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研究課題名（和文） 原子間力顕微鏡による三相界線ナノ構造のダイナミック解析

研究課題名（英文） Analysis of Dynamic Structure of Three Phase Contact Line with Atomic Force Microscope

研究代表者

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研究成果の概要（和文）： 数値モデリング、軌道解析、赤外線サーモグラフィー、および数学的解析を使用して、毛細管力、蒸発、および熱マランゴニ効果の相互作用によって揮発性液滴三相界線のダイナミクスをスケールできることを示した。状態図を使用してこれらの時空間相互作用を定量化した。三相界線の拡散法則は、タナーの法則を、飽和蒸気圧が10^1～10^4Paの油から冷媒までの液体と、熱伝導率が 10^-1～10^3W/m/Kの基板上に拡張することによって導出された。さらに、三相界線付近の流れパターンの遷移に関する普遍的な基準を導出し、界面流の接線速度を数学的に分解することによって毛細管速度とマランゴニ速度の時空間変化を定量化した。

研究成果の学術的意義や社会的意義

制御可能な液体輸送は、電子機器の冷却、化学分析、生物医学診断において重要な役割を果たす。アプリケーションにおける実際のケースでは、ほとんどの液体は揮発性であるため、通常は蒸発が伴う。本研究は、実際のシナリオに直接対応する、熱伝導性基板上で蒸発する液滴の予測可能な拡散と流動状態の理論的基盤を提供する。状態図による支配的なメカニズムの分解は、質量流束の強さや液体と固体の熱特性に対応する流れの遷移など、既存の文献で物議を醸している問題のいくつかに対する普遍的な基準を提供する。研究の結論は、液体と固体の特性がよく調和したエレクトロニクス冷却および熱管理デバイスの新しい技術の開発に応用できる。

研究成果の概要（英文）： Extesive explorations have been carried out on the flow structure and spreading law of three phase contact line. With numerical modelling, trajectory analysis, infrared thermography, and mathematical decomposition, we show that the wetting dynamics of volatile droplets can be scaled by the spatial-temporal interplay between capillary, evaporation, and thermal Marangoni effects. We quantify these complex interactions using phase diagrams. A spreading law of evaporative droplets is derived by extending Tanner’s law (valid for non-volatile liquids) to a full range of liquids with saturation vapor pressure spanning from 101 to 104 Pa and on substrates with thermal conductivity from 10-1 to 103 W/m/K. We further derive a universal criterion for the transition of flow pattern near three phase contact line of evaporating droplets, and quantify the spatiotemporal variations of capillary velocity and Marangoni velocity by mathematically decomposing the tangential velocity of interfacial flow.

研究分野： 熱工学

キーワード： 三相界線　蒸発　液滴　熱マランゴニ効果　ラプラスプレッシャー　ファンデルワールス力

１．研究開始当初の背景

Three phase contact line (TPCL, 固気液三相界線) plays a decisive role in the dynamics of partial wetting systems (Bonn, D. *et al. Rev. Mod. Phys.* 81.2, 2009), and directly affects the efficiency of various phase change processes. "Contact line" as it is named, the TPCL is not a simple geometric line but is rather a region with complex structures. The dynamic structure can be more complex with relative motion taking place at the liquid-solid interface. Additionally, the region of TPCL has been evidenced to dominate the fast evaporation of partial-wetting liquids as well as liquids from nanochannels and nanopores (Xie, Q. *et al. Nat. Nanotech.* 13.3, 2018).

Over the past decades, several theoretical hypotheses on the dynamic structure of contact line have been proposed to describe the various wetting dynamics; this includes the precursor film theory by Nobel Laureate De Gennes (1932-2007) (*C.R. Acad. Sci. Ser. B, 1979*). On the other hand, since the inner region of TPCL is in the scale of tens of nanometers high, it is difficult to be detected with all kinds of optical techniques due to the light wavelength limitation. Consequently, direct experimental evidence is rather limited for the detection of nanoscopic structures of TPCL. Additionally, no explicit conclusions have been reached on the quantitative effect of the nanoscale surface geometry and the multiscale energy barriers on TPCL development.

２．研究の目的

This project aims to fully reveal the dynamic structure of three phase contact line (TPCL) at micro and nanoscale, and to quantify the role of surface energy barriers and liquid properties on the nanoscopic structure of TPCL. Due to the limitation of temporal resolution of the current Atomic Force Microscope, it has been hard to trace the fast evolution of nanostructure of TPCL with sufficient information for physics analysis. Additionally, due to my change of affiliation, it has been inconvenient to make further modifications to the existing atomic force microscope. As a result, I have changed my research method for the study of three phase contact line. Specifically, I focus on the microflow and spreading dynamics of TPCL combining experimental, numerical, and theoretical approaches. The efforts aim to address the controversial issues on the spreading law and flow transition of TPCL as discussed in existing literature in the past decade, and to propose general conclusions and criterions for controllable flow state and contact line motion.

３．研究の方法

Research methodologies (Particle Tracking and Trajectory Analysis, Infrared Thermography, and Direct Numerical Simulation) are referred to two recent publications in Applied Physics Letters (Editor's Pick, DOI: 10.1063/5.0197919) and Journal of Fluid Mechanics (DOI: 10.1017/jfm.2024.385).

４．研究成果

4.1 Spreading law of evaporative droplets

Droplet spreading is ubiquitous and plays a significant role in liquid-based energy systems, thermal management devices, and microfluidics. While the spreading of non-volatile droplets is quantitatively understood, the spreading and flow transition in volatile droplets remains elusive due to the complexity added by interfacial phase change and non-equilibrium thermal transport. Here we show, using both mathematical modeling and experiments, that the wetting dynamics of volatile droplets can be scaled by the spatial-temporal interplay between capillary, evaporation, and thermal Marangoni effects. We elucidate and quantify these complex interactions using phase diagrams based on systematic theoretical and experimental investigations. A spreading law of evaporative droplets is derived by extending Tanner's law (valid for non-volatile liquids) to a full range of liquids with saturation vapor pressure spanning from 10^1 to 10^4 Pa and on substrates with thermal conductivity from 10^{-1} to 10^3 W/m/K (Figure 3). Besides its importance in fluid-based industries, the conclusions also enable a unifying explanation to a series of individual works including the criterion of flow reversal and the state of dynamic wetting, making it possible to control liquid transport in diverse application scenarios.

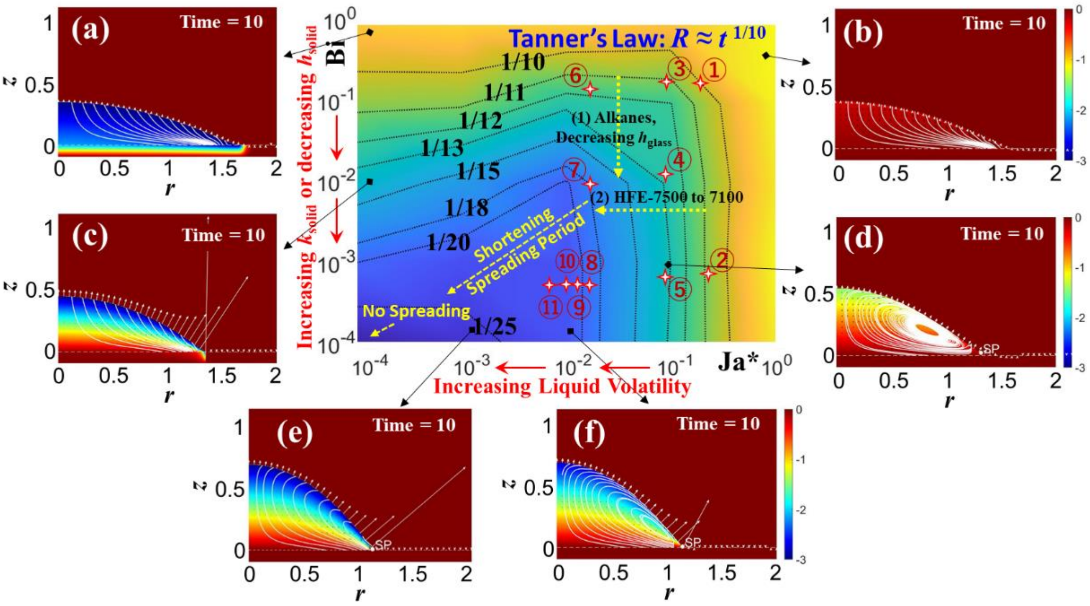

Figure 3 Phase diagram for the spreading rate of droplets along with demonstrations of flow and temperature fields in representative conditions. Contour lines of the spreading exponent are marked out with corresponding values.

4.2 Flow structure near three phase contact line of low-contact-angle evaporating droplets

Flow structure near three phase contact line (TPCL) of evaporating liquids plays a significant role in liquid wetting and dewetting, liquid film evaporation and boiling, etc. Despite the wide focus it receives, the interacting mechanisms therein remain elusive and in specific cases, controversial. Here, we reveal the profile of internal flow and elucidate the dominating mechanisms near TPCL of evaporating droplets, using mathematical modelling, trajectory analysis, and infrared thermography. We indicate that for less volatile liquids such as butanol, the flow pattern is dominated by capillary flow. With increasing liquid volatility, *e.g.,* alcohol, the effect of evaporation cooling, under conditions, induces interfacial temperature gradient with cold droplet apex and warm edge. The temperature gradient leads to Marangoni flow that competes with outwarding capillary flow, resulting in the reversal of interfacial flow and the formation of a stagnation point near TPCL (Figure 4). The spatiotemporal variations of capillary velocity and Marangoni velocity are further quantified by mathematically decomposing the tangential velocity of interfacial flow. The conclusions can serve as a theoretical base for explaining deposition patterns from colloidal suspensions, and can be utilized as a benchmark in analyzing more complex liquid systems.

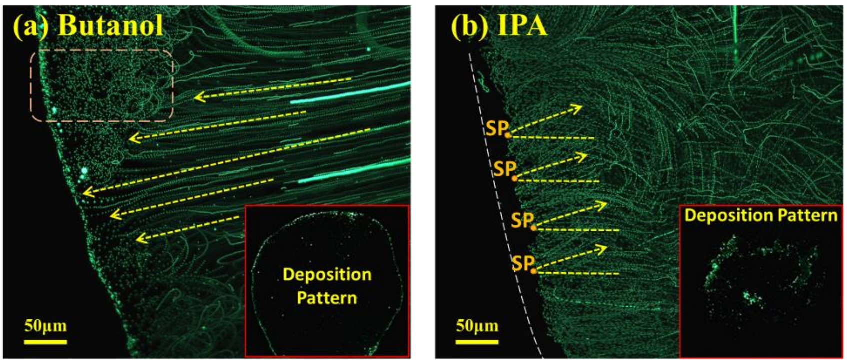

Figure 4 Trajectory of tracing particles reveals the flow field near TPCL of evaporating drops. (a) An overall outwarding flow is observed along the bottom of a butanol droplet ($p_{\mathrm{sat,Butanol}} = 580$ Pa) - small disturbances exist while the particles ultimately move towards and get deposited near TPCL. (b) Flow near the bottom of an IPA droplet ($p_{\mathrm{sat,IPA}} = 4420$ Pa) changes its direction at a position ~ 20 μm from the TPCL, eliminating the coffee ring effect with more particles deposited in the central region.

4.3 Hertz-Knudsen Type Expression of Interfacial Mass Flux for Partial-Wetting Liquids

Hertz–Knudsen equation, also known as Knudsen-Langmuir equation, is derived based on the statistics of vapor molecules detaching from/adsorbing onto the liquid surface, and has been commonly utilized in evaluating the evaporation and condensation mass flux due to its simplicity and efficiency. Despite its wide utilization, two empirical parameters contained in the relation (the evaporation and condensation coefficients) inexplicably span 3 orders of magnitude in a series of approaches to correlate experimental data.

In this research, we mathematically derive the expression of interfacial mass flux for evaporation of droplets and thin films based on the Hertz-Knudsen equation, the chemical potential difference across the liquid-air interface, and the ideal gas assumption, as Eq. (1),

$$\hat{J} = \hat{p}_{\mathrm{v,sat}}\sqrt{\frac{\hat{M}}{2\pi\hat{R}_g\hat{T}_g}}\left(\frac{\hat{M}}{\hat{\rho}\hat{R}_g\hat{T}_g}\left(\hat{p}-\hat{p}_g\right)+\frac{\hat{M}\hat{L}}{\hat{R}_g\hat{T}_g^2}\left(\hat{T}_S-\hat{T}_g\right)+ln\left(\frac{1}{\chi_{vapor}}\right)\right), \tag{1}$$

where $\hat{p}_{\mathrm{v,sat}}$ is the saturation vapor pressure, $\hat{M}$ is the molar mass of the liquid, $\hat{R}_g$ is the gas constant, $\hat{T}_g$ is the temperature of gas phase, $\hat{p}$ is the pressure of the liquid phase, $\hat{p}_g$ is the total pressure of the gas phase, $\hat{L}$ is the latent heat of vaporization, $\hat{T}_S$ is the temperature at the liquid-gas interface, and χ_{vapor} is the relative vapor concentration - ratio of vapor pressure to the saturation vapor pressure in the gas phase.

After scaling, the expression becomes Eq. (2),

$$\mathrm{Ja}\, J = \delta p + \psi\left(T_{\mathrm{i}} - T_g\right) + \ln\left(\frac{1}{\chi_{\mathrm{vapor}}}\right), \tag{2}$$

where Ja is defined as Jacob number, $\mathrm{Ja} = \frac{\hat{k}_0 \Delta T}{\hat{H}_0 \hat{L} \hat{p}_{\mathrm{v,sat}}} \sqrt{\frac{2\pi \hat{R}_g \hat{T}_{\mathrm{g}}}{\hat{M}}}$, measuring the joint thermal effects at the interface by evaporation cooling and heat dissipation into the liquid, $\delta = \frac{\hat{M}\hat{\eta}_\sigma \Delta\hat{T}}{\hat{\rho}_0 \hat{R}_g \hat{T}_{\mathrm{g}} \hat{H}_0}$, measure of Kelvin effect, and $\psi = \frac{\hat{M}\hat{L}\Delta\hat{T}}{\hat{R}_g \hat{T}_{\mathrm{g}}^2}$, indicating the effect of local temperature difference on the mass flux.

Through systematic experiments on droplet evaporation and spreading, we found that this expression overpredicts the interfacial mass flux by 100~500 times (in comparison to the experimental values). Additionally, the more volatile the liquid is, the more it overpredicts. The order of magnitude of overprediction corresponds with a number of work on water at 1 bar, *e.g.*, Pruger (1940) and Delaney et al. (1964) as summarized in Fig. 3 (evaporation coefficients), as well as Berman (1961) (film condensation) and Maa (1969) (direct condensation) as in Fig. 4 (condensation coefficients) in the work of Marek & Straub (2001). The variation trend of overprediction, i.e., more overprediction for more volatile liquids (weaker molecular bond at the interface), also corresponds with Fig. 7 in the work of Marek & Straub (2001) where weaker hydrogen bonds lead to smaller evaporation coefficients (J. Fluid Mech., 2024, doi: 10.1017/jfm.2024.385).

Based on the degree of overprediction and the trend, we propose the modification formula,

$$\mathrm{Ja}^* = 500 \ \frac{log_{max} - log Ja}{log_{max} - log_{min}} \mathrm{Ja}, \tag{3}$$

for Jakob number Ja, where a unified correction is made for all test liquids with varying volatility.

In the modification formula, we evaluate the liquid volatility by the order of magnitude of Ja (or rather, saturation vapor pressure). log_{max} is the maximal order of magnitude of Ja, log_{min} is the minimal order of magnitude of Ja for liquids that are available in nature and in normal fluid dynamics research, *i.e.*, $log_{max} = 0$, $log_{min} = -4$ based on our calculations (note that there might be cases that exceed this range in extreme conditions, but we do not consider such cases which are rare in nature and lab). With this general fitting, we correctly predict the evaporation mass flux for additional testing cases, *e.g.*, by randomly setting the substrate temperature for a randomly selected liquids in our lab, which validates the proposed formula.

We are currently in progress with a series of continuous experiments to further validate the proposed expression of interfacial mass flux in different scenarios of evaporating partial wetting liquids. In the expression, the liquid side pressure, $p = -\frac{\varepsilon^2 \sigma}{\mathrm{Ma}}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right) - \frac{A}{h^3}$, contains the curvature effect of liquid-air interface (Laplace pressure) as well as the van der Waals force in the simplest form, $-\frac{A}{h^3}$, which only becomes significant when the liquid film thins to sub-micro and nano scale. We are also conducting a series of theoretical investigations on the adaptability of the proposed expression in correctly describing the evaporation near contact line with better mathematical description of the interacting physics in this region.

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

—

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
ギリシャ	Aristotle University of Thessaloniki			
英国	University of Edinburgh			