

Kinetics of Capillary Condensation in a Nanoscale Pore

M. M. Kohonen,* N. Maeda, and H. K. Christenson

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, Canberra A.C.T. 0200, Australia

(Received 16 February 1999)

The rate of growth of capillary condensates in a model wedgelike pore has been studied using the surface force apparatus. The method described allows the direct measurement of the diffusion-limited growth of liquid condensates with interface radii of curvature as small as 20 nm. The observed rates of condensation of vapors of *n*-pentane, *n*-hexane, cyclohexane, and water are close to, but consistently lower than, values calculated from a model based on Langmuir's theory of droplet growth. [S0031-9007(99)09289-3]

PACS numbers: 68.10.Jy, 64.70.Fx, 68.45.Da

The exchange of matter between the condensed and the gaseous phase is a central feature of many natural and industrial processes. Although the study of evaporation and condensation at macroscopic planar surfaces has a long history, very little work has been done on systems involving small fluid domains with curved surfaces [1]. An important example of such a system is the formation of water droplets in the atmosphere, where the kinetics of droplet growth determines the properties of clouds [2,3]. Another problem of current interest is the dynamic behavior of fluids confined in porous media [4]. Numerous studies have been concerned with understanding the effects of confinement on the dynamics of phase separation processes [5]. The phenomenon of capillary condensation, whereby an undersaturated vapor can coexist with the liquid phase in small pores [6,7], is a particularly important example of a phase separation process occurring in confined systems. The kinetics of this process is of direct relevance to the study of the ageing of the mechanical properties of granular materials [8] and the kinetics of adsorption in porous media [6], but has received very little attention.

The equilibrium aspects of capillary condensation have been studied extensively using the surface force apparatus (SFA) [9]. It has been shown [10] that for nonpolar liquids the equilibrium surface radius of curvature r of liquids condensed between mica surfaces in contact is accurately described (down to $r \approx 4$ nm) by the Kelvin equation,

$$r = -\frac{\gamma v_m}{kT \ln S}, \quad (1)$$

where γ is the surface tension of the liquid, v_m is its molecular volume, and $S = p/p_0$ is the vapor saturation ratio (p is the actual vapor pressure and p_0 the saturation vapor pressure of the liquid). The mechanism giving rise to the capillary condensation transition when two surfaces are brought together has also been studied using the SFA [11] but none of these earlier studies has addressed the problem of the dynamics of condensate growth. We have now applied for the first time this technique to measure the kinetics of capillary condensation of various liquids.

The experiments involve bringing two back-silvered muscovite mica surfaces, which are mounted in a crossed-cylinder geometry, into contact in an atmosphere consisting of a mixture of nitrogen gas and the undersaturated vapor of a given liquid. Capillary condensation occurs in the annular wedge formed by the two surfaces in contact [Fig. 1(a)]. The geometry of this model wedgelike pore is locally equivalent to a truncated sphere on a flat surface [Fig. 1(b)]. The interference fringes produced by passing white light through the surfaces are recorded using a CCD camera connected to a computer, and the geometric parameters of the pore (R and ϕ) and the rate of growth of the capillary condensate are obtained from a subsequent analysis of the fringe images. The analysis of the fringes as well as other aspects of the procedure is described in detail elsewhere [9–13].

All experiments were performed at 25.0 ± 0.05 °C. Vapors of various liquids were obtained by introducing excess liquid onto the bottom of the sealed SFA chamber. Because of a slight heating effect of the light beam which passes through the surfaces (≤ 0.3 °C) the saturation ratio at the surfaces is slightly less than 1 (typically $S \approx 0.995$). In experiments with *n*-pentane, *n*-hexane, and cyclohexane a drying agent (usually phosphorus pentoxide) was also introduced into the chamber to exclude water vapor. All organic liquids were of analytical grade, used as received. Water was filtered, distilled, and deionized prior to use.

Previous attempts to study the capillary condensation of water vapor using the SFA were hampered by the accumulation of involatile material in the liquid condensate [10]. Although the identity of the involatile material is uncertain, it has been shown that such contaminants can be removed by dipping the mica surfaces in an acidic water solution [14]. In this work all surfaces were dipped in a dilute hydrochloric acid solution and dried with a gentle stream of nitrogen before mounting in the SFA; no subsequent accumulation of involatile material was observed with any of the liquids studied.

A theoretical model of the dynamics of capillary condensation in the model pore illustrated in Fig. 1 can

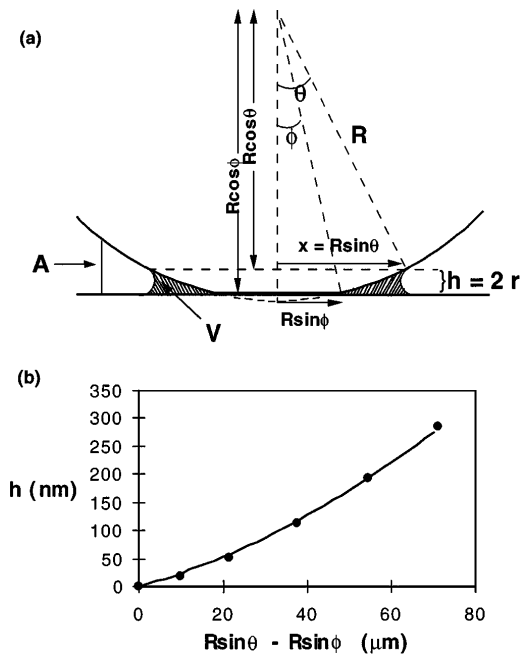


FIG. 1. (a) Schematic cross section of the surfaces in the equivalent sphere-on-a-flat-surface configuration in adhesive contact with a condensed annulus. R is the radius of curvature of the surfaces, h is the surface separation at the liquid-vapor interface of the condensate ($\approx 2r$, twice the radius of curvature of the interface), $x = R \sin \theta$ is the radius of the annular condensate, and $R \sin \phi$ is the radius of the flattened contact zone. (Typically, $R \approx 2$ cm, $\phi \approx 0.015$ rad, and $20 < h < 500$ nm for the measurements presented here.) $V \approx 4\pi Rr^2$ is the volume of the annulus and $A = 2\pi x[R \cos \phi - (R^2 - x^2)^{1/2}]$ is the area of an annular shell at distance x . (b) The filled circles show the measured surface profile inside a water condensate. The solid line is the surface profile calculated from the truncated-sphere-on-a-flat-surface model of the geometry (based on the measured values of R and ϕ); the agreement between measured and calculated profiles indicates that this model is an accurate description of the pore geometry.

be obtained based on Langmuir’s treatment [15] of the diffusion-limited growth of atmospheric water droplets. Consider an annular shell of area A at distance x , outside of the liquid condensate [Fig. 1(a)]. If Q is the rate of change of mass of the liquid condensate, then from simple diffusion theory, assuming the steady state has been reached,

$$dc = \frac{Q dx}{DA}, \tag{2}$$

where c is the concentration (mass per unit volume) of the vapor at x , and D is the diffusion coefficient. Integrating Eq. (2) between the limits $x = a$ and $x = b$, and converting from concentration to pressure units gives

$$p_b - p_a = \frac{QR_g T}{DM_w} \int_a^b \frac{dx}{A}, \tag{3}$$

where R_g is the gas constant, T is the temperature, and M_w is the molecular weight. If $x = a$ is taken to be at the liquid-vapor interface of the condensate (of radius of

curvature r), then p_a can be calculated using Eq. (1), and if $x = b$ is taken to be large enough then $p_b = p$, the vapor pressure in the chamber. If V is the volume of the condensate and ρ is the density of the liquid then, $Q = \rho(dV/dr) \times (dr/dt)$. Finally, substituting this expression for Q into Eq. (3) and performing the integration gives

$$\frac{dr}{dt} = \frac{DM_w p_0}{R_g T \rho} G(r; R, \phi) [S - \exp(-\gamma v_m / kTr)], \tag{4}$$

where $G(r; R, \phi)$ is a function of r and the measured geometric parameters R and ϕ [16].

Typical measured growth curves for the various liquids studied, together with theoretical curves generated by numerical integration of Eq. (4), are shown in Figs. 2 and 3. Adsorption from the vapor phase gives rise to thin films (of thickness ≈ 3 nm) on each surface which are squeezed out from between the surfaces when they jump into contact from a separation of approximately 20 nm [11,17]. The initial value of r in the subsequent growth of the liquid annulus by capillary condensation is thus determined by the volume of liquid squeezed out from between the surfaces, and varies between the different liquids and different S values. The values of S used to generate the theoretical curves are obtained from the experimentally determined equilibrium sizes of the condensates via Eq. (1), and so agreement between

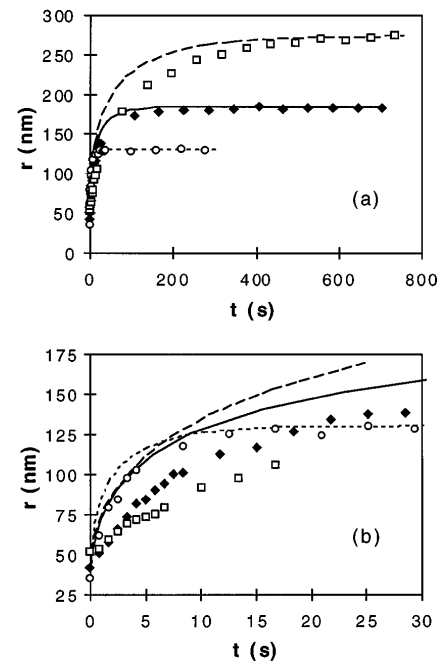


FIG. 2. (a) The growth of capillary condensates in the model pore shown in Fig. 1(a). The points represent experimental data and the lines are theoretical curves calculated using Eq. (4). Data are shown for n -pentane with $S = 0.9945$ (open circles, dotted line), n -hexane with $S = 0.9949$ (filled diamonds, solid line), and cyclohexane with $S = 0.9961$ (open squares, dashed line). (b) The same data as in (a), plotted on a smaller scale to reveal more detail concerning the initial dynamics.

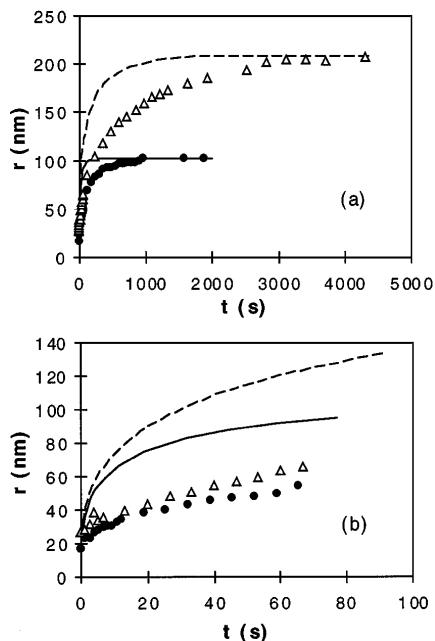


FIG. 3. (a) The growth of water condensates at two different saturation ratios. The points represent experimental data and the lines are theoretical curves calculated using Eq. (4). Data are shown for $S = 0.9949$ (filled circles, solid line) and $S = 0.9975$ (open triangles, dashed line). (b) The same data as in (a), plotted on a smaller scale to reveal more detail concerning the initial dynamics.

the measured and theoretical *equilibrium* values of r is guaranteed (i.e., the theoretical and measured curves must coincide for sufficiently large t).

It appears that the simple model described above provides a reasonable prediction of the time scale over which the condensates reach their equilibrium sizes, at least for nonpolar liquids. This model does tend to overestimate the rate of growth however, particularly for small values of r . For water, which displays the largest deviations, the theoretical and observed initial rates of growth differ by a factor of 10. Langmuir's theory, upon which Eq. (4) is based, is the most basic treatment of the diffusion-limited growth of droplets and neglects a number of effects which may explain the deviations between theory and experiment observed in our measurements.

The derivation of Eq. (4) is based on modeling the vapor phase as a continuous field up to the surface of the liquid condensate. When the characteristic dimensions of the condensate are comparable to the mean free path of the vapor molecules this description may not be an accurate one. For the case of diffusion-limited growth of a spherical liquid droplet with a radius comparable to the mean free path, a more detailed theoretical analysis leads to predicted growth rates which are slower than those obtained from Langmuir's basic treatment [3]. Using elementary kinetic-molecular theory [18] the mean free path of the vapor molecules in our measurements is estimated to be approximately 50 nm, which is comparable to the distance

between the confining walls of the pore at the position of the liquid-vapor interface of the condensate. The fact that the observed growth rates of the condensates are slower than predicted may thus be attributed in part to the breakdown of the continuum assumption.

Another effect which is neglected in Langmuir's treatment is the existence of a temperature differential between the surface of the liquid condensate and the surrounding vapor phase. The condensation of vapor results in the release of heat (i.e., the latent heat of evaporation) which gives rise to an increase in temperature, ΔT , of the condensate relative to the temperature of the surrounding vapor, T_v . An increase in temperature of the condensate results in a decreased rate of growth, because the difference between the vapor pressure of the condensed liquid and the pressure of the surrounding vapor, which is the driving force for condensation, is reduced. The magnitude of ΔT depends on the latent heat of evaporation of the liquid, the rate of condensation of vapor, and the thermal conductivity of the condensate surroundings. For typical conditions of atmospheric water droplet growth a simple calculation predicts $\Delta T \leq 0.003$ °C [19].

Although we have not attempted an *a priori* calculation of the expected increase in temperature for the case of capillary condensation, it is relatively simple to modify the rate equation [Eq. (4)] to incorporate the effect of a given temperature differential [20]. Using this modified rate equation the temperature differential which would give rise to a given observed rate of growth can be calculated. For the initial growth rates the values of ΔT calculated in this manner are approximately 0.3 °C for all the liquids studied.

It seems unlikely that the heat released by the condensation of vapor could give rise to such relatively large values of ΔT . We have considered the possibility that extra heating could arise from the change in surface energy which occurs when the mica surfaces jump into contact and the adsorbed liquid films coalesce to produce the initial condensate. If it is assumed that the energy released by the destruction of the two liquid-vapor interfaces associated with the adsorbed liquid films is absorbed entirely by the expelled liquid, then the expected temperature increase of the condensate is of the order of several degrees. However, a simple calculation suggests that the heat released from the coalescence of the surface films should be dissipated by conduction is less than a microsecond. It is thus unlikely that the deviations between theory and experiment observed in our measurements can be attributed solely to a temperature differential between the condensate and the surrounding vapor.

In summary, the results presented in this Letter constitute the first direct measurement of the kinetics of capillary condensation. In a broader sense they also represent an extension of previous studies of the "diffusion-limited" evaporation/condensation dynamics of liquid domains with highly curved surfaces. In particular, we have presented

measurements for interface radii of curvature as low as 20 nm, an order of magnitude lower than has previously been studied [21]. Further work is in progress to extend our measurements to liquids of lower vapor pressures and to systems of mixed vapors, a problem which is of particular interest in atmospheric science because of the importance of multicomponent condensation nuclei in the formation of atmospheric aerosols [3].

We thank D. R. M. Williams for useful discussions, and T. Sawkins and A. Hyde for technical assistance.

*Corresponding author.

Email address: mmk110@rsphysse.anu.edu.au

- [1] H. K. Cammenga, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1980), Vol. 5.
- [2] P. Y. Chuang, R. J. Charlson, and J. H. Seinfeld, *Nature* (London) **390**, 594 (1997).
- [3] H. R. Pruppacher and J. D. Klett, *Microphysics of Clouds and Precipitation* (Reidel, Dordrecht, 1978), and references therein.
- [4] *Molecular Dynamics in Restricted Geometries*, edited by J. Klafter and J. M. Drake (Wiley, New York, 1989).
- [5] See, e.g., D. D. Awschalom, J. Warnock, and M. W. Shafer, *Phys. Rev. Lett.* **57**, 1607 (1986); A. Chakrabarti, *Phys. Rev. Lett.* **69**, 1548 (1992); H. Tanaka, *Phys. Rev. Lett.* **70**, 53 (1993).
- [6] S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press, New York, 1982).
- [7] R. Evans and P. Tarazona, *Phys. Rev. Lett.* **52**, 557 (1984).
- [8] L. Bocquet, E. Charlaix, S. Ciliberto, and J. Crassous, *Nature* (London) **396**, 735 (1998).
- [9] J. N. Israelachvili and G. E. Adams, *J. Chem. Soc. Faraday Trans. 1* **74**, 975 (1978); J. L. Parker, H. K. Christenson, and B. W. Ninham, *Rev. Sci. Instrum.* **60**, 3135 (1989).
- [10] L. R. Fisher and J. N. Israelachvili, *J. Colloid Interface Sci.* **80**, 528 (1981).
- [11] H. K. Christenson, *Phys. Rev. Lett.* **73**, 1821 (1994).
- [12] H. K. Christenson, *Phys. Rev. Lett.* **74**, 4675 (1995).
- [13] J. N. Israelachvili, *J. Colloid Interface Sci.* **44**, 259 (1973).
- [14] H. K. Christenson, *J. Phys. Chem.* **97**, 12 034 (1993).
- [15] I. Langmuir, *Phys. Rev.* **12**, 368 (1918); General Electric Research Laboratory, New York, Report No. RL-223, 1944.
- [16] The actual form of the function $G(r; R, \phi)$ depends on the choice of the upper limit of the integral in Eq. (3); however, the results of integrating Eq. (4) are insensitive to this choice, provided $x = b$ is chosen large enough. A convenient choice is $b = R$, which gives $G(r; R, \phi) = (4rR)^{-1} \{ (2(R + R \cos \phi))^{-1} \ln[(R + (R \cos \phi - 2r)^2)/R] + (2(R \cos \phi - R))^{-1} \ln[(R - (R \cos \phi - 2r)^2)/R] + R \cos \phi (R^2 - R^2 \cos^2 \phi)^{-1} \ln[(R \cos \phi - (R \cos \phi - 2r)^2)/R \cos \phi] \}$.
- [17] D. Beaglehole, E. Z. Radlinska, B. W. Ninham, and H. K. Christenson, *Phys. Rev. Lett.* **66**, 2084 (1991); D. Beaglehole and H. K. Christenson, *J. Phys. Chem.* **96**, 3395 (1992); J. E. Curry and H. K. Christenson, *Langmuir* **12**, 5729 (1996).
- [18] I. N. Levine, *Physical Chemistry* (McGraw-Hill, New York, 1988), p. 457.
- [19] M. Neiburger and C. W. Chien, in *Physics of Precipitation*, edited by Helmut Weickmann, Geophysical Monograph No. 5, NAS-NRC No. 746 (American Geophysical Union, Washington, DC, 1960).
- [20] Reference [3], p. 419.
- [21] R. S. Bradley, M. G. Evans, and R. W. Whytlaw-Gray, *Proc. R. Soc. London A* **186**, 368 (1946), and references therein.