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Spreading diffusion and its relation to sliding friction in molecularly thin adsorbed films

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The Einstein relations between frictional transport and diffusion coefficients are applied to the special case of a molecularly thin adsorbed film in order to demonstrate the equivalence between film-substrate sliding friction and the collective spreading diffusion properties of the film on its substrate.

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I. INTRODUCTION

Einstein's discovery that frictional transport coefficients could be related to diffusion coefficients ranks among the more important results of early 20th century physics [1]. This discovery occurred within the context of Brownian motion of mesoscopic particles in a condensed matter fluid. Through direct observation of the self-diffusive properties of the particles, a firm experimental foundation was given to the notion that fluctuations (implicit in the statistical mechanics of Boltzmann and Gibbs) were due to atomic motions occurring within the fluid.

The crucial theoretical step in Einstein's reasoning was to note that what appeared as friction in one experimental situation would appear again as diffusion in another experimental situation. The connection between the two situations has come to be called the Einstein relation.

The Einstein relation is applicable to numerous problems in condensed matter physics [2]. We apply it here to the particular case of friction due to sliding (interfacial viscosity) of an adsorbed monolayer (or molecularly thin film) and the mass diffusion coefficient of the layer as it spreads out on its substrate.

We have previously described how the sliding friction coefficient of an adsorbed film can be experimentally measured by means of a quartz crystal microbalance (QCM) [3]. The primary physical implication of our work is to note that such measurements can also provide quantitative information on the collective spreading properties of the film, direct observation of which [4] may not be straightforward.

In Sec. II we apply the thermodynamic arguments of Einstein to the mass diffusion and the sliding friction coefficient of a molecularly thin adsorbed film. In addition, we review the simplicity of Einstein's reasoning for the particular context of an adsorbed film. In Sec. III the same results are rigorously derived by means of the fluctuation dissipation theorems of quantum statistical physics [5]. The latter derivation is given for completeness of theoretical presentation. It also serves as a proof that the original reasoning by Einstein remains applicable even when atomic motions are treated within a quantum mechanical framework. We conclude with a discussion of physical considerations in Sec. IV.

II. STATISTICAL THERMODYNAMICS

Consider N film particles, each with mass m, adsorbed on an area A_s. The behavior of the film is governed by the equilibrium equation for two-dimensional thermodynamics [6]:

$$d\phi = s\,dT + \Gamma\,d\mu \,, \tag{1}$$

where ϕ is the spreading pressure (the force per unit length exerted on an arbitrary boundary within the film), s is the entropy per unit area, and $\Gamma = N/A_s$ is the number of particles per unit area.

Suppose that the particles were forced to concentrate near one point on the surface, creating spacial nonuniformities in the spreading pressure of the film. As a result, film particles would drift from regions of high spreading pressure to regions of low spreading pressure. How long would it take for the particles to spread out so as to uniformly cover the surface (on a macroscopic scale)? From the sliding friction viewpoint, the film is described by the Darcy law [7]:

$$-\nabla\phi = \eta_2 \mathbf{v}_d \,, \tag{2}$$

where η_2 is an interfacial friction coefficient defined as $F_f/A_s = \eta_2 v_d$, which relates the frictional force F_f to the film drift velocity v_d.

The Einstein argument allows one to alternatively view the spreading as a diffusive process described by the relation

$$-D\nabla\Gamma = \Gamma \mathbf{v}_d \,, \tag{3}$$

where D may be viewed as a "spreading diffusion" coefficient.

In order for Eq. (2) to be consistent with Eq. (3), the existence of a density gradient must necessarily imply the existence of a gradient in the spreading pressure. The explicit form of this interdependence is obtained by expressing the gradient of the spreading pressure as

$$\nabla\phi = \left[\frac{\partial\phi}{\partial\Gamma}\right]_T \nabla\Gamma \,, \tag{4}$$

so that Eqs. (2) and (3) can be combined to obtain the Einstein relation between η_2 and D:

$$D=\left(\frac{\Gamma}{\eta_2}\right)\left(\frac{\partial\phi}{\partial\Gamma}\right)_T . \tag{5}$$

Equation (5) is the central result of this work. It can be put into a form more convenient for experimental application via the thermodynamic relations implicit in Eq. (1):

$$\left(\frac{\partial\phi}{\partial\Gamma}\right)_T=\left(\frac{\partial\phi}{\partial\mu}\right)_T\left(\frac{\partial\mu}{\partial\Gamma}\right)_T=\Gamma\left(\frac{\partial\mu}{\partial\Gamma}\right)_T , \tag{6}$$

allowing Eq. (5) to be rewritten as

$$D=\frac{\Gamma^2}{\eta_2}\left(\frac{\partial\mu}{\partial\Gamma}\right)_T=\frac{\Gamma}{m}\left(\frac{\rho_2}{\eta_2}\right)\left(\frac{\partial\mu}{\partial\Gamma}\right)_T=\frac{\Gamma\tau}{m}\left(\frac{\partial\mu}{\partial\Gamma}\right)_T , \tag{7}$$

where $\rho_2=m\Gamma$ is the mass per unit area of the film and $\tau=\rho_2/\eta_2$ is a characteristic film slip time which has previously been discussed in great detail [3]. (The slip time is related to the decay of the film momentum fluctuations and corresponds to the time for the film's average drift velocity to fall to $1/e$ of its original value.) The relation between τ and film momentum fluctuations will become more apparent in Sec. III, where the fluctuation dissipation theorems are discussed as the basis of the Einstein relations stated in Eqs. (5) and (7). Although the mathematical manipulations of Sec. III are more involved than those of this section (which follow from Einstein's original reasoning), the physics of the final answer will be the same.

III. MASS DENSITY FLUCTUATIONS

The correlation function describing mass fluctuations in a molecularly thin film under equilibrium conditions involves the mass density operator at wave vector Q, taken for convenience to be along the x axis in the plane of the film:

$$\rho_Q=\frac{m}{\sqrt{A}}\sum_{j=1}^{N}e^{-iQx_j} . \tag{8}$$

The dynamic linear response function (for the mass density) to an applied potential is given by

$$\chi(Q,\zeta)=\frac{i}{\hbar}\lim_{A\to\infty}\int_0^\infty dt\, e^{i\zeta t}\langle[\rho_Q(t),\rho_Q^*(0)]\rangle , \tag{9}$$

which is analytic in the upper half complex frequency plane $\mathrm{Im}\zeta>0$. The dispersion relation for $\chi(Q,\zeta)$ reads

$$\chi(Q,\zeta)=\frac{2}{\pi}\int_0^\infty d\omega\frac{\omega}{\omega^2-\zeta^2}\mathrm{Im}\chi(Q,\omega+i0^+) , \tag{10a}$$

$$\mathrm{Re}\chi(Q,\Omega+i0^+)=\frac{2}{\pi}\mathrm{P}\int_0^\infty d\omega\frac{\omega}{\omega^2-\Omega^2}\mathrm{Im}\chi(Q,\omega+i0^+) , \tag{10b}$$

where P indicates the principal part of the integral and $\mathrm{Im}\chi(Q,\omega+i0^+)$ determines (completely) the response function.

The response function is well studied within the context of neutron and x-ray scattering experiments. The dynamic structure function $S(Q,\omega)$ for such scattering studies can be found from $\chi(Q,\zeta)$ using [5]

$$\mathrm{Im}\chi(Q,\omega+i0^+)=\left(\frac{\pi m^2\Gamma}{\hbar}\right)[1-e^{-\hbar\omega/k_BT}]S(Q,\omega) . \tag{11}$$

Applying known general expressions [5] to the specific case at hand, we obtain the form of $\chi(Q,\zeta)$ for certain asymptotic limits.

(i) The dynamic response function must reduce to the thermodynamic response function in the low frequency long wavelength limit:

$$\lim_{Q\to 0}\lim_{\zeta\to 0}\chi(Q,\zeta)=m^2\left(\frac{\partial\Gamma}{\partial\mu}\right)_T=\left(\frac{\rho_2}{c_T^2}\right) , \tag{12}$$

where c_T is the (isothermal) speed of sound in the film. Equations (10) and (12) imply the thermodynamic sum rule

$$\lim_{Q\to 0}\frac{2}{\pi}\int_0^\infty\frac{d\omega}{\omega}\mathrm{Im}\chi(Q,\omega+i0^+)=\frac{\rho_2}{c_T^2} . \tag{13}$$

(ii) In the high frequency limit, the response function must be that corresponding to "free particles:"

$$\lim_{\zeta\to\infty}\left(\frac{\zeta^2}{Q^2}\right)\chi(Q,\zeta)=-\rho_2 , \tag{14}$$

which together with Eq. (10) implies the oscillator strength sum rule

$$\frac{2}{\pi}\int_0^\infty d\omega\,\omega\,\mathrm{Im}\chi(Q,\omega+i0^+)=\rho_2Q^2 . \tag{15}$$

(iii) If the long wavelength limit in Eq. (14) is taken for finite frequency, then one obtains the acoustic impedance of the film $Z(\zeta)$ from

$$\lim_{Q\to 0}\left(\frac{\zeta^2}{Q^2}\right)\chi(Q,\zeta)=\left(\frac{i}{\zeta}\right)Z(\zeta)-\rho_2 . \tag{16}$$

The real and imaginary parts of the acoustic impedance (each is an experimentally measurable quantity by means of a QCM) may be obtained by taking the limit of real frequency:

$$Z(\omega+i0^+)=R(\omega)-iX(\omega) . \tag{17}$$

The complete acoustic impedance is determined by the acoustic resistance via the dispersion relation

$$Z(\zeta)=-\frac{2i\zeta}{\pi}\int_0^\infty d\omega\, R(\omega)/(\omega^2-\zeta^2) , \tag{18a}$$

$$X(\Omega)=\frac{2\Omega}{\pi}\mathrm{P}\int_0^\infty d\omega\, R(\omega)/(\omega^2-\Omega^2) . \tag{18b}$$

The asymptotic limits discussed thus far allow for the representation of $\chi(Q,\zeta)$ as a sound wave (phonon) propagator with a self-energy part $\Pi(Q,\zeta)$ defined as

$$\chi(Q,\zeta)=\rho_2Q^2/[c_T^2Q^2-\zeta^2-\Pi(Q,\zeta)] . \tag{19}$$

In the long wavelength limit, the self-energy part defines the "slipping impedance" $Z_s(\zeta)$ of the film against the substrate:

$$\lim_{Q\to 0}\Pi(Q,\zeta)=i\zeta\frac{Z_s(\zeta)}{\rho_2} . \tag{20}$$

It is interesting to note that Eqs. (16), (19), and (20) imply a simple acoustical engineering rule for computing the mechanical impedance of a film on a QCM: The acoustic impedance is that which would be computed if the film were rigidly fixed to the substrate, but connected in parallel to an impedance Z_s representing the "slipping" of the film on the substrate:

$$\frac{1}{Z(\zeta)}=-\frac{1}{i\zeta\rho_2}+\frac{1}{Z_s(\zeta)} . \tag{21}$$

Now let us return to the Einstein relation.

The zero frequency limit of the "slipping impedance" can be identified with the interfacial friction coefficient

$$Z_s(0)=\eta_2 , \tag{22}$$

so that the slipping impedance $Z_s(\zeta)$ may be described as a frequency dependent interfacial viscosity. Equation (21) can, for many purposes, be approximated by neglecting the frequency dependence of $Z_s(\zeta)$. Equations (21) and (22) then imply a simple Drude form for the acoustic impedance:

$$Z_{\mathrm{Drude}}(\zeta)=-\frac{i\zeta\rho_2}{1-i\zeta\tau} , \quad \tau=\frac{\rho_2}{\eta_2} . \tag{23}$$

In this regard it should be remembered that Eq. (21) is quite rigorous, while Eq. (23) represents a form for the acoustic impedance which in practice is often adequate. Equation (23) has previously been discussed in great detail [3]. The more rigorous equation (21) will be treated in a future work.

In both the long wavelength and low frequency limits, the above considerations can be summed up by the following statements:

$$\chi(Q,\zeta)\to\frac{\rho_2 Q^2\tau}{(c_T^2 Q^2\tau-i\zeta)} , \quad \text{as } (Q,\zeta)\to(0,0) . \tag{24}$$

The density fluctuations propagator of Eq. (24) has a diffusion pole with

$$D=c_T^2\tau , \tag{25}$$

which is the Einstein relation of Sec. II derived from a response function viewpoint. For a perfectly "smooth" substrate, sound waves propagate freely and the characteristic slip time is infinite. For an actual substrate (with nonzero interfacial friction and finite slip time), the density fluctuations ultimately become diffusive, proportional to the square of the (isothermal) sound velocity times the slip time as described by the Einstein relation of Eq. (25).

IV. DISCUSSION

Sliding friction coefficients and slip times have been measured [8] for physisorbed films on gold and silver substrates. Slip times for liquid monolayers of materials such as krypton, xenon, nitrogen, water, and cyclohexane are observed to be on the order of ns (for QCM's which oscillate at 8 MHz). The corresponding friction coefficients range from ≈ 8 dyn/cm^2 per cm/s for a material of relatively light molecular weight (water) to ≈ 120 dyn/cm^2 per cm/s for a more massive material such as xenon. The spreading diffusion coefficients for such films, deduced from Eq. (7), are on the order of 1 cm^2/sec [9] (less for rough surfaces [8]). This is in qualitative agreement with the experimentally observed equilibrium times and supports the interpretation of D as the rate at which the film can spread into an equilibrium configuration. The observation of higher friction coefficients for films adsorbed on rough surfaces is intuitively appealing. It is also intuitive that a lower diffusion rate should be associated with a rougher surface, since the film particles must travel longer distances along the surface in order to accomplish the same net horizontal displacements.

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