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# On the Temperature of Surfaces

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## Abstract

The concept of the temperature of a surface is introduced from the viewpoint of the physical chemistry of surfaces. The surface, near surface and microlayer regions of the interface are defined. Most methods measure the temperature of the microlayer or at best the near surface region and may err in representing the surface temperature. Methods based on capillary ripples actually measure the surface temperature since surface tension (or surface tension tensor when a monolayer has been spread or adsorbed at the interface) is the main restoring force that controls their propagation. Light scattering methods are described for determining the elevation of very small amplitude capillary waves through the computation of various correlation functions from which the surface tension can be estimated. Procedures for estimating the surface temperature are described.

## The Surface Temperature

In order to speak of the "temperature of a surface" a length scale for the surface must be specified: the interface spans a length over which the normal derivative of the density is non–zero, Figure 1. It is well understood theoretically and experimentally that away from critical temperatures, the width of the interface is at most a fraction of a nanometer and corresponds to a few atomic or molecular dimensions. (See ref. (1,2).)

It is useful to define two additional length scales. The *near–surface* extends to about 10 nm. The near surface properties are some superposition of surface and volume properties which may, with careful analysis, be separated to some extent. The *microlayer* can be thought of as extending to roughly 1 micrometer from the surface. The properties determined in the microlayer *cannot* be separated into distinct surface and volume effects.

A property such as the *surface temperature* refers only to the first few molecular (atom) diameters of the interface; rigorously, it is not either the near–surface temperature or the microlayer temperature. Most methods in fact report the near surface or microlayer temperature. When the system (e.g. two–phase with one component) is at equilibrium, the temperature is uniform so that $T' = T_{surf} = T''$; even the microlayer temperature represents the temperature of the entire system. When the system is not in equilibrium, the near surface or microlayer temperatures may differ significantly from the surface temperature. The hypothesis that the near surface and surface temperatures are the same must be established experimentally or supported by careful analysis.

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Ellipsometry, reflectrometry (especially in the x-ray wave lengths) as well as theory and computer simulation provide the basis for asserting that the liquid/vapor interface is at most a few tenths of nanometers in thickness. One representation of the density profile through the interface is that of the mean field, Figure (1):

$$n(z) = \frac{1}{2}\left[n^{(+)} + n^{(-)}\right] + \frac{1}{2}\left[n^{(+)} - n^{(-)}\right] \tanh\frac{z}{\xi} \tag{1}$$

where n is the volume density, $n^{(+)}$, $n^{(-)}$ the densities on either side of the interface, and z is taken along the normal. When $T < T_c$ and $\left|\frac{T - T_c}{T_c}\right| >> 10^{-2}$, $\xi \sim .3$ nm. The actual value of $\xi$ depends on T. In addition the interface fluctuates. Define the Gibbs surface associated with the interface by the integral

$$0 = \int_{-a}^{\zeta} \left[n(z) - n^{(-)}\right] dz + \int_{\zeta}^{a} \left[n(z) - n^{(+)}\right] dz \tag{2}$$

where $-a$ and a are taken so that $(n(\pm a) - n^{\pm}) \sim 0$.

The fluctuating interface can be represented by the differential manifold[2,3]

$$\Sigma: = \begin{cases} x = x \\ y = y \\ z = \zeta(x,y,t) \end{cases} \tag{3}$$

One must think of $\zeta$ as a random variable, for the plane interface, or as a small fluctuation away from the average trace of a curved interface. The representation[2] for a plane interface

$$\zeta = \sum_{\vec{q}} \zeta_{\vec{q}}(t) e^{i\vec{q}\cdot\vec{x}} \tag{4}$$

for unit area leads to

$$<\zeta^*_{\vec{q}}\, \zeta_{\vec{q}}> = \frac{kT}{\gamma q^2 + g\Delta n} \tag{5}$$

(for unit area of surface) where k is the Boltzmann factor, T the temperature, $\gamma$ the surface tension, $\vec{q}$ the wave number, $\Delta n = n^{(+)} - n^{(-)}$ the density difference and g the gravity constant. This formula has been studied experimentally and is considered accurate although a molecular level theory is incomplete.

Clearly, the measurement of $<\zeta^*_{\vec{q}}\, \zeta_{\vec{q}}>$ will provide an estimate of the true surface temperature. However, the surface tension, $\gamma$, depends on temperature. So that the temperature dependence of the surface tension should be known.

In addition, the spectrum of the fluctuations can be calculated (Ref (2) and references therein)

$$G(\omega,q) = F(<\overset{*}{\zeta}_{\vec{q}}(0)\ \zeta_{\vec{q}}(t)>) \tag{6}$$

where $<\overset{*}{\zeta}_{\vec{q}}(0)\ \zeta_{\vec{q}}(t)>$ is the autocorrelation function of the $\vec{q}$ component of the elevation function and $F(\cdot)$ is the Fourier transform.

Even though $\sqrt{<\zeta_q^2>}$ << .1 nm, continuum mechanics provides a formula for $\zeta_{\vec{q}}$ which is known to be accurate for small $|\vec{q}|$ (the "long" wave length limit). There is a substantial body of experimental work that supports this conclusion so long as $|\vec{q}|$ is sufficiently small that macroscopic formulas are valid. A fairly delicate argument leads to the following result (Ref (2) and references therein)

$$G_{\vec{q}}(\omega) = \frac{kT}{\gamma q^2 + g\Delta n} (\underline{\underline{M}}^{-1})_{11}\, [q,\omega,n,\mu,\gamma,\ldots] \tag{7}$$

where , . . ., represents surface visco–elastic coefficients appropriate for systems for which a monomolecular film can form; a one component, two phase system admits only $\gamma$.

Note that the determination of $G_{\vec{q}}(\omega)$ provides the surface temperature as well as the surface tension. However, there are conditions that must hold when the system is dynamic, and $\nabla T \neq 0$. The distribution function for $\{\zeta_{\vec{q}}\}$ must not change form from that of equilibrium when the system is dynamic; local equilibrium is assumed. Furthermore a sufficient area must be sampled so that area averaging is satisfactory; for an $\ell$ by $\ell$ surface patch, $\ell >> \frac{1}{q}$ where $q \sim 1000\ \mathrm{cm}^{-1}$.

In fact, the functions $<\overset{*}{\zeta}_q \zeta_q>$ and $G_q(\omega)$ can be determined by light scattering which will be described briefly.

## Light Scattering Spectroscopy

Early in the century, the Maxwell equations for the scattering of light from thermally excited capillary waves[2,3] was worked out with the result that in the far field for $\zeta_{\vec{q}} << \lambda_o$, with $\lambda_o$ the wave length of the incident light, the scalar electric field follows $E_{\vec{q}} = \zeta_{\vec{q}} \times f$ where f depends on the geometry of the scattering experiment (angles of incidence and scattering) and the refractive indices of the phases that join at the surface. Obviously, at least one of the phases must be transparent. Indeed $<\overset{*}{E}_{\vec{q}}\ E_{\vec{q}}> = f^2 <\overset{*}{\zeta}_{\vec{q}}\ \zeta_{\vec{q}}>$. However, the electric field is detected by a square–law device (photodiode or PMT detectors) so that the autocorrelation function actually generated is that of the current, $i = \overset{*}{E}_q\ E_q$. Thus a heterodyne system is required so that $<i(0)\ i(t)>$ can be related directly to $<\zeta_{\vec{q}}(0)\ \zeta_{\vec{q}}(t)>$ without loss of phase information[2,4,5].

A general schematic of the methodology[2,4,5] is shown in figure 2. The essential feature is that a spatially filtered image of a grating of known wave number is projected onto the interface. The quality of the optical processing in projecting the grating onto the surface is crucial. The liquid surface is usually the highest quality optical component in the system and can be thought of as a very high quality but very inefficient phase grating following the rule[4,5]

$$R = R_0(1 + \eta)e^{-i\varphi} \qquad (8)$$

where R is the reflection coefficient of the surface, $R_0$ is the reflection coefficient of the ideally smooth surface, $\eta(x,y) << 1$ is the amplitude variation over the illuminated spot and $\varphi(x,y)$ is the phase variation. The phase function is $\varphi_{\vec{q}}(x,y) = 2k_0\zeta_{\vec{q}}$ wherein a real function representation of $\zeta_{\vec{q}}$ is appropriate[4,5].

The product $RS^{(-)}$ provides the modulation of the reflected beam, $S^{(+)}$ by the capillary ripples; a particular component $\zeta_{\vec{q}}(t)$ modulates $S^{(+)}$ $(= RS^{(-)})$ depending on the structure of $S^{(-)}$ as determined by the grating, $F_1$, $L_1$ and $L_2$. However, since the incident laser beam is of finite extent, the reflected beam $S^{(+)}$ carries a distorted representation of $\zeta_{\vec{q}}(t)$. Fortunately, the "instrument function" can be computed accurately[4]. The one most characteristic dimensionless group for the instrument function is $k_g\sigma$ where $k_g$ is the wave number of the grating as projected on the surface and $\sigma$ the cross section of the Gaussian incident beam ($4\sigma$ is the "beam diameter"). While not absolutely essential, the incident beam should be cleaned up so as to be accurately Gaussian since this makes the computation of the instrument function relatively simple.

It is practical to use optical components to manipulate the optical field $S^{(+)}$ so as to eliminate the zero–order beam and pass only the reference beam that is modulated by $\varphi$. The optical quality required for this step is modest, the entire reference beam must be collected excluding all other beams (higher order or lower order beams). The beam need not be of accurate Gaussian cross section and some distortion of the phase by the collection optics can be tolerated.

The computation of the correlation function $\langle i(0)\, i(t)\rangle = R_i(t)$ from the time series generated by the detector yields $\langle E^*_q(0)\, E_q(t)\rangle$ and therefore[4,5]

$$R_i(t) = \int_{-\infty}^{+\infty} dq_x \int_{-\infty}^{+\infty} dq_y \, \langle \zeta^*_q(0)\, \zeta_q(t)\rangle \, F(q_x - k^S_g, q_y) \qquad (10)$$

where $k^s_g$ is the wave number of the grating as projected on to the surface (if the magnification is 1 then $k_g = k^S_g$). The instrument function F depends on $k^S_g\sigma$ so that

$k^s_g\sigma \to \infty$, $F \to \delta(q_x - k^s_g)\,\delta(q_y)$ and $R_i \to \langle \overset{*}{\zeta}_q(0)\,\zeta_q(t)\rangle$, see references (4,5).

A second dimensionless group useful for designing an experiment[2,4,5] is $Y = (\omega_0\tau_0)^2$ where $\frac{1}{\tau_0} = 2\frac{(\mu' + \mu'')}{(n' + n'')}q^2$ where $\mu'\mu''$ are the shear viscosities in the volume of the phases surrounding the interface and $n'$, $n''$ the densities. The frequency, $\omega_0$ is defined by $1 = (n' + n'')\omega_0^2/\gamma q^3$ which obtains for the ideal, clean surface, between fluids of vanishing viscosity.

When $Y >> 1$ the capillary ripples are propagating and

$$\langle\overset{*}{\zeta}_q(0)\,\zeta_q(t)\rangle = \frac{kT}{\gamma q^2 + g\Delta n}\,e^{-\Gamma_q t}\cos\omega_q t \tag{11}$$

is a good representation of the autocorrelation function. The correlogram determined experimentally allows the estimation of $\Gamma_q$ and $\omega_q$ (and their uncertainties and correlation) by fitting equation (11) through a maximum likelihood algorithm. In general $\omega_q$ is determined to ~ .2% and $\Gamma_q$ to ~ 1%. It then is easy to compute any two parameters $n,\mu,\gamma,\ldots$ by using the dispersion equation, Det $\underline{\underline{M}} = 0$, from equation (7).

The construction of equation (7) and in particular the response function matrix $\underline{\underline{M}}$, has been done several times and is too lengthy to produce here; see references (2,3) for a guide to the literature. The analysis requires a careful construction of the mass and momentum balance at the surface including coupling to the substrate through the jump of the three dimensional pressure tensor across the interface projected along the normal to the interface as well as in the plane of the interface[2,3]. The boundary conditions include:

$$\frac{d\zeta}{dt} = \hat{n}\cdot\vec{v}|_0$$

and

$$\frac{d\vec{\xi}}{dt} = \vec{v}|_0 \cdot \underline{\underline{U}}\,\hat{n}$$

where $\vec{v}|_0$ is the volume velocity field evaluated at the surface and projected either along the normal, $\hat{n}$, or into the plane by the tensor $\underline{\underline{U}}_{\hat{n}}$. The conditions for linearization obtain since $\zeta << \frac{1}{q}$ in the spectrometer specifications. $\underline{\underline{M}}$ is constructed from the set of linear equations that result from a Fourier trahsform in space and a Laplace transform in time. The $M^{-1}_{11}$ component representing $\zeta$ is used in equation (7) while Det $\underline{\underline{M}} = 0$ is the dispersion equation mentioned above.

## Remarks on Implementation of the Fourier Transform Spectrometer

A research instrument, as figure (2) suggests, has required substantial room on an optical bench. Optics of focal lengths of ~ 1 meter are often used. We have built a much more compact system for various applications. Our latest instrument uses a ~ 40 mw diode laser, $\lambda_0 \sim 830$ nm, which is only a few centimeters long, wide and high. The power supply is built into this package. With care, a lens system of f ~ 200 mm works well to provide the necessary Fourier transforms and further, the optical path can be folded. The detector is a photodiode and is small. This system delivers correlograms of research quality without special manipulation of the output of the laser; the beam is elliptical but of Gaussian cross section in each direction. We are now working to reduce the size to that of a package measuring centimeters instead of meters.

A second problem with the light scattering methodology has been sensitivity to vibration. When the surface tilts slightly at low frequency ($\lesssim 10$ Hz) due to building vibration the correlograms become so badly distorted that $\Gamma_q$, $\omega_q$ cannot be determined. This has been overcome by a beam directing device in a feed–back circuit that locks the reference beam onto the detector accurately. The correlogram is then clean of the flicker effect; the slight distortion of the correlogram due to fluctuations of the angle of incidence of the laser beam about the normal is ignorable.

We have designed and are implementing a "single board" correlator that is driven by a PC (80286 processor + 80287 coprocessor) which provides a compact, clean system for data analysis.

We expect to have the first integrated prototype ready for a ship–board experiment in October, 1989 involving the measurement of the calm ocean surface tension <u>in</u> <u>situ</u>.

## Discussion

The light scattering procedures for measuring the "true" surface temperature rather than the near–surface or microlayer temperature are two

- Measure the averaged, surface light scattering irradiance which is proportional to $<\zeta_q^* \zeta_q>$ and thereby determine T through equation (5).
- Measure the correlation function of the scattered light, compute estimates of $\Gamma_q$ and $\omega_q$ and determine T through their variation with T.

The determination of the averaged, surface light scattering irradiance is difficult because the signal is small and subject to distortion by flare. Moreover, even with the careful application of an interference filter with a narrow band–pass at the wavelength of the laser, the radiance of the heated, liquid metal pool may swamp the detector. However, since the laser can be modulated easily, lock–in detection is possible and should be effective in separating out the signal due to scattered light. The strong q dependence of the scattered irradiance also provides a way of separating out the part of the signal to be analyzed. These methods require some information about the equilibrium surface tension dependence with temperature but a limited data set should be sufficient because of the relatively small changes involved.

The measurement of the correlation function is quick and accurate. The radiance coming from the heated, liquid metal pool is uncorrelated but does contribute to the "dark" noise. An interference filter should make this effect tractable. Note that the reference beam is much more intense than the scattered light and so the signal-to-noise ratio will be substantially better than in the first procedure.

However, the relationship between $\Gamma_q$, $\omega_q$ and T is complex in that the surface tension dependence on temperature is involved as well as that of the density and viscosity. Even so, the methodology has the potential of being relatively easy to calibrate ($\omega_q$, $\Gamma_q$ with T for each material) under equilibrium conditions which provide working curves for determining T and $\gamma$ for non-equilibrium systems.

While the theory of light scattering spectroscopy can be generalized to include temperature gradients, at this time we depend on the local equilibrium assumption. If light scattering can be observed from a small enough spot then local equilibrium can be asserted and an estimate of the surface tension or temperature, averaged over the illuminated spot, can be computed. However, as the spot is made smaller, q becomes less well determined by the optical system and thereby the estimate of the surface tension and temperature is less certain.

With the technology we have in place now, the minimum spot size that is practical is about 2 mm. It is likely that we can work with .2 mm spot sizes by using gratings with $k_g >$ 1000 $cm^{-1}$ but how well this works in practice must be determined. Note: The spot can be moved over the surface so that a profile can be developed.

It is entirely possible to do surface spectroscopy from curved surfaces. Indeed little needs to be changed for cylinder systems of 1 cm or so in length and a few mm in diameter or for spheres of 1 cm or so in diameter. It is an interesting question whether by careful application of Fourier transform optics it is possible to design an optical system that will separate out the higher frequency normal modes of a spherical drop for spectral analysis. Based on unpublished calculations done for spherical drops irradiated by an ultra–sound field we feel it is possible.

The question is whether an optical field can be produced in practice so that normal mode oscillation driven by thermal fluctuations in a small drop can be detected as a time series and analyzed. Indeed, it is not necessary to consider thermal fluctuations alone, external fields (e.g. sound or ultra–sound) can be used to drive the surface oscillations of the drop. The spectroscopy of such driven waves is also possible using the laser methods developed by the CWRU group.

It has been our experience that the light scattering methodology is the method of choice in determining the surface tension and interfacial tension of a system. It is fast, accurate and does not require manipulation of the sample. It is my opinion that this is the method of choice for determining the equilibrium surface tension of melts at high temperature. Whether the technology can be adapted for small samples with curvature can be determined by Fourier optical computations and a set of careful measurements.

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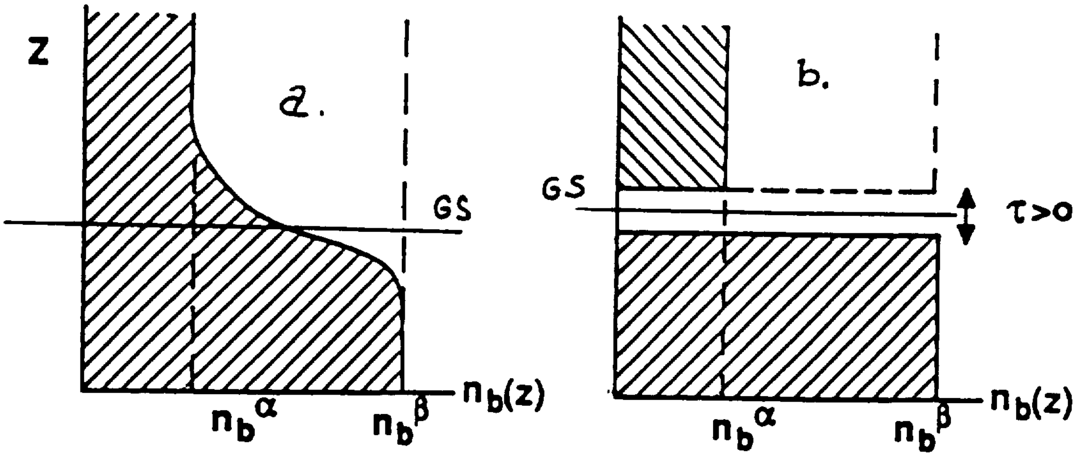

Figure 1 The density variation through the interfacial region between a liquid and its vapor. a) The variation of density as determined by theory and simulation. b) A model that can be defined to be consistent with the macroscopic continuum thermodynamics of interfacial behavior. In either case, the interfacial thickness, $\xi$, is < 1.0 nm for liquids at temperatures at least a few degrees below the critical temperature. $\xi \to \infty$ as $T \to T_c$, the critical temperature. The two lines, GS, represent the Gibbs surface.

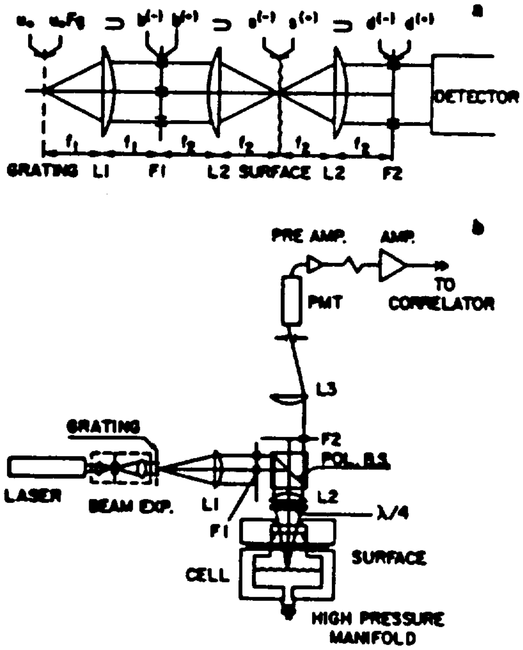

Figure 2 (a) Fourier optics method of design for a surface-light-scattering spectrometer. The symbol $\supset$ implies a Fourier transform. Transmission (or reflection) functions relate $b^{(-)}$ to $b^{(+)}$, $s^{(-)}$ to $s^{(+)}$, and $d^{(-)}$ to $d^{(+)}$. In particular, for the surface $s^{(+)} \simeq R_0(1 + \eta + i\phi)s^{(-)}$ where $\eta$ depends on the monolayer density and is ignorable. The phase function $\phi$ depends on the ripple profile and is modeled easily. The grating transmits a zero-order beam of relatively high intensity which is passed along with higher order diffracted beams which can be filtered spatially by F1. (b) Schematic of an implementation for high-pressure work. Note that the grating along with filters F2 and F1 provide a heterodyne configuration. It is easy to block all beams at F1 except the zero-order beam so as to obtain a homodyne configuration. Note that the grating is imaged onto the surface. The polarizing beam splitter (POL.B.S.) and λ/4 plate isolate the laser from the reflected beams.