Electronic Supplementary Material (ESI) for Soft Matter.

Supplemental material to
Viscoelasticity and elastocapillarity effects in the impact of drops on a repellent surface

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We provide here details on i) the heat transfer involved in the impact of drops in cold Leidenfrost conditions, ii) the measurement of the dynamic surface tension of micro-emulsions and wormlike micelles, iii) validation of the assumption made for the initial condition for the expansion velocity.

HEAT TRANSFER

Here we estimate the heat transfer when a drop at room temperature impacts a thin layer of liquid nitrogen at $T_\mathrm{s} = -196.15$°C with T_s the liquid nitrogen boiling point. The heat transfers from the warm drop to the liquid nitrogen, thus inducing its evaporation. The nitrogen vapor is supported by the liquid nitrogen layer underneath until this latter is completely evaporated (see Figure SM1). From this situation, two questions arise: how long does it take for the liquid nitrogen layer to completely evaporate once in the vicinity of the drop and what is the temperature of the drop at maximal expansion?

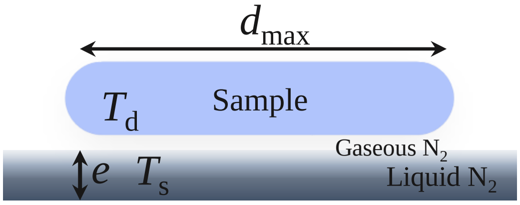

Figure SM1: Schematic representation of the drop in the vicinity of the liquid nitrogen after impact. T_d is the drop temperature, e is the thickness of the liquid nitrogen film and T_s its boiling point. Before impact, $e \approx 50$ nm [1].

Time to evaporate the liquid N_2

Heat transfer processes that involve change of phase of a fluid are dominated by convection because of the fluid motion induced during the process [2]. Thus, the rate of heat change between the vapor and the liquid N_2 is given by:

$$hS\Delta T = L\frac{dm_{\mathrm{N}_2}}{dt} \tag{1}$$

Here, m_{N_2} is the mass of liquid nitrogen to evaporate, $\frac{dm_{\mathrm{N}_2}}{dt}$ is its vaporization rate, $L = 199$ kJ/kg [3] is the latent heat of vaporization, h (in W/m^{2}K) is the convection heat transfer coefficient, S, the area of contact and $\Delta T = T_\mathrm{v} - T_\mathrm{s}$ where T_v is the N_2 vapor temperature and T_s, the temperature of the liquid nitrogen. We assume the temperature of the N_2 vapor to be homogeneous and equal to the mean between the temperatures of the drop and liquid N_2 $\left(T_\mathrm{v} = \frac{T_\mathrm{d}+T_\mathrm{s}}{2}\right)$ with $T_\mathrm{s} = -196.15°\mathrm{C}$, and $T_\mathrm{d} = 20°\mathrm{C}$, the initial drop temperature.

The time for the liquid nitrogen under the drop to evaporate is

$$t_\mathrm{evap} \approx \frac{m_{\mathrm{N}_2}}{\frac{dm_{\mathrm{N}_2}}{dt}} = \frac{m_{\mathrm{N}_2}L}{hS\Delta T} \tag{2}$$

with $m_{\mathrm{N}_2} = \frac{1}{4}\pi e d^2_\mathrm{max}\rho_{\mathrm{N}_2}$. ρ_{N_2} is the liquid N_2 density. The thickness of the liquid nitrogen film, e, is approximately 50nm as measured by ellipsometry [1]. The diameters used for the estimation of the surface of contact, S, are $d_\mathrm{max} = 20,\ 25,$ and 30 mm. Using $\rho_{\mathrm{N}_2} = 809$ kg/m^3 [3], the mass of liquid nitrogen to evaporate are $1.3\ 10^{-8},\ 2\ 10^{-8},$ and $2.8\ 10^{-8}$ kg.

The convection heat transfer coefficient, h, is not an intrinsic property of the fluid but is a parameter determined experimentally and which depends on variables influencing convection (surface geometry, the nature of fluid motion, the properties of the fluid, and the bulk fluid velocity). Nonetheless, it can be derived from the natural convection Nusselt number, Nu, for the upper surface of a cold plate [2].

$$h = \frac{k\mathrm{Nu}}{l} \tag{3}$$

with $k = 18.3\ 10^{-3}$ W/mK, the thermal conductivity of the bulk fluid measured at $-73.15°\mathrm{C} \approx T_\mathrm{v} = -87.85°\mathrm{C}$ [4] and l, the characteristic length of the contact area (Surface/Perimeter). The Nusselt number reads[2]

$$\mathrm{Nu} = 0.27\mathrm{Ra}_\mathrm{L}^{1/4} \tag{4}$$

with Ra_L, the Rayleigh number [2]

$$\mathrm{Ra}_\mathrm{L} = \frac{g\beta\Delta T l^3}{\nu^2}\mathrm{Pr} \tag{5}$$

with $g = 9.81$ m/s, the acceleration due to gravity, $\beta = \frac{1}{T_\mathrm{v}}$, the thermal expansion coefficient, $\nu = 7.65\ 10^{-6}$ m^2/s, the kinematic viscosity of nitrogen vapor at -73.15°C [4] and Pr $= 0.736$, the Prandtl number at -73.15°C [4]. The Prandtl number is the ratio between the momentum diffusivity over the thermal diffusivity.

We finally obtain $h = 9.6$, 9.1 and 8.7 W/m^{2}K which gives respectively $t_\mathrm{evap} = 7.7$, 8.2, and 8.6 ms for the three different maximum diameters. The drop will therefore be supported by evaporating liquid nitrogen during the whole expansion process as $t_\mathrm{evap} \geq t_\mathrm{max}$.

Temperature of the drop at t_max

Now that we made sure the drop is supported by the evaporating N_2 layer during the expansion, we solve the equation for the heat exchange between the drop and the N_2 vapor. As a first-order approximation, we consider Newtons law of cooling for which we assume no thermal gradient in the sample. [4–7]

In this case, the main mode of heat transport is conduction as its contribution is one order of magnitude higher than the contribution from convection and two orders of magnitude higher than the contribution from radiation. Thus, the heat exchange between the drop and the N_2 vapor is given by

$$-m_\mathrm{drop} C_\mathrm{p} \frac{dT}{dt} = k \frac{S}{e} (T - T_\mathrm{s}) \tag{6}$$

with $C_\mathrm{p} = 4.18$ kJ/kgK, the specific heat of water, m_drop, the mass of the drop with $\rho_\mathrm{drop} \approx \rho_\mathrm{water}$, $k = 18.3\ 10^{-3}$ W/mK, the thermal conductivity of the N_2 vapor measured at $-73.15°\mathrm{C} \approx T_\mathrm{v} = -87.85°\mathrm{C}$ [4], S, the surface of contact, e, the thickness of the vapor layer, T, the temperature of the sample and T_v, the N_2 vapor temperature. After integration, equation 6 reads

$$T_\mathrm{max} = (T_\mathrm{d} - T_\mathrm{s}) exp\left(\frac{-k t_\mathrm{max} S}{m_\mathrm{drop} C_\mathrm{p} e}\right) + T_\mathrm{s} \tag{7}$$

with T_max, the temperature of the drop at maximal expansion (at $t = t_\mathrm{max}$).

Using a surface S calculated from the mean diameter from d_0 to d_max, d_mean, we estimate the temperature at maximal extension for three viscoelastic samples impacted at $v_0 = 4.2$ m/s: M14ϕ8r9 ($t_\mathrm{max} = 1.5$ ms and $d_\mathrm{mean} = 6.57$ mm), M14ϕ8r8 ($t_\mathrm{max} = 3$ ms and $d_\mathrm{mean} = 10.98$ mm) and WMϕ9α4 ($t_\mathrm{max} = 6.4$ ms and $d_\mathrm{mean} = 14.85$ mm). The estimated temperature of the sheet at maximal expansion for samples M14ϕ8r9, M14ϕ8r8 and WMϕ9α4 are respectively 19.96°C, 19.80°C and 19.21°C.

This simple heat transfer model shows that even though the temperature gradient between the drop and the liquid nitrogen is important, the N_2 vapor layer between the two successfully insulates the drop from thermal variation during the expansion process.

DYNAMIC SURFACE TENSION

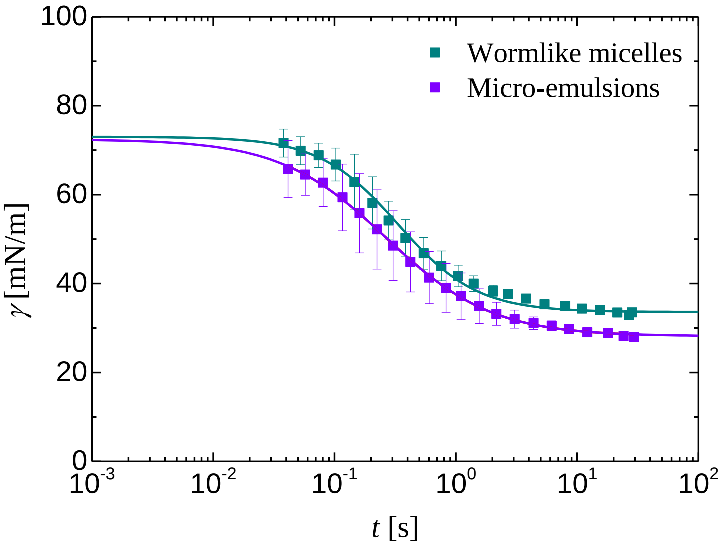

Figure SM2: Dynamic surface tension measurements for wormlike micelles and micro-emulsions. Error bars come from the average of three experiments. The lines are the fits obtained with equation 8.

The dynamic surface tension (DST) of micro-emulsions and wormlike micelles measurements were performed using a maximum bubble pressure tensiometer from Sita. The experimental measurements shown in Figure SM2 result from an average from measurements on 3 different micro-emulsions (M14ϕ8r8, M14ϕ10r6 and M14ϕ8r6) samples and 3 wormlike micelles samples (WMϕ9α4, WMϕ7α1.8 and WMϕ5α0.48). The experimental data are fitted with [8]

$$\gamma - \gamma_{inf} = \frac{\gamma_0 - \gamma_{inf}}{1 + \left(\frac{t}{t^*}\right)^n} \tag{8}$$

With γ_{inf}, the equilibrium value of the surface tension, γ_0, the surface tension of the solvent, t^*, a fitting parameter with units of time and n, a fitting exponent.

These experiments clearly indicate that, in the timescale of the experiment (10 ms), the relevant surface tension is the surface tension of the solvent.

INITIAL CONDITION FOR THE EXPANSION VELOCITY

The initial condition $\dot{d}(t=0)=2v_0$ comes from the initial velocity of the expanding sheet, $\frac{dr(t\to 0)}{dt}$, which is comparable to the impact velocity of the drop. Figure SM3 shows the experimental measurement of this assumption for representative $d(t)$. Linear fits are performed on the first three data points and the slopes of these fits give $\dot{d}(t=0)\approx 2v_0$.

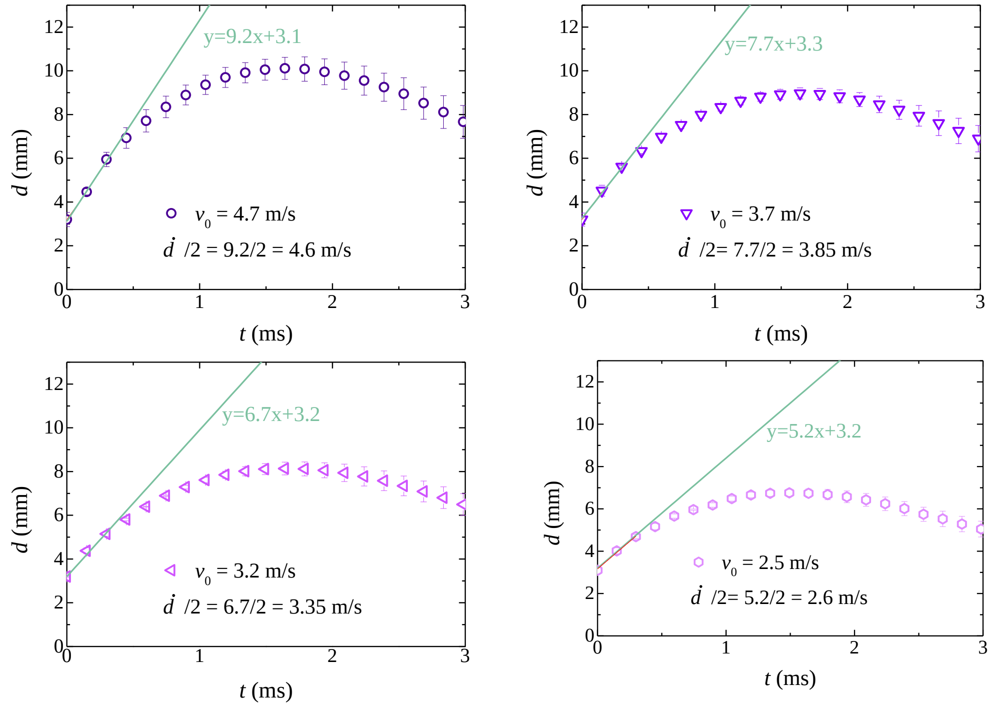

Figure SM3: Time evolution of the effective diameter, d, for sample M14ϕ8r9 at impact velocities $v_0 = 4.7$, 3.7, 3.2 and 2.5 m/s with linear fit of the first 3 data points to evaluate $\dot{d}(t=0)$. We find $\dot{d}(t=0)\approx 2v_0$.

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