In this Letter a diffuse-interface model featuring phase change, transition to supercritical conditions, thermal conduction, compressibility effects and shock wave propagation is exploited to deal with the dynamics of a cavitation bubble. At variance with previous descriptions, the model is uniformly valid for all phases (liquid, vapor and supercritical) and phase transitions involved, allowing to describe the non-equilibrium processes ongoing during the collapse. As consequence of this unitary description, rather unexpectedly for pure vapor bubbles, the numerical experiments show that the collapse is accompanied by the emission of a strong shock wave in the liquid and by the oscillation of the bubble that periodically disappears and reappears, due to transition to super/sub critical conditions. The mechanism of shock wave formation is strongly related to the transition of the vapor to supercritical state, with a progressive steepening of the compression wave to form the shock which is eventually reflected as an outward propagating wave in the liquid.

Shock formation in the collapse of a vapor nano-bubble

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Vapor bubble collapse is a fascinating classical problem involving vapor-liquid phase transition and extreme pressures and temperatures that may find application in different fields like ultrasound medicine or material science.

Typical experiments concern ultra-fast imaging of the bubble interface and the analysis of light and sound emitted after the collapse. Basic work concentrated on free cavitation bubbles, although nano-bubbles at solid walls are becoming an increasingly active research field.

Intermingled phenomenologies, such as interface dynamics, thermodynamics of phase change, and dissolved gas diffusion, are a challenge to theoretical modeling. Indeed, a unified description encompassing all these aspects is still lacking. The available models combine different ingredients starting from a system consisting of two distinct adjoining regions, liquid (sometimes compressible) and vapor phase, respectively. The pressure in the vapor is taken to be the saturation pressure and the phase transition is accounted for through suitable kinetic equations and latent heat release.

The diffuse interface model discussed in the present Letter is uniformly valid for all phases (liquid, vapor and supercritical) and phase transitions involved, embedding compressibility effects, capillary forces as well as thermal conductivity. The approach enables an unprecedented analysis of collapse, where the bubble interface speed may exceed the speed of sound. This leads to the formation of a shock wave focused towards the bubble that is successively reflected back, as an outward-propagating spherical wave in the liquid. Contrary to classical models, latent heat of condensation and rapid compression are found to locally bring the vapor in supercritical conditions, originating a composite system comprising vapor phase, supercritical fluid and liquid. This explains the observed rebounds usually considered a typical feature of incondensable gas bubbles. Indeed, as shown below, the liquid-vapor interface may disappear and reappear again, according to the local thermodynamic conditions.

The physical model. We exploit a diffuse interface description of the multiphase flow based on the van der Waals gradient approximation of the free energy functional. The model embeds thermodynamically consistent capillarity effects and accounts for phase change and transition to supercritical conditions. In the spirit of density functional theory, the free energy functional reads

\[ F[\rho, \theta] = \int_V \left( \bar{f}_0 (\rho, \theta) + \frac{\lambda}{2} |\nabla \rho|^2 \right) \, dV, \]

where \( \lambda \) is a coefficient controlling surface tension and interface thickness. \( \bar{f}_0 (\rho, \theta) \) is the free energy per unit volume at temperature \( \theta \) and density \( \rho \) that, for a van der Waals fluid, takes the form

\[ \bar{f}_0 (\rho, \theta) = \bar{R} \rho \theta \left[ \frac{1}{\delta} + \log \left( \frac{\rho K \theta^\delta}{1 - b \rho} \right) \right] - a \rho^2, \]

with \( \delta = \bar{R}/c_v \), \( \bar{R} \) the gas constant, \( c_v \) the constant volume specific heat, \( a \) and \( b \) the van der Waals coefficients, and \( K \) a constant related to the de Broglie length. The conservation equations for mass \( \partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \), momentum \( \partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{\tau} \), and total energy, \( \partial_t E + \nabla \cdot (\mathbf{u} \mathbf{E}) = \nabla \cdot [\mathbf{\tau} \rho + \lambda \rho \mathbf{v} \mathbf{u} \nabla \rho + k \nabla \rho] \), where \( k \) is the thermal conductivity, are derived in the Supplemental Material, Section A. The stress tensor,

\[ \mathbf{\tau} = -p_0 I + \lambda \left( \frac{1}{2} |\nabla \rho|^2 + \rho \nabla^2 \rho \right) I - \nabla \nabla \rho + \mathbf{\tau}^v, \]

accounts for capillarity, \( \lambda, p_0 = \bar{R} \rho \theta/(1 - b \rho) - a \rho^2 \) being the pressure and \( \mathbf{\tau}^v = \mu \left[ (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - 2/3 \nabla \cdot \mathbf{u} I \right] \) the viscous stress. A given temperature dependence of the...
interfacial energy,
\[
\sigma = \int_{-\infty}^{+\infty} \lambda \left( \frac{d \rho}{d n} \right)^2 \, dn ,
\]
where \(n\) is the coordinate normal to the interface, can be reproduced by assuming \(\lambda(\rho, \theta)\).

**Simulation details.** The system constitutes a quite non-standard problem that calls for specialized numerical techniques. We list here a few issues to provide a flavor of the numerics used in the simulations, see *Supplemental Material, Section B* [22] for a more complete discussion of the numerical method: i) The extremely thin liquid-vapor interface calls for a high numerical resolution; ii) Liquid, vapor, and supercritical fluid compressibility gives rise to shock waves propagating in a non-uniform, multiphase environment; iii) The system manifests a compound nature, partly controlled by acoustics (hyperbolic behavior) and partly induced by viscosity and capillarity (diffusion and dispersion, respectively); iv) Although the sound speed, \(c^2 = \partial p_0/\partial \rho|_p\), with \(\eta\) the specific entropy, is well defined in most of the phase space \((c^2 > 0)\), a region exists below the spinodal where \(c^2 < 0\). This hybrid behavior [23] is cause of failure for the standard hyperbolic solvers.

**Bubble dynamics and shock evolution.** The present Letter describes numerical simulations of spherically symmetric, pressure-induced bubble collapse. The vapor nano-bubble with radius \(R_{eq} = 100\) nm is initially in equilibrium and the collapse is initiated by an overpressure enforced on the liquid, \((p_\infty - p_c) / p_c = \Delta p / p_c > 0\), where \(p_c\) is the liquid equilibrium pressure. Cases differing for overpressure and for thermal conductivity, measured by \(Pr = 3\mu R/(8k)\), are considered to analyze their effects on the collapse dynamics. In all cases the initial temperature is \(\theta_c/\theta_\infty = 0.5\) and the surface tension is \(\sigma / (p_c R_{eq}) = 0.045\), corresponding to a realistic value \(\sigma = 0.09\) N/m for water. Here and throughout the subscript \(c\) denotes critical values.

After the application of the overpressure, the bubble starts shrinking while an expansion wave propagates in the surrounding liquid, see *Supplemental Material, Section C* [22]. After the expansion wave passes by, the liquid pressure comes back to \(p_\infty > p_c\). Figure 1 shows successive snapshots of the collapsing bubble. The time evolution of the bubble radius is provided in Fig. 2 for different \(\Delta p / p_c\) and \(Pr\). The dynamics consists of a sequence of rebounds and collapses associated with shock formation. The collapse time of a macroscopic bubble is estimated as \(t_c = 0.915 R_{eq} \sqrt{p_\infty / (p_\infty - p_c)}\), with \(p_v\) the bubble equilibrium pressure, where capillary, viscous and compressibility effects are neglected [10, 11]. For nano-bubbles, however, surface tension is crucial and the numerical results suggest the scaling
\[
t_c = 0.915 R_{eq} \frac{p_\infty}{p_\infty - p_c + 2\sigma / R_{eq}} = 0.915 R_{eq} \sqrt{\frac{p_\infty}{\Delta p}}.
\]
Before the first collapse, the radius evolution is independent of thermal conductivity with a slight sensitivity to the overpressure. Although predicted by models of indecondensable gas bubbles [11], rebounds are missed by simplified models which neglect the inner vapor dynamics. The rebounds are affected by thermal conductivity and overpressure, Fig. 2. The radius where the first collapse phase ends, and the successive rebound starts, increases with the overpressure, suggesting the presence of an indecondensable gaseous phase inside the bubble. The increase of the overpressure leads to faster dynamics, see

![Figure 1](image1.png)  
**Figure 1.** Successive snapshots of the system configuration. Density field (top) and pressure gradient intensity (bottom) in arbitrary units for \(p_\infty - p_c = 0.01 p_c\) and \(Pr = 0.2\). The bottom plots highlight the position of bubble interface and radiated shock.

![Figure 2](image2.png)  
**Figure 2.** Time evolution of the bubble radius for various cases with the prediction of the Keller model [12] shown by the dotted line. The collapse of the bubble is induced by an overpressure in the liquid, \(\Delta p = p_\infty - p_c\). The other control parameters are \(Pr\) defined in the text, a measure of thermal conductivity, and \(Re = \sqrt{p_c R_{eq} / \mu}\) and \(C = \lambda p_v^2 / (\mu R_{eq}^2)\), playing the role of a Reynolds and a Weber number, see *Supplemental Material, Section A* for their detailed definition. In correspondence with the first bubble rebound a shock wave is radiated in the liquid. The shock position \(s(t)\) is shown in the inset.
the expression of $t_c$, resulting in increased pressure inside the bubble. An enhanced thermal conductivity, solid lines in Fig. 2 reduces the subsequent oscillations of the bubble by diffusing thermal energy from the hotter bubble to the colder liquid, recovering the isothermal Keller model with no-rebonds in the limit $Pr \to 0$.

The shock position $s = s(t)$ is provided in the inset of Fig. 2. The seemingly different velocity is an artifact of the $\Delta p$-dependent time scale $t_c$. In fact $w = \dot{s}$ is fairly constant. Away from the bubble, the shock propagates in the still liquid that, after the expansion wave, relaxed back to $p_\infty$, $\theta_\infty = \theta_c$. The shock speed $w$ is determined by the state ahead of the shock ($p_\infty, \rho_\infty, \theta_\infty = 0$) and by an additional parameter, the density $\rho_b$ behind the shock, say, see [24] and [21] for details concerning a van der Waals fluid. The small compressibility of the liquid ($\rho_b - \rho_\infty)/\rho_\infty \ll 1$, allows the linearization $w = c_\infty + \alpha_\infty (\rho_b - \rho_\infty)/\rho_\infty$, where $c_\infty$ is the unperturbed sound speed in the liquid and $\alpha_\infty (p_\infty, \rho_\infty) = \rho_\infty dw/d\rho|_\infty$. It turns out that $w \approx c_\infty$ for the cases explicitly reported here (more precisely, $(w - c_\infty)/c_\infty \leq 3\%$).

The main plot in the top panel of Fig. 3 shows the pressure profile through the bubble center for the initial phase of the process up to the bubble collapse. The corresponding density profiles are provided in the inset. Initially (solid, dashed and dash-dotted lines), the location of the interface is identified by an extremely sharp density drop. The bubble shrinks while the vapor density, pressure, and temperature (main plot in the bottom panel) increase. Successively, the shrinkage accelerates, the gaseous phase is compressed, its temperature raises and the fluid transitions to supercritical conditions ($p/p_c > 1, \theta/\theta_c > 1$). During this phase the inner vapor core is surrounded by a shell of supercritical fluid whose density increases through a strong density gradient to eventually adjoin the external liquid. Later, the vapor disappears altogether, transformed into a low density supercritical fluid. Subsequently pressure and temperature peaks in the profile keep increasing. For $\Delta p/p_c = 1.4$ they reach instantaneous values of the order of $p/p_c \approx 1700$, $\theta/\theta_c \approx 9$, Table I (corresponding to $p \approx 37 \times 10^3$MPa and $\theta \approx 6 \times 10^3$K for water). The late collapse phase is dominated by a strong pressure wave propagating in a homogeneous supercritical fluid which focuses into a converging shock (see Supplemental Material, Section C [22] for the comparison with a supercritical converging shock). Pressure and temperature extrema are reached at the first collapse time $t_c$, when the inner low density core disappears.

The thermal aspects are described by

$$\rho c_v \frac{D\theta}{Dt} = -\rho \frac{\partial \eta}{\partial \theta} \frac{D\rho}{Dt} + \tau^v \cdot \nabla u + \nabla \cdot (k \nabla \theta).$$

The heat release rate per unit volume during phase change at constant temperature is $q_L \dot{\rho}$ where $q_L = \rho \theta [\eta_L(\theta) - \eta_L(\rho_L)]/[\rho_L(\theta) - \rho_L(\theta)]$, and the subscripts $L$ and $V$ denote liquid and vapor states along the coexistence curve (binodal), respectively. In order to single out the latent heat contribution, it is instrumental to consider the splitting $-\rho \partial \eta / \partial \theta |_{\theta} = H q_L + \alpha$, where $H$ is the characteristic function of the coexistence region ($H = 1$ for states below the coexistence curve and 0 otherwise), with $\alpha$ defined accordingly. Profiles of latent heat release rate, $H q_L$, are displayed in inset a) of Fig. 3 when $\alpha \dot{\rho}$ is too small to be appreciated in the plot. At later times, inset b), the fluid in the bubble becomes supercritical, i.e. $H q_L = 0$, and the term $\alpha \dot{\rho}$ becomes substantial.
Figure 5. System evolution in the $p$ – $\rho$ plane. As background information, the plot provides the main thermodynamic features of the van der Waals system, namely critical isotherm and isobar, and binodal curve. The solid curves in the top panel refer to successive time instants during the late phase of shock focusing toward the center. The pressure increase in the supercritical fluid is apparent. The inset shows density (solid line) and pressure (dashed line) radial distributions in the region very close to the bubble center. The bottom panel refers to time instants immediately after the shock reflection, with the expansion of the fluid inside the inner core and the shock wave propagating toward the liquid.

(for ideal gases $\alpha = \tilde{R} \theta$, while in general $\alpha = \theta \beta_p/(\kappa_\theta \rho)$, where thermal compressibility and thermal expansion coefficient are $\kappa_\theta = -(1/v)\partial v/\partial \theta|_p$ and $\beta_p = (1/v) \partial v/\partial \theta|_p$, respectively).

After reaching the bubble center, the shock is reflected and propagates toward the liquid, Fig. 4. The pressure peaks ahead of the shock follows the scaling law $p_s \propto 1/s$, inset of Fig. 4, as predicted by the compressible Hickling-Plesset model for incondensable gas bubbles. After reflection, the fluid near the bubble center expands back and reduces quickly its temperature and pressure coming back to vapor with reappearance of the bubble. The expansion continues up to a maximum radius when the motion reverts and the process repeats itself.

The pressure-density loci $p = p(\rho, t)$ are plotted in

Table I. Pressure and temperature peaks in the collapsing bubble as a function of the initial overpressure. The intensity of the pressure wave at one radius from the bubble center is shown in the last column.

Table I

| $\rho_{\infty}/p_c$ | $\rho_{\max}/p_c$ | $\Theta_{\max}/\Theta_e$ | $(p_{\infty} - p_c)/|p_c|$ |
|-------------------|-------------------|--------------------------|--------------------------|
| 1.43              | 1764              | 8.58                     | 31.7                     |
| 0.95              | 339               | 4.53                     | 22                       |
| 0.63              | 190               | 3.53                     | 15.9                     |
| 0.073             | 52.8              | 2.01                     | 6.6                      |

Fig. 5. The top panel refers to the late phase of shock focusing, successive to the configurations of Fig. 4, when the conditions are already supercritical. The spatial distribution of density and pressure plotted in the inset corresponds to the outermost curve in the main panel. Across the shock, pressure and density increase along the portion $A - B$ of the curve. Behind the shock, the pressure decreases smoothly while the density oscillates due to capillarity-induced dispersion, portion $B - C - D$. The progressive strengthening of the shock wave is apparent.

The pressure-density loci after shock wave reflection are reported in the bottom panel of Fig. 5. The pressure progressively decreases, until subcritical conditions are recovered and the vapor bubble reappears.

**Discussion & conclusions.** Phase change and transition to super-critical conditions play a crucial role in the collapse of a vapor bubble. Indeed, independently of the intensity of the initial overpressure, a strong pressure and temperature increase is experienced that induces the transition to incondensable gaseous state. As a consequence, a vapor bubble substantially resembles an incondensable gas bubble, making the boundary between the two kinds less sharply defined than usually assumed. The pressure and temperature peaks increase with $(p_{\infty} - p_c)/p_c$ as the strength of the emitted shock wave does, see Table |. At fixed thermal conductivity, a limiting overpressure exists below which the bubble condenses altogether. Above the critical overpressure oscillations set in, with the bubble periodically reforming and emitting a shock upon collapse. From the above considerations it should be expected that a collapsing bubble could trigger a synchronized collapse of its neighbors. Indeed, the pressure at the distance $r = R_{eq}$ from the bubble center is substantially larger than the initial overpressure, Table |. Accounting for the $1/r$ decay of the pressure peak, the pressure of the wave exceeds the initial overpressure in a region extending for, typically, $20R_{eq}$.

The present model for vapor-bubbles collapse is easily extended under several respects: a) Incondensable gas dissolved in the liquid can be taken into account; b) More realistic transport coefficients can be assumed, e.g. dependence of viscosity and thermal conductivity on
thermodynamic conditions can be included; c) A different equation of state can be adopted.

An aspect that certainly deserves further investigation is the capillary effect that may emerge in slightly supercritical fluids due to the strong density contrasts maintained by the shock wave.

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[1] L. Rayleigh, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 34, 94 (1917).
[2] R. P. Taleyarkhan, C. West, J. Cho, R. Lahey, R. Nigmatulin, and R. Block, Science, 295, 1868 (2002).
[3] C.-D. Ohl, Physics, 3, 65 (2010).
[4] R. Pech and B. Gompf, Physical review letters, 84, 1328 (2000).
[5] G. Sankin, W. Simmons, S. Zhu, and P. Zhong, Physical review letters, 95, 034501 (2005).
[6] K. Weninger, C. Camara, and S. Putterman, Physical Review E, 63, 016310 (2000).
[7] M. P. Brenner and D. Lohse, Physical review letters, 101, 214505 (2008).
[8] J. H. Weijs and D. Lohse, Physical review letters, 110, 054501 (2013).
[9] X. Zhang, H. Lhuissier, O. R. Enríquez, C. Sun, and D. Lohse, Langmuir, 29, 9979 (2013).
[10] C. E. Brennen, *Cavitation and bubble dynamics* (Cambridge University Press, 2013).
[11] M. S. Plesset and A. Prosperetti, Annual Review of Fluid Mechanics, 9, 145 (1977).
[12] J. B. Keller and I. I. Kolodner, Journal of Applied Physics, 27, 1152 (1956).
[13] M. S. Plesset and R. B. Chapman, J. Fluid Mech, 47, 283 (1971).
[14] S. Fujikawa and T. Akamatsu, Journal of Fluid Mechanics, 97, 481 (1980).
[15] I. Akhatov, O. Lindau, A. Topolnikov, R. Mettin, N. Vakhitova, and W. Lauterborn, Physics of Fluids, 13, 2805 (2001).
[16] Y. Hao and A. Prosperetti, Physics of Fluids (1994-present), 11, 2008 (1999).
[17] D. Anderson, G. McFadden, and A. Wheeler, Annual review of fluid mechanics, 30, 139 (1998), ISSN 0066-4189.
[18] F. Dell’Isola, H. Gouin, P. Seppecher, et al., Comptes Rendus de l Académie des Sciences-Series IIB-Mechanics, 320 (1995).
[19] D. Jamet, O. Lebaigue, N. Coutris, and J. Delhaye, Journal of Computational Physics, 169, 624 (2001).
[20] R. Evans, Advances in Physics, 28, 143 (1979).
[21] N. Zhao, A. Mentrelli, T. Ruggeri, and M. Sugiyama, Physics of fluids, 23, 086101 (2011).
[22] see Supplemental Material at [http://nonso.dove](http://nonso.dove) for details.
[23] M. Affouf and R. E. Caflisch, SIAM Journal on Applied Mathematics, 51, 605 (1991).
[24] R. Courant and K. O. Friedrichs, *Supersonic flow and shock waves*, Vol. 21 (Springer, 1976).
[25] R. Hickling and M. S. Plesset, Physics of Fluids (1958-1988), 7, 7 (2004).