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Measurement of Surface Velocity Fields

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Several preliminary remarks may be helpful before describing briefly a new technique for measuring surface velocity fields. All will appreciate that non-zero velocity fields at a free surface can be caused by bulk flows coupling to the surface. It is less well appreciated that surface velocity fields can be generated by other mechanisms so that bulk flows will result. In this case surface tension gradients provide the driving force for the velocity fields. Surface curvature can complicate the measurement as well as the calculation of velocity fields from first principles.

So far as we can determine $\nabla\sigma$ (σ is the surface tension or perhaps the surface tension tensor) is zero for 1 component systems kept at constant temperature. Since σ depends on temperature, a temperature gradient parallel to the surface will generally cause the development of a surface velocity field. Those trained in fluid mechanics tend to emphasize the effects of temperature gradients on surface flows.

The surface tension or interfacial tension of most any liquid-fluid system depends on composition in ways that are often very sensitive to concentration levels of certain components called surfactants. Long chain fatty acids, alcohols, amines and "soaps" in general are very effective in producing large excesses of these components at the surface. As a result the surface tension lowers. At equilibrium, the "Gibbs equation" holds

$$\Gamma = -\frac{1}{kT} \frac{\partial\sigma}{\partial \log c}$$

where Γ is the surface excess (sometimes takes in units of molecules/cm²), k is the Boltzmann constant and c the bulk concentration level of the surface active agent. From a molecular viewpoint, Γ is an excess defined across a sharp surface by the integral

$$\Gamma = \int_{-\infty}^{+\infty} (\rho(z) - \rho^{\pm}) dz$$

where z is taken along the normal to the interface and ρ^{\pm} is the density of the fluid far into the fluid on either side of a "dividing surface" and $\rho(z)$ the local density through the interface. A discussion of important details such as the choice of the surface is not appropriate here.

For most systems far from the critical temperature, the distance over which $(\rho(z) - \rho^{\pm}) \neq 0$ holds is of molecular dimensions, viz. ca 10 Å - 40 Å. This characteristic range of thickness is that which surface chemists usually think about in studies of adsorption and desorption and catalysis as well as surface flows. Other characteristic distances are often involved depending on the nature of the flows being analyzed. Unfortunately this can be misleading.

A striking example where intuition may lead to serious error occurs when certain surfactant molecules are allowed to spread at the air-water interface. A close packed monolayer of a long chain fatty acid will have $\Gamma \sim 5 \times 10^{14}$ molecules/cm². Since such materials are relatively insoluble in the substrate the concentration amounts to about 10⁻⁹ molar which is a very dilute solution. However, the surface tension will have gone from about 72 mN/m for pure water to less than 30 mN/m. Further since the "Gibbs elasticity" $-\Gamma \frac{\partial \sigma}{\partial \Gamma}$ is large, there can be large surface tension gradients with only small dilations, $\frac{\Gamma - \Gamma_0}{\Gamma_0}$.

These fundamental notions from the field of surface chemistry¹ can be easily demonstrated. Partially fill a petri dish with water, sprinkle a small amount of clean, dry talcum powder over the surface and then touch the tip of your finger

to the surface of the water. A monolayer will start to spread on the surface pushing the talcum away from the finger. The effect is rapid and obviously involves substantial surface tension gradients.

Since such a small amount of material can cause substantial surface flows, it is obvious that contamination will be an important factor to control whenever such flows are important. This factor should be kept in mind when developing designs for the floating zone process in zero gravity. Unfortunately, it may well be that surface contamination factors are not well enough controlled in many crystal growth situations. For example, note well that so called "deionized distilled water" can be sufficiently contaminated with amine surfactants so as to lower σ by a few mN/m and develop a non-trivial excess at the surface.¹

The velocity fields confined to the surface can be measured by techniques that are rather similar to them used for bulk measurements. For example, seed particles can be floated at the air-water interface that will provide trajectories from which the velocity field can be determined at least approximately. Laser doppler methods can be used. However, the particles are large compared to the thickness of the interfacial region so that bulk effects are averaged in with the surface fields. This may be satisfactory depending on the characteristic length scales.

My group is developing new methodology based on the fluctuations intrinsic to any fluid surface. Even at equilibrium, liquid systems are agitated on the microscale as molecules move and collide on very short time scales (10^{-14} sec or less). The effects of these collisions average in cooperative ways producing small amplitude fluctuations observable on a liquid-fluid surface in macroscopic time and length scales by various techniques. The appropriate measurements can be made by various scattering methods² including laser light scattering spectroscopy.

Surface fluctuations develop into either propagating or non-propagating waves of very small amplitude. The situation can be modeled accurately by the conventional methods of hydrodynamics. The theory is too long and complicated to discuss here³ other than to point out a starting place.

The surface elevation from a fixed plane is taken to be a summation of decoupled, harmonic surface waves

$$\zeta(\vec{x}^s, t) = \sum_{\vec{q}} A(\vec{q}) e^{i(\vec{q} \cdot \vec{x}^s - \hat{\omega}_{\vec{q}} t)}$$

where \vec{q} is the surface wave number, and $\hat{\omega}_{\vec{q}} (= \omega'_{\vec{q}} + i\omega''_{\vec{q}})$ is the complex frequency. The light scattering technique picks out a particular \vec{q} for analysis so that the spectrum (or the equivalent autocorrelation function) of the surface waves is determined. The spectrum can be analyzed to produce the frequency ($\omega'_{\vec{q}}$) and damping factor ($\omega''_{\vec{q}}$) associated with waves characterized by the wave number \vec{q} . The wave number, q , is $\frac{2\pi}{\lambda_{rip}} \hat{e}$ where λ_{rip} is the wave length of the surface waves and \hat{e} the direction of propagation. Light scattering techniques allow one to select both λ_{rip} and \hat{e} .

The sensitivity of the light scattering measurement to surface profile fluctuations is incredible in that $\sqrt{\langle A(\vec{q}) A(\vec{q}) \rangle}$ is on the order of $1 \text{ \AA} (10^{-8} \text{ cm})$ for a good signal/noise ratio to obtain.

The dispersion relations ($\hat{\omega}_{\vec{q}} = \hat{\omega}_{\vec{q}}(\vec{q}, \dots)$) required for analysis are generated from the hydrodynamical field equations by a rather tedious calculation⁴ when all of the details of the surface response is included. I note only that $|A(\vec{q})|/\lambda_{rip}$ ratios are always small enough so that all of the field equations can be linearized; linear response function techniques can be applied easily. When the viscosity of the medium is zero, the dispersion equation is simply

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$$\frac{\rho \omega'^2}{\sigma q^3} = 1 \quad (1)$$

with $\omega'' = 0$.

In a typical light scattering experiment, $100 \text{ cm}^{-1} < q < 2000 \text{ cm}^{-1}$ so that $\omega' \sim 500 \text{ kHz}$ (Note $\omega' = 2\pi\nu$). This is a convenient frequency range for measurement. Further, the scattering region only needs to be large enough so that the required averages can be done properly. A careful design of the lens system used to focus light onto the surface does allow spacial discrimination ranging from ca $50 \mu\text{m}$ as the minimum characteristic distance. In fact, we have designed such a system in order to determine local values of σ and the velocity fields over a fluid surface of about 100 cm^2 area. With the incident beam focused on a given location in the surface, the scattered light is analyzed for $\hat{\omega}$ from which the local σ and the velocity information can be determined. The geometrical factors can be controlled experimentally so that \vec{q} is specified and not just $|\vec{q}|$. As a result, velocity information is available and not just the speed.

The model invoked so as to determine the surface velocity includes the substrate velocity field as a part of the potential function used in solving the relevant field equations: $\phi = -Ux + \phi'$ where U is the speed of the fluid flow in direction x and x is the direction of wave propagation. The jump conditions at the surface, Σ , include

$$\frac{\partial \zeta}{\partial t} + U \frac{\partial \zeta}{\partial x^s} = - \left. \frac{\partial \phi}{\partial z} \right|_{\Sigma} + \left. \frac{\partial \Psi}{\partial x} \right|_{\Sigma}$$

where Ψ is the stream function. The resulting dispersion equation is of the form

$$f(q, \omega', \omega'', \sigma, U, \dots) = 0$$

where $q = |\vec{q}|$ and \dots implies that there are other parameters that must

be included (viscosity, etc.). The experiment can be run for different q values so that it is possible to determine both σ and U independently. Clearly it will be more convenient to know σ by an independent experiment so that only U need be determined during one observation.

Work is in progress directed toward the development of an apparatus to measure this surface laser doppler velocity (SLDV) effect quantitatively. The first experiments will be done in collaboration with Dr. Fowle (Arthur D. Little) who has developed an apparatus for the study of temperature gradient effects in thin liquid films. We will attempt to resolve in time and space velocity fields on the slowly flowing surfaces of pure liquids (water, mercury, etc.) using our SLDV techniques. If our estimations of precision, accuracy and discrimination are verified, we will design a SLDV system for the float zone experiment that we hope will be flown in about five years.

It is also possible to generate waves on the surface of a liquid. The methodology has been developed by a number of workers³ so that ω is fixed and $\hat{q} (= q' + iq'')$ is determined very accurately. This approach can also be used to determine σ and U and the sensitivity, precision and accuracy will be of a higher order than that obtained by the use of fluctuations as described in this paper. Unfortunately, the use of wave generators provides a complication that makes the simplicity of the light scattering method very attractive. Nevertheless, we are experimenting with new pulsing techniques that may lead to a superior instrument for determining velocity fields on the surface of a liquid.

Summary

I have emphasized the need to consider the effects of very small concentrations of impurities on the surface properties of liquids. I have described a new methodology for determining the surface velocity vector

as a function of location and time by the analysis of thermal fluctuations of the surface profile in a small domain around the point of interest. These fluctuations turn out to be waves so that the method amounts to the analysis of the local phase and group velocities of the waves as modified by a flow field. The apparatus now being constructed will be used in a series of experiments involving flow fields established by temperature gradients imposed along a surface. The SLDV methodology is difficult at this stage of development and may turn out to be impractical if the expected signal to noise ratio of the spectrum is not observed. With this in mind we are experimenting with driven wave arrangements that will provide the appropriate information but with a more awkward experimental arrangement.

References

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