamically consistent description of the equilibrium between fluid and vapor and of its coupling to the temperature field. With reasonable choices of material parameters, our theory predicts that, on the time scale of relevance to the experiments, bubbles can only nucleate when the fluid is heated well beyond coexistence. The growth of the bubbles is extremely rapid and will lead to a disturbance of the pressure field of the fluid of the type observed experimentally.

A. Experimental background

The observations have been made in degenerate four-wave mixing experiments using laser pulses of ~ 25 ns duration. Two strong laser pulses with slightly different propagation directions overlap in the sample. A time-dependent refractive index grating (whose period is determined by the angle between the beams) is induced in the sample via nonlinear effects. This is interrogated by a probe laser pulse which is diffracted by the grating. The time dependence of the diffracted beam intensity is recorded electronically and

this may be used to study the time-dependent processes which occur in the fluid following its disturbance by the pump beams.

Experiments¹ have been carried out on aqueous suspensions of carbon (graphite) particles using Nd/YAG laser pulses at a wavelength of $1.06 \mu\text{m}$ and using gold particles of various sizes with a frequency doubled Nd/YAG. Under these conditions, the particles may absorb the laser radiation and become very hot; various observations suggest that temperatures of the order of 2000 K are reached. The particle sizes and concentration are such that there are many particles in a volume corresponding to the grating wavelength (cubed). In both cases, under appropriate conditions, the intensity of the diffracted signal shows a very rapid increase and then oscillates with a period which is characteristic of the sound frequency of the fluid (i.e., it has the appropriate magnitude and scales linearly with the grating period). This implies that the refractive index change which is detected in the experiment is formed in the suspending fluid and is not due to a change in the intrinsic polarizability of the particles caused by the heating process.⁵

Were this refractive index change to be brought about simply by heat transfer to the fluid surrounding the particles and its subsequent expansion, it would be describable as a simple *thermal effect*, well known in molecular absorbing fluids.⁶ The characteristic transients associated with this effect are known and can be modeled accurately.⁷ Under the experimental conditions, the heating process would occur over the laser pulse duration, i.e., over several acoustic periods. Under the experimental conditions, the diffracted pulse would rise, following the pump pulse shape and relax slowly by thermal diffusion; no oscillatory features would be seen.

The experimental observations have been shown¹ to be consistent with the relaxation of the hydrodynamic fields of the fluid following a very sudden disturbance to the temperature and density fields of the fluid during the pump illumination. The time scale of this impulse must be short compared to the acoustic period¹ which is typically 5 ns in the experiments, i.e., the disturbance must occur on a time scale roughly 20 times shorter than the pump pulse dura-

^{a)}Permanent address: Sektion Physik der Universität München, Theresienstrasse 37, D 8000 München 2, Germany.

^{b)}Permanent address: Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom.

^{c)}Unité de Recherche Associée 1325 du CNRS.

tion. In further attempts to characterize the origin of this disturbance, evidence was presented to show that any bubbles which form in the process are not caused by dissolved gas.¹ The authors of Ref. 1 therefore postulated that the origin of the disturbance was the rapid growth of vapor bubbles around the hot particles. The degenerate four-wave mixing experiment picks up a coherent superposition of the pressure fields emanating from the heated particles.

B. Time scale considerations

In order to provide a justification for the theoretical description of the growth of the bubble which we introduce below, it is necessary to consider the relationships of the time scales of numerous physical processes which could influence this process *under the conditions which pertain to the experiments described above*. The experimentally controllable parameters which set the time scale are the pump illumination period (say 25 ns), the period of the acoustic oscillation (typically 5 ns), and the size of the particles ($R_p = 0.1 \mu\text{m}$)—the latter determines the rate of certain relaxation processes. We envisage that, when the particle absorbs photons, this energy is degraded into heat on a subpicosecond time scale and that furthermore the distribution of temperature within the particle rapidly becomes uniform. Therefore, the particles behave as a heat source for the surrounding fluid and the temporal profile of the surface temperature follows the integrated form of the laser pulse, effectively instantaneously. That is, the surface temperature will rise to a maximum in about 25 ns (the time taken for the pulse to rise and decay), a time which we designate τ_0 ; it will then relax relatively slowly as the heat is transferred to the fluid. The ultimate long time limit is set by the time it takes for the heat to diffuse away into the surrounding fluid, i.e., $(D_T/R_p^2)^{-1} \approx 50 \text{ ns}$ (using the thermal diffusivity appropriate to water at 300 K). The time scale of the process which we hope to identify is shorter than these two limits ($\approx 1 \text{ ns}$), but considerably longer than the time it takes to convert photons to heat at the particle surface. We believe that it is set by the details of the energy transfer between the hot surface and the (initially) cool fluid, i.e., by properties of the boundary layer and it is to this region that we now turn our attention.

Initially, we are looking for the creation of an interface between the low density vapor and high density liquid phases. The subsequent propagation of the interface brings in other considerations which we will discuss below. The extent of the interface will be a microscopic correlation length ζ (the range of the direct correlation function in equilibrium theories of interfacial structure⁸) of the order of 0.1–1 nm. The relevant microscopic time scales concern the rate of heat and mass diffusion across this interface. The rate of heat transport will be $\tau_{\text{th}}^{-1} = D_T/\zeta^2$ or roughly 10 ps. If we take the relaxation time for mass transport τ_m to be the relaxation time of the dynamical structure factor of the liquid for wave vectors $\approx 2\pi/\zeta$, we expect to find τ_m longer than τ_{th} by a factor of 2–10.⁸ τ_{th} is the lower time scale of our analysis; on longer times, the interface may develop and move. Note that τ_{th} is comfortably longer than the internal thermalization time of the particle and much

shorter than τ_0 . What the difference between the time scales of heat and mass diffusion implies is that the kinetics of the formation of the interface, which involves mass transport between two phases of different density, will be slower than the transport of heat. This means that it is likely that the creation of the interface will lag behind the creation of the appropriate thermodynamic conditions, i.e., there may be a substantial lag between the local temperature of the liquid exceeding the “boiling point” and the appearance of the vapor bubble. The normal mechanism for bubble formation (in slowly heated liquids) is the spontaneous appearance of a density fluctuation which then acts as a nucleation center. In the rapid heating conditions relevant to the experiments, one may expect that there is insufficient time for such a fluctuation to arise before the liquid is heated well beyond normal liquid/vapor coexistence conditions and is approaching the point at which it is unstable (the spinodal). When vaporization does begin to occur, the fluid will be cooled locally as heat will be absorbed to overcome the latent heat of this process; the appearance of the interface involves a coupling of the density and temperature fields.

In this discussion of the interface creation, we have asserted that the relaxation of the density across the interface can be treated as diffusive. In the theory developed below, this assumption is manifest in the use of a “locally conserved” order parameter. If the distance scales were large (ζ), this simplification would be inappropriate and the mass transport would have an important contribution from sound waves, i.e., there would be an important coupling to the momentum field. However, the density relaxation on very short distance scales in a liquid (as seen in the dynamical structure factor for large wave vector) is dominated by diffusive processes. Distinctive sound peaks appear in the dynamical structure factor for water only for wave vectors smaller than $\approx 0.3 \text{ \AA}^{-1}$. In a more exact treatment, the acceleration of the liquid by the growing interface would be included at the price of considerably increased complexity (see also the discussion of Oxtoby and Harrowell⁹).

The paper is organized as follows: after having described a simple phase field model in Sec. II, we present analytical and numerical results of this model in Sec. III. The results support strongly the picture of a rapid vapor-bubble formation at temperatures close to the spinodal of the liquid at the surface of the colloidal particle. Finally, Sec. IV is devoted to a conclusion and discussion of this mechanism.

II. THE MODEL

As pointed out in the Introduction, the local temperature as well as the density (or more generally an order parameter) field are coupled and this coupling is crucial for the formation of a vapor bubble around a colloidal particle. So we require coupled equations describing the time development of these two quantities. These can be developed in analogy to a phase field model that was invented to describe crystal growth.^{2,3}

Since the width of the gas layer around the particle is much smaller than the particle diameter R_p , we can map the spherical spatial geometry onto a one-dimensional semiinfinite one characterized by a spatial variable z . This is true at least for the early stage of the bubble formation process. If we choose the particle surface to be located at $z=0$, we can also symmetrize the problem thus dealing only with profiles that are symmetric with respect to inversion in z .

First, we introduce a dimensionless temperature field

$$u(z,t) = \frac{c}{L} [T(z,t) - T_0], \quad (2.1)$$

where T_0 is the coexistence temperature between liquid and gas inside a bubble of radius R_p for normal conditions.¹⁰ This is our thermodynamic reference state around which we expand all quantities. c is the molar heat capacity, crudely assumed to be equal in the liquid and gas, and L is the latent heat of vaporization per mole. Then the heat diffusion equation for u can be written as follows:

$$D_T \frac{\partial^2 u}{\partial z^2} - \frac{\partial u}{\partial t} = -\frac{\partial m}{\partial t} - \phi(t)\delta(z). \quad (2.2)$$

Here, m is a dimensionless order parameter. For $T=T_0$, m equals 0 for the gas and 1 for the liquid phase, i.e., $m = (\rho - \rho_G)/(\rho_L - \rho_G)$, where ρ_G and ρ_L are the bulk gas/liquid densities at coexistence. The right-hand side of the heat diffusion equation (2.2) can be understood as a heat source. It consists of the external heat $\phi(t) \geq 0$ flowing into the liquid from the particle surface and the heat sink $\partial m/\partial t < 0$ which corresponds to the latent heat needed to vaporize the liquid. $\phi(t)$ is related to the laser pulse intensity; its time variation scale is the same as that of the laser pulse (τ_0). For our model, $\phi(t)$ is a given input which will be specified later; we choose $\phi(t)$ such that $\phi(t) = 0$ for $t < 0$.

The dynamics of passage between the two phases can be viewed as motion over a potential energy barrier. In general, motion of the system along this potential surface (i.e., the change in the density profile for a given temperature field) may be described by an equation of the Cahn-Hilliard form (see Ref. 11)

$$\frac{\partial m}{\partial t} = \Gamma \Delta \frac{\delta F(m,u)}{\delta m} + \frac{k_B T}{\Gamma} R(t), \quad (2.3)$$

where the first term represents the systematic motion due to the thermodynamic driving force and $R(t)$ is a random term reflecting thermal fluctuations. Γ is a transport coefficient which sets the microscopic time scale for the relaxation of the density and Δ is the Laplacian. Under thermodynamic conditions, where the vapor is more stable than the liquid, but for which a barrier exists between the liquid and vapor minima in the bulk free energy, passage over the barrier (nucleation) may be caused by the random thermal fluctuations.

In Eq. (2.3), F is the grand canonical free energy functional per unit area

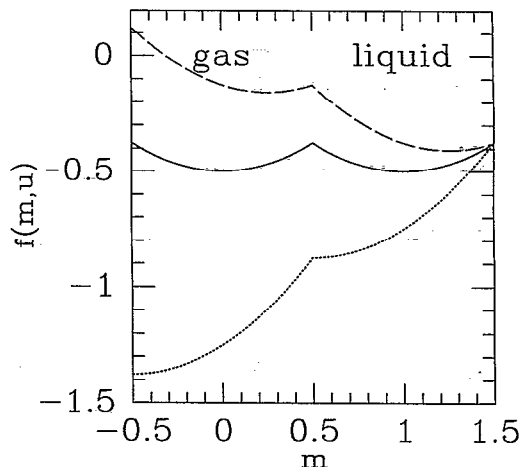


FIG. 1. A sketch of $f(m,u)$ (in units of λ) as a function of m for different temperatures ($\delta=1$): coexistence temperature T_0 (solid line), liquid temperature T_L corresponding to an initial situation (broken line); and spinodal temperature (dotted line). We have chosen the m -independent additive function $f_0(u)$ to be $f_0(u) = -\lambda(1+3u)/2$.

$$F(m,u) = \int_{-\infty}^{\infty} dz \left\{ \frac{1}{2} \lambda \xi^2 \left[\frac{\partial m(z,t)}{\partial z} \right]^2 + f[m(z,t), u(z,t)] + \gamma \delta(z) \right\}. \quad (2.4)$$

The first term in the integrand is square gradient correction to the bulk free energy, λ being an energy density scale and ξ a bulk correlation length ($\lambda \xi^2$ is proportional to the liquid-vapor surface tension). γ is the surface tension between the colloidal particle and the fluid; we take γ to be a constant. The local part $f(m,u)$ is the grand canonical free energy density for a uniform fluid. This function may be viewed loosely as the potential along which the system must move in order to pass from the liquid to the vapor and is sketched in Fig. 1. The shape of the potential changes with temperature. At coexistence, $f(m,0)$ has equal minima, which correspond to the liquid and vapor, separated by a barrier. As the temperature is raised, the vapor minimum becomes more stable than the liquid, but they are still separated by a barrier until, as indicated in the dashed curve in Fig. 1, the spinodal temperature is reached. We model $f(m,u)$ as two intersecting parabolas¹² for $u=0$ and do a linear expansion in u ,^{2,3}

$$f(m,u) = \frac{1}{2} \lambda \max[m^2(m-1)^2] + \frac{1}{2} \lambda \delta m u + f_0(u). \quad (2.5a)$$

The dimensionless coupling constant δ turns out to be

$$\delta = 2\rho_0 L^2 / \lambda M_W c T_0, \quad (2.5b)$$

where M_W is the molecular weight and ρ_0 is the mass density of the liquid phase at coexistence. It is obvious from the Cahn-Hilliard equation (2.3) that the m -independent function $f_0(u)$ can be changed without affecting the dynamics.

We remark that since we have chosen the grand canonical ensemble, we consider a constant chemical poten-

tial μ in the liquid and gas. Thus, $f(m,u)$ equals $-P$, where P is the pressure. For equilibrium thermodynamics, only the global minimum of $f(m,u)$ with respect to m has a physical meaning. However, we can define a nonequilibrium pressure field by

$$P(z,t) = -f[m(z,t),u(z,t)]. \quad (2.6)$$

Let us now discuss the role of the fluctuations embodied in the Langevin forces $R(t)$ in Eq. (2.3). These fluctuations cause spontaneous or homogeneous nucleation by allowing the system to jump over a finite free energy barrier. The time between the occurrence of fluctuations large enough to cross the barrier depends exponentially on the barrier height.⁴ For water at the boiling point, e.g., spontaneous nucleation events occur on a time scale which is much longer than our experimental time scale. Being random events, the times at which nucleation occurs at different particles which have had the same heating history would be uncorrelated (whereas all would reach the spinodal at the same time). However, as the fluid is heated close to the spinodal, the free energy barrier becomes very small and the occurrence of a suitable fluctuation becomes likely within the time resolution of the experiment (say, one quarter of an acoustic period, or 1 ns). Despite the fact that such events are, strictly speaking, spontaneous nucleation processes, we will refer to them as spinodal decompositions since, within the limitations of our observation, their timing is set by the achievement of a thermodynamic condition, rather than by a random process. With the random forces present, the mathematical treatment of Eq. (2.3) is complex and henceforth we shall neglect them. The effect of the fluctuations, *as perceived in our experiment* can be incorporated into the equations if one views $f(m,u)$ as a *renormalized* potential. Small barriers present in the bare function $f(m,u)$ are smeared out in the renormalized potential such that spinodal decomposition with the renormalized potential can correspond physically to nucleation slightly before the spinodal point is reached.

We start from a spatial constant liquid profile at $t=0$,

$$u(z,t=0) = \frac{c}{L} (T_L - T_0) = u_0 < 0, \quad (2.7a)$$

$$m(z,t=0) = 1 - \delta u_0/2 = m_0, \quad (2.7b)$$

T_L being the liquid temperature before laser heating and m_0 is such that it corresponds to a stable state, i.e., $f(m,u)$ has its global minimum at $m=m_0$ (see Fig. 1). Introducing normalized profiles $\bar{u}(z,t) = u(z,t) - u_0$ and $\bar{m}(z,t) = m(z,t) - m_0$, and adopting natural order parameter length and time scales $l_m = \sqrt{2}\xi$ and $\tau_m = l_m/\Gamma\lambda$, we can rewrite Eqs. (2.2) and (2.3) as

$$\frac{\partial \bar{u}}{\partial t} - \frac{\partial \bar{m}}{\partial t} = \frac{1}{2p} \frac{\partial^2 \bar{u}}{\partial z^2} + \bar{\phi}(t)\delta(z), \quad (2.8a)$$

$$\frac{\partial \bar{m}}{\partial t} = -\frac{\partial^2}{\partial z^2} \left(-\bar{m} + \frac{1}{2} \frac{\partial^2 \bar{m}}{\partial z^2} - \frac{\delta \bar{u}}{2} + \theta(t-t_0) \{ \theta[z-z_0(t)] - \theta[z+z_0(t)] \} \right). \quad (2.8b)$$

Here, only two dimensionless parameters enter, namely, the coupling δ and $2p = \tau_{th}/\tau_m$ and $\bar{\phi}(t/\tau_m) \equiv \tau_m \phi(t)/l_m$. These equations are solved in Sec. III. The problem is that the liquid-vapor interface position $z_0(t)$ is an unknown function and has to be determined self-consistently¹² from

$$m[z_0(t),t] = \frac{1}{2}. \quad (2.9)$$

In addition, $z_0(t) = 0$ for $t < t_0$ and t_0 is obtained from

$$m(0,t_0) = \frac{1}{2}. \quad (2.10)$$

From Fig. 1, it is clear that t_0 corresponds to the time where the spinodal point of the liquid is reached at the particle surface. The liquid then becomes unstable for $t = t_0$ at $z=0$ and spinodal decomposition takes place.

We finish this section with some general remarks on the simplifications in our phase field model and their effect on detailed comparisons with experiment:

(1) Equations (2.8) contain drastic simplifications. In particular, c , L , D_T , p , Γ , δ , and γ are all taken to be constant, i.e., independent of m and u . In reality, this is not fulfilled. Nevertheless, we believe that our model captures the essential physics, i.e., a competition between heat transfer and mass transport. At least the qualitative behavior should not depend drastically on such details. However, for a quantitative study, the abovementioned parameters as well as $f(m,u)$ have to be chosen more realistically. In particular, one can use liquid state or density functional theory to get an explicit form for $f(m,u)$ starting from the microscopic interaction potential. In our modeling of $f(m,u)$, one major defect is that the bulk liquid density decreases rapidly as the temperature increases; see the position of the liquid minimum in Fig. 1 as a function of temperature. This will have some consequences for the interpretation of the data in the next section.

(2) Our model also neglects the effect of polydispersity in the sizes of the colloidal particles, which is certainly present in the experimental systems. The properties of particles of different size may differ with regard to the nature of the heating transient and to the propagation of the density and temperature fields at surfaces of differing curvature. This will lead to a distribution in the times at which particles reach the spinodal under the same laser fluence. We have already noted that the experimental observation has a lower limiting time scale of the order of 1 ns, so that events occurring within this window are perceived as simultaneous. Furthermore, we note that the volume in which the grating is formed in the experiments is large enough to contain a very large number of particles of the same radius.

(3) Finally, another important approximation was to neglect the coupling between the density and momentum fields of the fluid. When the bubble is formed, large density nonuniformities are created; in our description, these nonuniformities must then relax by diffusion. In reality, the density nonuniformities will generate a nonuniform pressure field which will accelerate the fluid, i.e., there will be an important relaxation channel through the sound mode. Because we neglect this coupling, our description of the propagation of the interface, after its initial formation, is

not realistic (and we have not pursued it). To obtain a more realistic model with which to study the growth of the bubble, we should couple the order parameter and temperature equations (2.2) and (2.3) to the Navier–Stokes equation of the fluid, i.e., we should fuse our model with that studied by Prosperetti¹³ (in which the kinetics of interface formation was neglected). A recent successful study for the isothermal case (neglecting the temperature variations) was done in the context of crystal growth by Harrowell and Oxtoby.⁹

III. RESULTS

Equations (2.8) are linear for $t < t_0$, so the profiles can be found *exactly* by Fourier transformation

$$\begin{bmatrix} \bar{u}(z,t) \\ \bar{m}(z,t) \end{bmatrix} = \frac{1}{\pi} \int_0^t dt' \int_0^\infty dK \cos(Kz) \exp[C_K(t-t')] \times \bar{\phi}(t') \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (3.1)$$

with the 2×2 matrix C_K ,

$$C_K = -K^2 \begin{pmatrix} \frac{1}{2p} + \frac{\delta}{2} & \frac{K^2}{2} + 1 \\ \frac{\delta}{2} & \frac{K^2}{2} + 1 \end{pmatrix}, \quad (3.2)$$

t_0 can be determined by solving Eq. (2.10) with the expression for $m = \bar{m} + m_0$ given in Eq. (3.1). Once t_0 has been obtained, the corresponding profiles $\bar{u}(z, t_0)$ and $\bar{m}(z, t_0)$ are given directly by the analytic expression (3.1).

On the other hand, for $t > t_0$, Eqs. (2.8) become nonlinear and an analytical expression for the profiles cannot be found. As pointed out in Ref. 14, one can map Eqs. (2.8) onto an explicit expression which involves the unknown function $z_0(t)$,

$$\begin{bmatrix} \bar{u}(z,t) \\ \bar{m}(z,t) \end{bmatrix} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dK e^{-iKz} \left\{ e^{C_K(t-t_0)} \begin{bmatrix} \bar{u}_0(K) \\ \bar{m}_0(K) \end{bmatrix} + \sqrt{\frac{2}{\pi}} \int_{t_0}^t dt' e^{C_K(t-t')} \begin{bmatrix} \bar{\phi}(t')/2 + g_K(t') \\ g_K(t') \end{bmatrix} \right\} \quad (3.3)$$

with

$$\begin{bmatrix} \bar{u}_0(K) \\ \bar{m}_0(K) \end{bmatrix} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dz e^{iKz} \begin{bmatrix} \bar{u}_0(z, t_0) \\ \bar{m}_0(z, t_0) \end{bmatrix} \quad (3.4)$$

and

$$g_K(t) = -K \sin[Kz_0(t)]. \quad (3.5)$$

Using Eq. (3.3), we can iterate the self-consistency condition (2.9) to get $z_0(t)$ and inserting this into Eq. (3.3), we obtain the profiles. With the numerical iteration procedure described in Ref. 14, we can solve for the time development of \bar{u} and \bar{m} .

To be concrete, we have chosen an exponential form for the external heat source for $t > 0$,

$$\bar{\phi}(t) = A(t/\tau_m) \exp(-t/\tau_0) \quad (3.6)$$

with $\tau_0 = 50$ in units of τ_m (consistent with the time scales discussed in the Introduction) and $A = 0.03$. Thus the external heat source has a maximum at $t = \tau_0 = 50\tau_m$. Furthermore, the coupling δ can be expressed via the liquid–gas surface tension σ (Ref. 14) as [cf. Eq. (2.5b)] $\delta \approx \xi L^2 \rho_0 / 3\sigma M_w c T_0$. For water at 100 °C, we get a large coupling $\delta \approx 1.5$ due to the large latent heat. Estimates for the ratio of the kinetic coefficients are harder to make. We have chosen $2p = \tau_{th}/\tau_m = 0.44$, so that thermal relaxation is about twice as fast as order parameter relaxation. In dense liquids at long wavelengths, thermal diffusion is much faster than density relaxation, but as kinetic theories have shown,¹⁵ the effective modes associated with heat and density become very similar at wavelengths comparable to the inverse of the correlation length, so that we expect our choice for p to be reasonably representative.

The result for the order parameter and temperature profiles are shown in Figs. 2(a) and 2(b). First of all, the spinodal point is reached at the colloidal surface at a time t_0 which is $0.75\tau_m$ after the maximum of the external heat source at $t = \tau_0 = 50\tau_m$. For $t \approx \tau_0$, the heat transfer from the colloidal particle to the liquid via its interface is very rapid, so that much of the heat cannot be transported away by thermal diffusion and the spinodal point is reached at $t = t_0$. The order parameter and temperature profiles for $t = t_0$, as given by the analytical expressions (3.1), are shown on a large scale for the spatial coordinate z in Figs. 2(a) and 2(b). At $t = t_0$, the spinodal decomposition has not yet begun, but the order parameter still varies considerably, reflecting the normal thermal expansion of the liquid. This effect is overemphasized in our calculations due to our choice of $f(m, u)$, where the equilibrium liquid density varies drastically with temperature. This variation should be less pronounced in a more realistic model for $f(m, u)$. One also sees that m is conserved since the density that is missing at $z = 0$ has diffused away and results in a nonmonotonic profile with a maximum at $z \approx 10l_m$. The temperature profile $u(z, t_0)$ is simply monotonically decreasing in z due to the diffusion of the heat coming from the external source. For $t < t_0$, nothing happens but a continuous heating of the surrounding liquid. For comparison in the inset, the corresponding profiles are also shown for a time $t = t_0 - \tau_m$ (dashed curve). After the spinodal point is reached, however, things change dramatically. On a very short time scale of about $0.1\tau_m$, the liquid starts to vaporize at the surface of the colloidal particle and a low-density “bubble” forms. The excess density diffuses away and builds up a barrier which hinders a continuation of the vapor-bubble growth [see the inset of Fig. 2(a).] At the same time, latent heat is needed where a vapor–liquid interface was created and the system cools down locally, although there is still further external heating [see the inset of Fig. 2(b).] This also leads to a slowing down of the growth process.

The general scenario which emerges is a rapid growing of a quasigas bubble induced by spinodal decomposition which occurs on a very short time scale compared with the

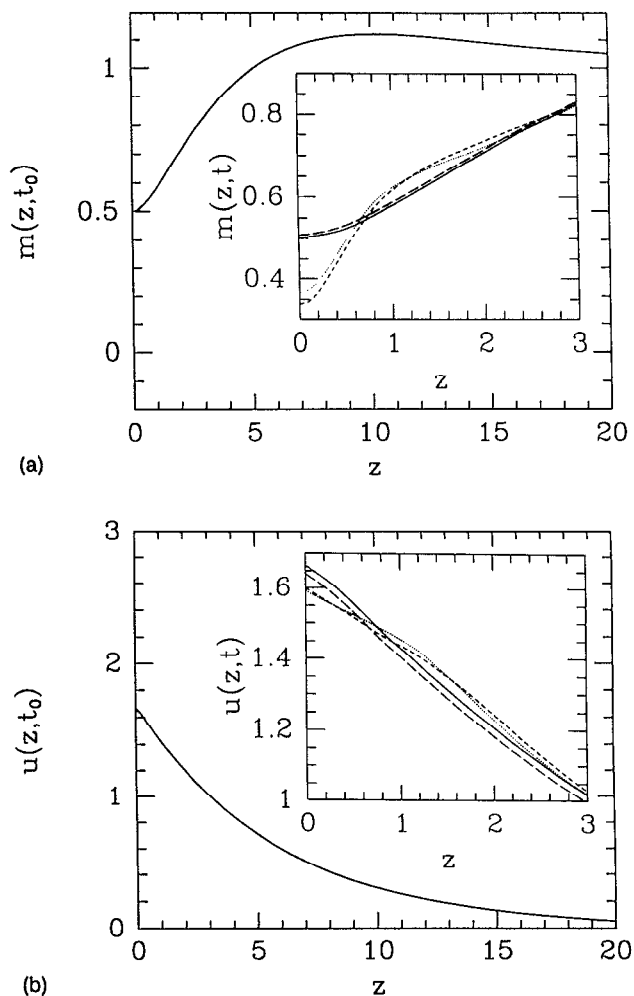


FIG. 2. Profiles of (a) the order parameter $m(z, t_0)$ and (b) the reduced temperature $u(z, t_0)$ when the spinodal point at the colloidal surface ($z=0$) is reached. The insets of (a) and (b) show the order parameter $m(z, t)$ and the reduced temperature $u(z, t)$ in the neighborhood of the colloidal surface ($z=0$) for four different times $t=t_0-1$ (long-dashed line), t_0 (solid line), $t_0+0.15$ (dotted line), and $t_0+0.25$ (short-dashed line). The parameters are $\delta=1.5$, $p=0.22$, and $u_0=-0.02$. For the external heat source, we take $\phi(t)=0.03t \exp(-t/\tau_0)$ and $\tau_0=50$. All times and lengths are in "order parameter" units of τ_m and l_m .

time scale τ_0 of the external laser pulse. This growth process which is very fast initially is then hindered since mass transport is relatively slow and the temperature decreases locally. This is illustrated clearly by the two profiles at $t=t_0+0.15\tau_m$ and $t=t_0+0.25\tau_m$ in the insets of Figs. 2(a) and 2(b). Our model only applies to relatively small times $t-t_0$; for longer times, other processes, e.g., a coupling to the liquid momentum field become more and more relevant.

In principle, one could have used a more general form for $f(m, u)$ than Eq. (2.5) and solve the corresponding system of partial differential equations (2.2) and (2.3) directly. However, here one has to handle with fourth-order derivatives with respect to z and to integrate the equations starting from $t=0$. So the location of the spinodal point (at a time t_0) and the processes that occur on a very short time scale (for $t > t_0$) are necessarily subject to numerical errors.

Our choice of $f(m, u)$ has the great advantage that an analytical solution exists for $0 \leq t < t_0$. So one can start with the exact solution at $t=t_0$ and integrate the equation only for relatively small times $t > t_0$.

IV. SUMMARY AND CONCLUSIONS

We have examined a model for vapor-bubble formation around a colloidal particle which has been heated rapidly (< 25 ns) well above the boiling point of the surrounding fluid. We have shown that the bubble formation leads to large disturbances in the density and pressure fields around the particle of the type which has been inferred from nonlinear optics experiments.¹ It has proven difficult to find alternative explanations for these transients.

A crucial aspect of our model is the idea that because of the rate at which the fluid is heated, normal fluctuation driven bubble nucleation events do not have time to occur and the bubble forms by spinodal decomposition. This leads directly to several consequences which seem to concur with what is observed:

(1) There is an energy threshold for the process which depends on the laser pulse length and particle size since to reach the spinodal, enough heat must be supplied to heat the fluid to the spinodal in a sufficiently short time to overcome the thermal diffusion.

(2) The onset of the rapid density change is delayed until well into the pulse since it takes some time to heat the fluid.

(3) The very rapid time scale on which the bubble forms is due to the high degree of local superheating which has occurred before; most of the superheated region is then able to vaporize very rapidly.

(4) The idea that the event is not triggered by a *random* nucleation event has a further consequence. Recall that the observation (degenerate four-wave mixing) picks up a *coherent* superposition of the pressure fields emanating from the heated particles. If these pressure pulses are triggered randomly, it is difficult to see how they could add up coherently. On the other hand, with the spinodal mechanism, all particles which have the same heating history nucleate bubbles at the same time.

The model includes, in a thermodynamically consistent way, the coupling between the temperature and density fields. A number of simplifying assumptions were made to simplify the solution of the kinetic equations, such as using the same transport coefficients for liquid and vapor and neglecting the temperature dependence of the latent heat. We do not expect simplifications of this type to have a major influence on the results since the phenomena exhibited by the equations are stable to wide parameter variations.

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