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Dynamics of the condensation of a saturated vapor into droplets

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A fluid-dynamic model of condensation is presented here. Under proper thermodynamic conditions a saturated vapor condenses into tiny droplets. This nonequilibrium process is characterized by a transfer of mass from the vapor to the incipient liquid, a thermal gradient at interface, and a release of heat from the gas to the interface (heat of condensation). These three fundamental physical aspects of the problem are taken into account in the present description. First, the thermal boundary condition for a spherical interface is derived. This surface equation, together with the balance mass equation and the thermal distribution of each bulk phase, results in a first-order nonlinear differential equation. For single noninteracting drops condensing onto a substrate (heterogeneous condensation) the equation predicts an exponent of $\frac{1}{3}$ for the time evolution of the droplet radius. But, for an assembly of interacting drops, the power-law exponent changes to one. For the homogeneous case of single noninteracting droplets, the equation gives a power exponent of $\frac{1}{2}$ and for an assembly of interacting drops, for small values of time, the radius of the drop grows linearly with time. These results are discussed and compared with experiment.

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I. INTRODUCTION

Most human beings recognize the effects of gravity and condensation as phenomena happening everywhere around in nature. Formation of tiny droplets on every flower or leaf is a routine spectacle in every early morning all around the planet. "Breath figures" or dew formation on windows or spectacles [1], transformation of clouds into rain, condensation of water in a cloud chamber [2], microemulsions and macroemulsions stability [3], creaming of emulsions [4], grain growth [5], etc., are problems of considerable interest and pose important questions to be understood in condensed-matter physics. In thermodynamics language this phenomena is known as a first-order phase transition. Heterogeneous and homogeneous [6] are the names for the two ways of a saturated vapor condensation. When vapor condenses on an inhomogeneous solid surface or a seed or a fast particle (Wilson chamber), the process is named heterogeneous condensation. But when a pure saturated vapor is condensed by density fluctuations, the condensation is called homogeneous. From the thermodynamic point of view [7], heterogeneous and homogeneous condensation differ on the density value at which each fit occurs. To trigger condensation, the latter process requires higher-density values than the former. This fact will be used later to characterize both ways of condensation. Measurements were reported on the growth of breath figures on solids [8,9], on liquids [10], and also the influence of wetting conditions in the formation of breath figures on fibers [11]. Models considering diffusion-limited droplet growth developed from a mean-field boundary approximation [12] and the influence of temperature gradients on the kinetics boundary layer problem for a condensing droplet have been developed [13] in order to understand the experiments. A dynamic-scaling approach was also developed for the description of the droplet-size distribution [14]. The kinetics of droplet growth was investigated using Monte Carlo simulations, scaling theory, and the Smoluchowski equation [15]. Simulation on the formation of large liquid drops by molecular aggregates was described and discussed for the stationary and falling case [16]. The laws of condensation onto a substrate or the homogeneous nucleation of a supersaturated vapor could also depend on the droplet's interaction. Interacting droplets grow faster than single ones. In an assembly of interacting droplets the growth is produced by coalescence. Bigger ones, following the Laplace law, grow faster to reduce the pressure of the system. Single drop condensation could be seen as a convective transfer of mass and heat from the gas phase to the liquid drop. In a coalescence process the convective transport of gas is irrelevant. The growth is ruled by the transport of liquid. Certainly here condensation will be viewed as a fluid-dynamic process but the thermal distribution and the associated thermal gradients at each phase will be such that no internal flow though Marangoni or Raleigh-Benard convection takes place.

II. THE THERMAL BOUNDARY CONDITION FOR A DROP

Before considering the specific fluid-dynamic problem of condensation of a saturated vapor into tiny droplets, it is necessary to know, in spherical symmetry, the interfacial thermal balance equation. This equation has been previously derived for the case of a plane surface of separation [17]. We follow here a phenomenological approach. We start by considering the conservation law [18] of the specific internal energy u of an inhomogeneous

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fluid (the interface)

$$\frac{\partial \rho u}{\partial t}=-\mathrm{div}(\rho u v+J_q)-P{:}\mathrm{grad}(v)\ , \tag{1}$$

where ρ is the density, v is the velocity, J_q is the heat flow, and P is the total pressure tensor. From here on it will be considered that there is not any gradient of temperature, velocity, or concentration on the surface of the drop. That is all the changes occur along the radial direction r. Then the hydrostatic part of the product $P{:}\nabla(v)$ reduces to

$$P{:}\mathrm{grad}(v)=\sum_{\alpha,\beta}P_{\alpha\beta}\frac{\partial v_\alpha}{\partial x_\beta}\simeq P_N\frac{\partial v_r}{\partial r}\ , \tag{2}$$

where P_N and v_r are the pressure and the velocity along the radial direction. Besides all these special restrictions on the gradients and on the tensor [19], we also assume that the system is in a steady-sate situation. However, under these assumptions, Eqs. (1) and (2) become

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left[\rho u v_r-\kappa\frac{\partial T}{\partial r}\right]\right]+P_N\frac{\partial v_r}{\partial r}=0\ , \tag{3}$$

where $\kappa(\partial T/\partial r)$ is the normal part of the heat flow vector J_q and κ is the heat conductivity. This last equation can be written as follows:

$$\frac{\partial}{\partial r}\left[r^2\left[v_r(\rho u+P_N)-\kappa\frac{\partial T}{\partial r}\right]\right]-v_r\frac{\partial}{\partial r}(r^2P_N)=0\ . \tag{4}$$

By integrating this equation between two concentric spheres, $r-\epsilon<r_s<r+\epsilon$, one at the gas and the other at the liquid side, and assuming that v_r is in this region a smooth function of r, we then have

$$\left[r^2\left[v_r\rho h-\kappa\frac{\partial T}{\partial r}\right]\right]_{r-\epsilon}^{r+\epsilon}-(v_r)_s[(r^2P_N)]_{r-\epsilon}^{r+\epsilon}=0\ . \tag{5}$$

h indicates the specific enthalpy ($h=u+P_N/\rho$). The velocity v_r has been approximated by its value at the Gibbs dividing surface $(v_r)_s$. By inserting the Laplace relation ($\Delta P=2\sigma/r$) into Eq. (5), it becomes

$$\left[v_r\rho h-\kappa\frac{\partial T}{\partial r}\right]_{r-\epsilon}^{r+\epsilon}+(v_r)_s\frac{2\sigma}{r}=0\ . \tag{6}$$

As it can be seen this thermal boundary condition takes into account the enthalpics and the thermal flow of each phase as well as the capillary pressure contribution. Equation (6) is a basic equation for the description of the condensation process.

III. DYNAMIC OF CONDENSATION

The process of condensation of a saturated vapor into droplets consists basically of an interchange of heat and mass, occurring at the surface of the drop. The former, regulated by Eq. (6), is rewritten as follows:

$$\left[\rho h\frac{\partial r}{\partial t}\right]_l^g+\frac{2\sigma}{r}\left[\frac{\partial r}{\partial t}\right]_s=\left[\kappa\frac{\partial T}{\partial r}\right]_l^g\ , \tag{7}$$

where the radial velocity $v_r=(\partial r/\partial t)$ and $(\ )_l^g$ indicates a difference of the corresponding property at both sides of the Gibbs dividing surface (the liquid and the gas sides, respectively). Let us write, for the steady-state situation, the continuity equation at the droplet's surface. It reads

$$\rho_l\left[\frac{\partial r}{\partial t}\right]_l=\rho_g\left[\frac{\partial r}{\partial t}\right]_g\ . \tag{8}$$

ρ_l and ρ_g indicate the liquid and gas density, respectively. As $\rho_l\gg\rho_g$, it then follows from Eq. (8) that

$$(\partial r/\partial t)_g\gg(\partial r/\partial t)_l\ .$$

Close to the interface, the gas particles move faster than the liquid ones. By remembering that the heat is transported from the gas (saturated vapor) to the liquid (the drop), Eq. (7), the surface energy balance equation, then becomes

$$\left[\frac{\partial r}{\partial t}\right]_g+\frac{2\sigma}{\rho_g L}\frac{1}{r}\left[\frac{\partial r}{\partial t}\right]_s=-\frac{\kappa_l}{\rho_g L}\left[\frac{\partial T}{\partial r}\right]_l+\frac{\kappa_g}{\rho_g L}\left[\frac{\partial T}{\partial r}\right]_g\ . \tag{9}$$

L represents the latent heat of condensation, κ_l and κ_g are heat conductivities of the liquid and gas, respectively. In the next applications of this equation, it will be assumed that the thermal gradients are such that no convective motion at the drop's surface is present; neither Raleigh nor Marangoni instability [20] is present.

A. Heterogeneous growth of single drops

In order to calculate the temperature gradient at the interface from the liquid and gas side, respectively, it is necessary to know the thermal distribution at both bulk phases. The temperature and the gradient can be found by solving the following differential equation:

$$\rho\frac{dq}{dt}=-\mathrm{div}J_q\ , \tag{10}$$

where dq is the sensible heat per unit mass transferred to the liquid droplet from the gas phase. J_q is the "heat flow" [18] and is given by the Fourier law ($J_q=-\kappa\,\mathrm{grad}T$). The thermal evolution of the droplet can be found by solving the following equation:

$$\frac{d}{dr}\left[r^2\frac{dT}{dr}\right]=-\frac{A_0}{\kappa_l}\ . \tag{11}$$

Here we have assumed that the sensible heat transferred to the liquid ($\rho\,dq/dt$)$=A_0$ is constant. The solution of the above equation is

$$T=-\frac{A_0}{6\kappa_l}r^2+C\ , \tag{12}$$

where C is a constant. For obtaining the thermal distribution of the gas phase, it is assumed that heat flows radially to the drop, then the temperature is given by

$$\frac{d}{dr}\left[r^2\frac{dT}{dr}\right]=0\ . \tag{13}$$

The heat flows from the gas to the drop, then the solution of Eq. (13) is

$$T=A/r+B\ , \tag{14}$$

where A and B are constant. After substitution of the respective thermal gradients, evaluated from Eqs. (12) and (14), into Eq. (9) we get the following nonlinear first-order differential equation:

$$\frac{\partial r}{\partial t}+\frac{2\sigma}{\rho_g L}\frac{1}{r}\frac{\partial r}{\partial t}-\frac{A_0}{3\rho_g L}r-\frac{A\kappa_g}{\rho_g L}\frac{1}{r^2}=0\ . \tag{15}$$

Here the subscript on the velocity has been dropped because it was assumed that

$$(\partial r/\partial t)_g\approx(\partial r/\partial t)_s\ .$$

The solution of this differential equation will provide us the condensation laws. It must be kept in mind that condensation of a vapor could be reached under two intrinsically different situations. When the saturated vapor condenses by fluctuations on a homogeneous surface of the system, the condensation is called homogeneous. The vapor is in a metastable state and the phase change is triggered at high-density values. Another situation is when there are imperfections on the wall. In this case the transition is named heterogeneous and occurs at lower densities than the former. For water drops of the order of μm the "coefficient" of the second term of Eq. (15) is

$$\frac{2\sigma}{\rho_g L}\frac{1}{r}<1\ .$$

Under this assumption Eq. (15) reduces to

$$\frac{\partial r^3}{\partial t}-\frac{A_0}{3\rho_g L}r^3-\frac{3A\kappa_g}{\rho_g L}=0\ . \tag{16}$$

The solution of this equation after expanding the exponential is

$$r^3=r_0^3+\left[\frac{r_0^3}{3}+\frac{3A\kappa_g}{A_0}\right]\frac{A_0}{\rho_g L}t\ . \tag{17}$$

Drops without interactions grow with time following a power of $\frac{1}{3}$.

Let us assume now that the temperature of the drop remains constant during the process of condensation; in such a situation the thermal gradient evaluated from the liquid side will be null and the growth equation (9) will reduce to

$$\frac{\partial r^3}{\partial t}-\frac{3A\kappa_g}{\rho_g L}=0\ , \tag{18}$$

then

$$r^3=\frac{A\kappa_g}{\rho_g L}t\ . \tag{19}$$

Also here we get the same power law as before [see Eqs. (17) and (19)]; the temperature distribution of the drop does not affect the condensation law of single drops. The $\frac{1}{3}$ growing power was found by experiment and by numerical simulation [9,10] and also predicted via a heuristic model [1].

B. Heterogeneous growth of an assembly of drops

The situation in this case is different than for single drops. Here the growth is basically governed by the coalescence of neighboring drops. Bigger drops grow at the expense of smaller ones (condition of mechanical stability). The present theory cannot be applied to an assembly of droplets having nearly the same size. The phenomenon of coalescence rescales the growth in a geometrical way. There are many cases where a monodispersed distribution of droplets is superimposed on a distribution of small droplets [14]. The present case has been done thinking on this type of polydisperse systems. It is assumed that the growing drop is surrounded by smaller ones of any size and it is practically circumvented by liquid. This bigger drop is imbibed in the same liquid. In Eq. (7) the energy flux due to the mechanical work performed on the system as well as the energy flux due to the gas phase are neglected. The drops' temperature and its gradient are given by Eq. (12). Under the above assumption, Eq. (9) reduces to

$$\frac{\partial r}{\partial t}-\frac{A_0}{3\rho_g L}r=0\ . \tag{20}$$

The solution for this equation is

$$r=r_0e^{(A_0/3\rho_g L)t}\ . \tag{21}$$

By expanding the exponential and considering $A_0/3\rho_g L<1$ [21] for times $t\leq 10^2$ Eq. (21) becomes

$$r=r_0+r_0\frac{A_0}{3\rho_g L}t\ . \tag{22}$$

Coalescence accelerate three times the growth of a single drop. Experiments and simulation agree with this result [1].

C. Homogeneous growth of a single drop

The homogeneous growth of a drop is produced when a supersaturated vapor is condensed by fluctuations of density. Let us suppose that the temperature of the liquid drop is nearly constant and that of the gas (the outside fluid) is given by Eq. (14). As we mentioned before, the vapor density here reaches higher values than in the heterogeneous case. Under these circumstances, it is assumed that

$$\frac{2\sigma}{\rho_g L}\frac{1}{r}>1\ ,$$

then Eq. (9) becomes

$$\frac{\partial r^2}{\partial t}-\frac{A\kappa_g}{\sigma}=0\ . \tag{23}$$

The solution of this equation is

$$r^2=\frac{A\kappa_g}{\sigma}t \ . \qquad (24)$$

In this case the radius grows with the power exponent $\frac{1}{2}$. This growth exponent is similar to the corresponding of a 3D droplet on a 1D substrate [1].

D. Homogeneous growth of an assembly of drops

As in the heterogeneous cases the growth of a drop is fundamentally controlled by the coalescence of the smaller droplets. The increase of the drop's mass by condensation of the saturated vapor is neglected in relation to the coalescence process. Here it is also assumed that

$$\frac{2\sigma}{\rho_g L}\frac{1}{r}>1 \ .$$

A central bigger drop is imbibed by smaller ones of the same liquid; the temperature and its gradient will be given by Eq. (12). Then Eq. (9) reduces to

$$\frac{\partial r}{\partial t}-\frac{A_0}{6\sigma}r^2=0 \ . \qquad (25)$$

The solution of this equation is

$$r=r_0+\frac{6\sigma}{A_0}\left[\frac{1}{t_0}-\frac{1}{t}\right] \ . \qquad (26)$$

It is seen from this equation that for small values of t, $r\approx t$, and at large values of t, $r\approx$const. The former asymptotic solution is similar to that found before for the heterogeneous case [see Eq. (22)].

IV. CONCLUSIONS

The condensation problem at the light of a fluid-dynamic approach has been studied here. First of all, we have found the surface thermal balance equation. This equation was obtained, for the steady-state situation, by integrating the three-dimensional energy balance equation. In the derivation, it was assumed that all the relevant changes occur along the radial direction of the drop and that there is no thermal or concentration gradient acting on the surface of the drop itself. The resulting equation [Eq. (9)] links, at the Gibbs dividing surface, the enthalpic, the thermal, and the capillary pressure contribution to the energy. By properly using this equation, it can be treated single noninteracting and assemble of interacting droplets for the heterogeneous and homogeneous condensation. The former case for both droplet's situation is represented by Eqs. (16) or (18) and (20), respectively. These equations were obtained by assuming that the capillary pressure contribution is neglected in relation to the thermal and enthalpic contributions. It must be kept in mind that the condensation density values of the saturated vapor for heterogeneous systems is lower than the respective values of the homogeneous ones. Then

$$1>\frac{2\sigma}{\rho_g L}\frac{1}{r}$$

clearly represents the condition for condensation onto a substrate. Water drops of the order of μm fulfill this condition. For single noninteraction and assembly of interacting droplets, the power growth exponents predicted here are $\frac{1}{3}$ and 1, respectively. These results agree with experiments [10] and numerical simulation [9]. It must be mentioned that the $\frac{1}{3}$ power law was also obtained by a model where it basically assumed a proportion between the rate of change of the drop's volume and the concentration gradient in the boundary layer [1]. The homogeneous growth of single drops and assembly of interacting drops have been considered by assuming in both cases that

$$1<\frac{2\sigma}{\rho_g L}\frac{1}{r} \ .$$

Here capillarity instead of the enthalpic contribution plays an essential role in the description. Noninteracting drops grow with the power exponent $\frac{1}{2}$. This growing power is similar to the one found experimentally on very thin thread under wetting conditions [11]. Finally, for small values of t, the homogeneous case of an assembly of droplets grows linearly with time. However, it can be concluded that the present fluid-dynamic approach takes into account the relevant feature of the condensation mechanism and predicts correct power laws.

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