Anomalous behaviour of droplet coalescence in a two-dimensional complex system

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HIGHLIGHTS

- The same experimental system exhibits normal and anomalous droplet coalescence under different conditions.
- The anomaly cannot be explained with existing theories and models.
- A simple simulation model is used to reproduce experimental results.

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ABSTRACT

Coalescence of myristic acid droplets on water surface is found to exhibit anomalous behaviour such as simultaneous increase of mean droplet size and droplet number with time at low surface pressure. The existing theories and models can describe droplet evolution at high surface pressure but fail to explain this anomaly at low surface pressure. We propose a more general model for coalescence that reproduces the anomaly at low surface pressure and agrees with other models at high surface pressure. Our model considers microscopic resolution, nucleation of droplets and desorption of droplets in addition to pure coalescence and can be applied to a wide variety of systems.

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1. Introduction

Coalescence is ubiquitous in nature. It plays an important role in the formation of various structures in biology, geology, nuclear physics, condensed matter physics, astrophysics and in many other branches of science and engineering [1–9]. In pure coalescence when no other mechanisms are present, mean radius of clusters increases whereas number of clusters decreases with time and their evolutions follow some power-laws, $\langle R(t) \rangle \sim t^{\alpha}$ and $N(t) \sim t^{-\beta}$ where α and β are two positive constants characterising the coalescence process [10,11]. Recently, the power-law behaviour of coalescence has been observed in cluster growth of gold nanocrystals [12], coarsening dynamics of lipid domains [13], thin nematic film on liquid substrate [14] and quasi-two dimensional viscous drops [15]. Various numerical techniques such as Newtonian hydrodynamics [16], molecular dynamics [17,18] and tight-binding molecular dynamics [19] have been employed to study coalescence in different systems. Paul Meakin has proposed a very simple model for diffusion-limited coalescence and investigated power-law behaviour in two and three dimensions [10]. The Smoluchowski equation [20,21] which is based on the population balance has been used to describe coalescence process in a wide variety of systems.

Although coalescence mechanism in its pure form is well-understood and has been extensively studied, coalescence in complex systems is less understood. Coalescence may appear to be very complex when it convolves with other mechanisms

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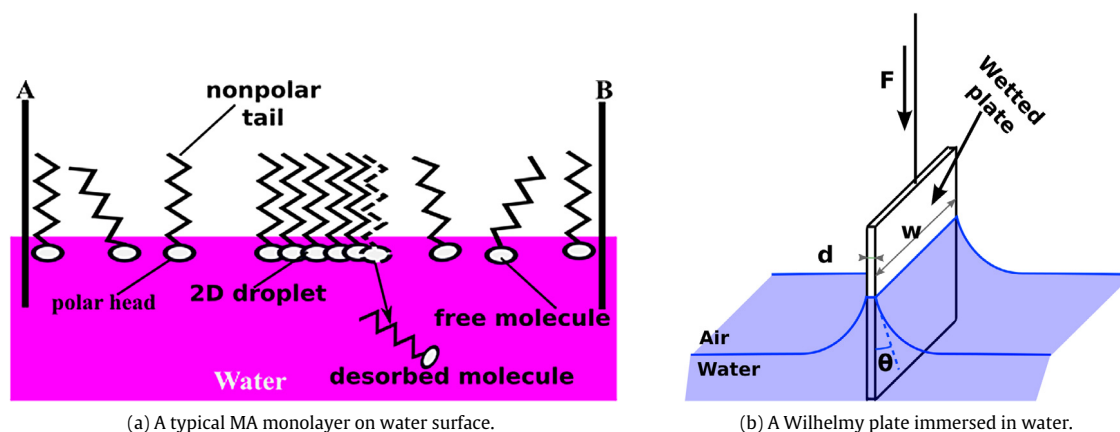
(a) A typical MA monolayer on water surface.

(b) A Wilhelmy plate immersed in water.

Fig. 1. Surface pressure (π) measurement: The schematic shows a typical Myristic acid (MA) monolayer consisting of free molecules and 2D droplets on water surface. The free molecules are not visible under a microscope. The droplets with size greater than microscopic resolution are seen. There could be desorption of molecules into water. The surface pressure is measured using Wilhelmy plate method. In this method, vertical forces are measured for different monolayer areas set by movable barriers A and B. For complete wetting, the contact angle (θ) is zero. The perimeter of the plate is 2(d + w). With known perimeter, the surface pressures are obtained for different monolayer areas (see text for details).

such as loss of materials to the surroundings and experimental limitations prevent viewing the entire system. Here, we investigate droplet evolution in a complex two-dimensional system, myristic acid (MA) droplets on water surface [22–24]. As friction on water surface is very low, this is an ideal system to study coalescence process. Also, the in-situ capture of the dynamics is possible with Brewster angle microscopy [25]. We study the droplet evolution in two extreme conditions – (i) at low pressure when there are a small number of small droplets and (ii) at high pressure when there are a large number of bigger droplets. The MA system exhibits an anomalous behaviour at low pressure. This cannot be explained with the existing theories and models. We propose a simple model that explains this anomaly at low pressure and agrees with other models at high pressure. To the best of our knowledge, this is the first study of two-dimensional droplet evolution where anomalous behaviour is observed. Also, this is the first attempt to model a complex two-dimensional system of droplets and explain the anomalous behaviour.

2. Experimental methods

2.1. System preparation

A myristic acid molecule consists of a polar carboxyl group, which is attracted by water and a nonpolar hydrocarbon tail, which is excluded by water. The solubility of myristic acid in water is found to be around 20 mg/L at room temperature [26]. Initially, myristic acid (Sigma-Aldrich, purity $>$ 99%) was dissolved in chloroform (Merck, purity $>$ 99%) to prepare a solution of concentration 3 mM. Then, the solution is spread on surface of Milli-Q water (resistivity 18.2 MΩ cm) in a KSV-NIMA Langmuir trough at room temperature (25 °C). A single layer of myristic acid molecules is formed on water surface as chloroform evaporates after 15 or 20 min. The surface pressure of this monolayer, and thus surface concentration of molecules can be varied with two barriers which can compress and decompress the molecules in the layer [22].

A typical MA monolayer consisting of free MA molecules and 2D MA-droplets is shown in Fig. 1(a). The orientation and packing of molecules, and the distribution of droplets change with surface pressure. The surface pressure (defined as $\pi = \gamma_0 - \gamma_m$ where γ_0 and γ_m are respectively surface tension of water without monolayer and with monolayer) is measured with Wilhelmy plate method [27,28]. In this method, a plate immersed in water experiences a resultant vertical force of $F = F_w - F_b + F_\gamma$ where F_w, F_b and F_γ are respectively weight of the plate, buoyant force on the plate and force due to surface tension. The resultant vertical forces are measured without monolayer (F_0) and with monolayer (F_m). With the complete wetting of Wilhelmy plate, $F_0 - F_m = (\gamma_0 - \gamma_m)/\text{perimeter} = \pi/\text{perimeter}$ as F_w and F_b are unchanged. As the perimeter of the Wilhelmy plate is known, the surface pressure can be obtained for a specific monolayer area. The area is changed by moving the barriers A and B (Fig. 1(a)) and surface pressure is measured for the new area. This process is repeated to obtain the Surface pressure–Area isotherm (see Fig. 2).

Fig. 2 shows that the surface pressure increases and MA monolayer passes through various two-dimensional phases when it is compressed [29,30]. The monolayer is initially in gaseous (G) phase when the molecules are not close enough to interact among themselves. Compression of the gas phase eventually leads to the liquid expanded (LE) phase. Upon further compression the liquid condensed (LC) droplets of myristic acid are formed on water surface at $\pi = 11$ mN/m. The surface pressure ranges for G, LE and LC phases are marked by small vertical bars in Fig. 2. The plateau region in the $\pi - A$ isotherm indicates the coexistence of LE and LC phases.