

## Surface Correlations and Exchange at a Spherical Liquid Interface

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The paper gives a new derivation of the rms displacement and slope of the surface of a spherical drop in the presence of thermally excited capillary waves. Calculations for a spherical surface have the advantage, over similar calculations for a plane surface, that they avoid the difficulty of having to choose an arbitrary upper limit for the wavelength. Expressions are obtained for time and distance correlation functions of the vertical displacement, of the difference in vertical displacement between different times or locations, of vertical velocity, and of the difference of vertical velocity between separate times or locations on the surface. The correlation function for the difference in vertical velocity between two points on the surface rapidly attains a constant, nonzero value as the separation of the points increases. The limiting value of the velocity difference is related to the speed of motion along the reaction coordinate when the process of accommodation into the bulk liquid is treated by transition-state theory. This leads to an estimate of the physical length of the critical region of the reaction coordinate that must be traversed if accommodation is to occur.

### Introduction

The relationship between the capillary-wave spectrum at a liquid surface and the mean-square displacement of the surface has been considered by many authors. Accounts of earlier work for a planar interface are given in the book by Widom and Rowlinson<sup>1</sup> and for planar and spherical interfaces by Henderson and Lekner.<sup>2</sup> In previous papers we have considered the thermal vibrations of a planar surface membrane in relation to the rate of escape of molecules from the surface,<sup>3</sup> the rate at which a surface molecule is accommodated into the body of the liquid,<sup>4</sup> and the angular dependence of the sticking coefficient for molecules striking the surface, arising from the distribution of tilt angles at the surface.<sup>5</sup> Recently Simpson and Rowlen<sup>6</sup> have discussed relationships between the capillary wave spectrum, correlation functions for vertical displacement, the local tilt angle of the surface, and the experimentally measured surface roughness.

In our earlier calculations we set the upper wavelength limit for the capillary wave spectrum at  $2L$ , where  $L$  is the wavelength at which capillary waves are superseded by gravity waves.<sup>7</sup> However, this is obviously an arbitrary procedure, and it is possible to envisage situations, such as the surface of a neutron star or a liquid with very low surface tension, where gravity waves would be dominant down to extremely short wavelengths. The main advantage of making calculations for a spherical surface is that this uncertainty about the upper wavelength limit is eliminated. In addition, the effect of gravity can be removed by supposing the droplet to be in a state of free fall, and conclusions about the surface of a moderately large drop can be expected to be essentially identical with those for a plane surface. Further, the calculations should ultimately provide information about the rate of exchange of material across the spherical interface, information which is of potential interest in such practical fields as the formation of acid rain,<sup>8</sup> the dynamics of emulsion polymerization,<sup>9</sup> and the physical chemistry of aerosols as studied, for example, in the work of Davidovits and colleagues.<sup>10</sup>

We begin by considering the nature of the packing of molecules at the liquid surface and the changes in coordination

number that can occur as a consequence of surface vibrations. Then we summarize some well-known mathematical results for the vibrations of a spherical drop and present a new calculation of the mean-square displacement and slope of the surface. Next we obtain some new expressions for displacement and velocity correlation functions for a single location at different times, and for the same time at different locations. Finally, we use the velocity correlation function for different locations as the basis of a new discussion of the rate at which a surface molecule is engulfed by the bulk liquid.

### Packing of Molecules at a Liquid Surface

For simplicity we consider only spherical molecules, or molecules whose rotation is sufficiently free that they can be regarded as spherical, and we assume that changes of coordination number in the surface skin of the drop do not alter the coordination to molecules in the layer immediately below the surface. Trivial observation, as of a layer of bubbles in a glass, suggests that flat layers of spherical molecules will tend to adopt 6-fold coordination, with the surrounding molecules arranged in hexagons in a manner which resembles the structure of graphite. Considering only the central molecule, the area per molecule, and hence the surface free energy, decreases as coordination number increases, but a heptagon has only slightly less area per molecule than a hexagon, a hexagon has markedly less area per molecule than a pentagon, and the average area per molecule is less for two hexagons than for one pentagon plus one heptagon. Studies of the geometry of fullerenes<sup>11</sup> show that the presence of some pentagons is required in order to produce a closed surface from a graphite sheet, and that a regular solid derived from a graphite sheet must contain exactly 12 pentagons. Every heptagon that is introduced into a closed surface must be balanced by an additional pentagon if the surface is to remain closed. Thus the thermal motion of the surface skin of a drop is likely to involve continual changes in coordination number for some of the surface molecules, and one can visualize how such motions might cause the coordination number to increase to a value characteristic of a subsurface molecule. For six spherical molecules in a flat hexagon and another at the

center, allowing for the fact that a molecule at an apex of the hexagon is shared equally among three hexagons, the surface area per molecule is  $2(3)^{1/2}a^2 = 3.464a^2$ , where  $a$  is the molecular radius. If we require the shortest wavelength of the surface oscillations to be  $4a$ , i.e., exactly two molecular diameters, the area per molecule has to be  $16a^2/\pi = 5.093a^2$  [see the discussion leading to eq 20]. In what follows we shall, for simplicity, write the surface area per molecule as  $\pi\sigma^2$ , but this quantity is not to be confused with the ordinary molecular cross section. Indeed, for an associated liquid such as sulfuric acid or water, the effective surface area per structural unit is liable to be considerably greater than the gas-phase cross section.<sup>5</sup> With the exception of some results given in Tables 1 and 2, all of the calculations reported in this paper used  $\sigma = 2 \times 10^{-8}$  cm.

### Mean-Square Displacement and Slope at a Spherical Surface

Equations 1–4 express some useful results that have been known for many years.<sup>12,13</sup> The instantaneous displacement  $\zeta_{lm}$  of the surface from its equilibrium position at the location  $\theta, \phi$  due to the vibration mode labeled  $l, m$ , with mean-square value  $\langle \zeta_{lm}^2 \rangle$ , can be written as

$$\zeta_{lm} = \zeta_{lm}^0 Y_{lm}(\theta, \phi) \cos(\omega_{lm}t + \epsilon_{lm}) \quad (1)$$

where  $\langle \zeta_{lm}^2 \rangle = (\zeta_{lm}^0)^2/2$ ,

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} e^{im\phi} P_{lm}(\cos\theta) \quad (2)$$

is a normalized spherical harmonic, the index  $m$  takes its usual  $2l+1$  values,  $\epsilon_{lm}$  is an unknown phase shift, and the circular frequency  $\omega_{lm}$  for all modes  $l, m$  with the same value of  $l$  is given by

$$\omega_{lm}^2 = l(l-1)(l+2)\gamma/\rho r^3 \quad (3a)$$

where  $\gamma$  is the surface tension and  $\rho$  the density of the liquid,  $r$  is the radius of the drop, and gravitation is neglected. The corresponding expression for a bubble is

$$\omega_{lm}^2 = (l+1)(l-1)(l+2)\gamma/\rho r^3 \quad (3b)$$

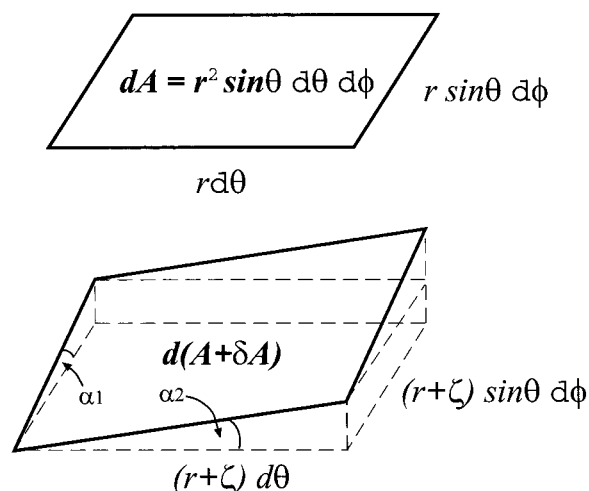
where  $\rho$  is now the density of the surrounding liquid. The surface waves are damped by the viscosity  $\eta$  of the underlying liquid so that their amplitude decays as  $\exp(-t/\tau)$ , where the characteristic decay time  $\tau$  for a drop is given by

$$\tau_{lm} = r^2/\{l(l-1)(2l+1)\eta\} \quad (4a)$$

and for a bubble by

$$\tau_{lm} = r^2/\{(l+2)(2l+1)\eta\} \quad (4b)$$

This damping by viscosity is the source of the time dependence of calculated correlation functions for surface quantities. In what follows we shall confine our calculations to the case of a droplet. Extension to a bubble is straightforward. Also, we shall ignore the density and viscosity of the second phase, which we assume to be a gas; more general expressions for  $\omega_{lm}$  and  $\tau_{lm}$  are given by Lamb.<sup>12</sup> To avoid having to employ numerical integration at an early stage, we shall also ignore the variation of surface tension with vibration frequency.<sup>6</sup>



**Figure 1.** Elements of surface area in spherical polar coordinates: (a) with no displacement; (b) with expansion and tilting.

For high-frequency vibrations, which in practice means for the great majority of vibrational modes, the time  $\tau_{lm}$  is much less than the period of vibration, which has two important consequences. The first is that temporal and spatial coherence decay very rapidly, which adversely affects time and distance correlations. The second is that the vibrations are strongly coupled to the heat bath of the bulk liquid, so thermal equilibrium is assured.

The spectrum of vibrational modes is delimited at the low-frequency end by  $l = 2$  and at the high-frequency end by the Debye cutoff,<sup>2</sup> which means that the total number of modes is equal to the number of degrees of freedom for vibration perpendicular to the surface of the drop, which in turn is equal to the number of molecules in the surface layer when motion due to internal modes of the molecules is neglected. If the effective surface area per molecule is written as  $\pi\sigma^2$ , the number of modes and the maximum value of  $l$  are given by

$$N_{\text{modes}} = 4r^2/\sigma^2 \quad (5)$$

and

$$N_{\text{modes}} = l_{\text{max}}(l_{\text{max}} - 1) \approx l_{\text{max}}^2 \quad (6)$$

The rms displacement and slope of the surface due to thermal motions are to be calculated by assigning to each mode an average energy  $k_B T$ , where  $k_B$  is Boltzmann's constant. For this purpose it is necessary to know the relationship between a displacement  $\zeta_{lm}$  and the resulting change in energy, as given by the change in surface area multiplied by the surface tension. This we now calculate.

The instantaneous effect of a surface vibration on an element of surface area is shown in Figure 1, where the original surface element  $r^2 \sin\theta d\theta d\phi$  of Figure 1a is seen, in Figure 1b, to be both expanded, because of the addition of  $\zeta$  to  $r$ , and tilted through the small angles  $\alpha_1$  and  $\alpha_2$ , which are given by

$$\alpha_1 = \partial\zeta/\partial\theta / (r + \zeta) \quad (7)$$

and

$$\alpha_2 = \partial\zeta/\partial\phi / \{(r + \zeta) \sin\theta\} \quad (8)$$

Hence for a single mode, after applying the cosine law twice and averaging  $\cos^2(\omega_{lm}t + \epsilon_{lm})$  over many cycles (or over many waves with random phases  $\epsilon_{lm}$ ), we obtain the change in energy

due to the change in surface area resulting from the displacement  $\xi_{lm}$  for mode  $l, m$  as

$$\delta E = \gamma \delta A$$

$$= 4\pi\gamma(\xi_{lm}^0)^2 \iint \left\{ (Y_{lm})^2 + \frac{1}{2} \left( \frac{\partial Y_{lm}}{\partial \theta} \right)^2 + \frac{1}{2\sin^2\theta} \left( \frac{\partial Y_{lm}}{\partial \phi} \right)^2 \right\} \sin\theta \, d\theta \, d\phi \quad (9)$$

where the ranges of integration are 0 to  $2\pi$  for  $\phi$  and 0 to  $\pi$  for  $\theta$ . Note that odd powers of the displacement integrate to zero over the surface of the sphere and are omitted. With the aid of the tabulated integral of  $(1-x^2)^{-1} \{P_l^m(x)\}^2 dx$  between  $-1$  and  $1$ ,<sup>14</sup> the third term immediately reduces to  $m(2l+1)/4$ . After a little more effort, the second term is found to be  $\{2l(l+1) - m(2l+1)\}/4$ . This last reduction involves application of the standard recursion formulas for associated Legendre polynomials and use of the result:

$$\int_{-1}^1 P_l^{m+1}(x) P_l^{m-1}(x) dx = \frac{-2}{2l+1} \frac{(l+m-1)!}{(l-m-1)!} \quad (10)$$

Hence we obtain finally

$$\delta E_{lm} = 2\pi\gamma(\xi_{lm}^0)^2(2 + l(l+1)) \approx 2\pi\gamma l(l+1)(\xi_{lm}^0)^2 \quad (11)$$

where the last approximation is generally a very good one, because the  $(2l+1)$ -fold degeneracy causes most modes to have large values of  $l$ , even for a very small droplet.

Thus the mean-square displacement for a single mode is

$$\langle \xi_{lm}^2 \rangle = k_B T / \{4\pi\gamma l(l+1)\} \quad (12)$$

To obtain the total rms displacement, the right-hand side has to be multiplied by  $2l+1$  and summed over  $l$  from 2 to  $l_{\max}$ . This can be done numerically if  $l_{\max}$  is not very large. For the usual situation with  $l_{\max} \gg 1$ , we can replace the sum by an integral over  $dl$  and obtain

$$\langle \xi^2 \rangle = (k_B T / 4\pi\gamma) \text{Ln}\{l_{\max}(l_{\max} + 1)/6\} \approx (k_B T / 4\pi\gamma) \text{Ln}\{2r^2/3\sigma^2\} \quad (13)$$

As is the case for a plane surface, this goes slowly to infinity as the area of the vibrating membrane tends to infinity, but here that area is well defined for any finite value of the drop radius.

The instantaneous slope of the surface due to a single mode is  $\tan \alpha_{lm}$ , where

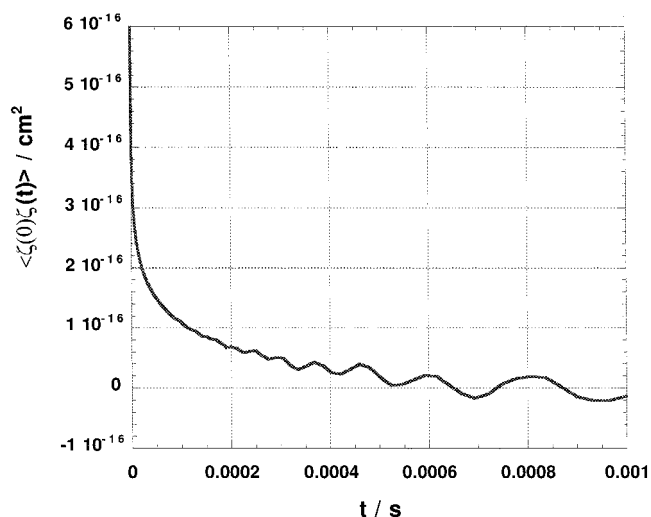
$$\alpha_{lm}^2 \approx \tan^2(\alpha_{lm}) = \alpha l^2 + \alpha 2^2 \quad (14)$$

Hence, after averaging  $\cos^2(\omega_{lm}t + \epsilon_{lm})$  over many cycles as before, we obtain

$$\alpha_{lm}^2 = (\xi_{lm}^0)^2 \left\{ \left( \frac{\partial Y_{lm}}{\partial \theta} \right)^2 + \frac{1}{\sin^2\theta} \left( \frac{\partial Y_{lm}}{\partial \phi} \right)^2 \right\} / 4r^2 \quad (15)$$

which gives the same value for the mean-square slope of every mode, namely:

$$\langle \tan^2 \alpha_{lm} \rangle = k_B T / (8\pi\gamma r^2) \quad (16)$$



**Figure 2.** Time dependence of  $\langle \xi(0)\xi(t) \rangle$  for a 1 mm radius water drop.

Multiplying eq 16 by  $N_{\text{modes}}$  gives

$$\langle \tan^2 \alpha \rangle = k_B T / 2\pi\gamma\sigma^2 \quad (17)$$

which is independent of the size of the drop.

For a water drop of radius 1 mm in free fall at 300 K, taking  $\sigma$  as  $2 \times 10^{-8}$  cm and  $\gamma$  as 73 dyne  $\text{cm}^{-1}$ , the calculated rms displacement and slope are  $3.7 \times 10^{-8}$  cm and  $25.4^\circ$ , respectively. These numbers are similar to values previously calculated for a plane water surface and for a drop.<sup>1,2,6</sup> The total number of modes is  $10^{14}$  and  $l_{\max}$  is  $10^7$ . For a  $1 \mu\text{m}$  droplet, the rms displacement is  $2.8 \times 10^{-8}$  cm, the rms slope is the same, the number of modes is  $10^8$ , and  $l_{\max}$  is  $10^4$ .

### Time, Distance, and Velocity Correlations

The damping factor  $\exp(-t/\tau_{lm})$  due to viscosity causes motions of the surface separated by time and distance to become uncorrelated while the mean-square values  $\langle \xi^2 \rangle$  and  $\langle \tan^2 \alpha \rangle$  remain constant. Consider first the instantaneous displacements  $\xi_{lm}(0)$  and  $\xi_{lm}(t)$  at the same location. On average,  $\xi_{lm}(t)$  will have a component  $\xi_{lm}(0) \cdot \exp(-t/\tau_{lm}) \cdot \cos(\omega_{lm}t + \epsilon_{lm})$  which is correlated with the displacement at time zero, where the unknown phase factor at time zero is  $\cos \epsilon_{lm}$ . The remainder of  $\xi_{lm}(t)$  will have random phase and so will average to zero when multiplied by  $\xi_{lm}(0)$ . Hence, using

$$\cos(\omega_{lm}t + \epsilon_{lm}) \cdot \cos \epsilon_{lm} = \{(\cos(\omega_{lm}t + 2\epsilon_{lm}) + \cos \omega_{lm}t)\} / 2 \quad (18)$$

and observing that the presence of the random phase  $\epsilon_{lm}$  causes the first term on the right-hand side of eq 18 to average to zero, we can write

$$\langle \xi_{lm}(0)\xi_{lm}(t) \rangle = \langle \xi_{lm}^2(0) \rangle \exp(-t/\tau_{lm}) \cos \omega_{lm}t \quad (19)$$

which has the correct limiting value when  $t$  goes to zero. The presence of the cosine term ultimately depends on the time between interactions with the heat bath being longer than  $\tau_{lm}$ , so eq 19 really represents a special case. For a fuller derivation of eq 19, see Appendix. In practice, setting the cosine factor equal to unity has negligible effect on  $\langle \xi(0)\xi(t) \rangle$  except at very long times. To obtain  $\langle \xi(0)\xi(t) \rangle$ , the right-hand side of eq 19 is averaged over all the modes  $l, m$  by numerical integration. Figure 2 shows the result of doing this for a water drop of radius 1

mm. Interesting but probably unobservable oscillatory behavior, arising from the noncancellation and slow damping of low-frequency cosine factors, is apparent at the longest times.

The correlation function  $\langle \zeta_{lm}(0)\zeta_{lm}(x) \rangle$ , where  $x$  is a spatial separation, can be calculated by essentially the same method. The distance  $x$  is related to a time  $t$  through the wave propagation velocity  $c$ , which is the product of the frequency given by eq 3a and the wavelength, defined as twice the distance between nodes, when measured around a great circle on the drop. There is a slight complication here, in that for a given mode the number of nodes is a function of direction, there being  $l - |m|$  nodes parallel to the equator and  $|m|$  nodes perpendicular to the equator.<sup>15</sup> so for a mode  $l, m$  we write the wavelength as  $2\pi r/k$ , where  $k^2 = (l - |m|)^2 + m^2$ , and the propagation speed is given by

$$c_{lm} = \{l(l-1)(l+2)\gamma/k^2\rho r\}^{1/2} \quad (20)$$

The time correlation function is independent of location, so

$$\langle \zeta_{lm}(0)\zeta_{lm}(x) \rangle = \langle \zeta_{lm}(0)\zeta_{lm}(t) \rangle \quad (21)$$

with  $t$  set equal to  $x/c_{lm}$ , and the global average  $\langle \zeta(0)\zeta(x) \rangle$  is obtained by numerical integration as before.

The instantaneous vertical velocity  $u_{lm}$  at some location, due to a single mode  $l, m$ , is given by

$$u_{lm} = d\zeta_{lm}(\omega_{lm}t + \epsilon_{lm})/dt = \omega_{lm}\zeta_{lm}(\omega_{lm}t + \epsilon_{lm} + \pi/2) = \omega_{lm}\zeta_{lm}(\omega_{lm}t + \kappa_{lm}) \quad (22)$$

where the change of  $\cos(\omega_{lm}t + \epsilon_{lm})$  to  $-\sin(\omega_{lm}t + \epsilon_{lm})$  on differentiating is replaced by a  $\pi/2$  phase shift, and  $\kappa_{lm} = \epsilon_{lm} + \pi/2$  is an unknown phase angle with exactly the same statistical properties as  $\epsilon_{lm}$ . Hence the time and distance correlation functions for vertical velocity are given by

$$\langle u_{lm}(0)u_{lm}(t) \rangle = \omega_{lm}^2 \langle \zeta_{lm}(0)\zeta_{lm}(t) \rangle \quad (23)$$

and

$$\langle u_{lm}(0)u_{lm}(x) \rangle = \langle u_{lm}(0)u_{lm}(t) \rangle \quad (24)$$

with  $t = x/c_{lm}$ .

To obtain the rms height separation and the relative velocity between two locations a distance  $x$  apart, we use the result<sup>6</sup>

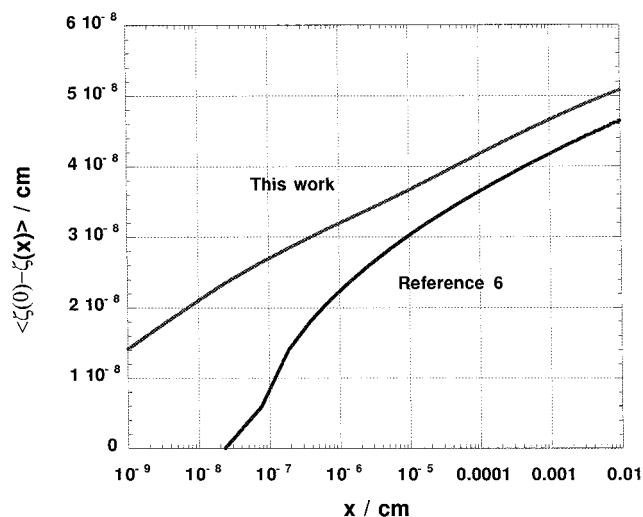
$$\begin{aligned} \langle \{\zeta_{lm}(0) - \zeta_{lm}(x)\}^2 \rangle &= \langle \zeta_{lm}(0)^2 + \zeta_{lm}(x)^2 - 2\zeta_{lm}(0)\zeta_{lm}(x) \rangle \\ &= 2\{\langle \zeta_{lm}^2 \rangle - \langle \zeta_{lm}(0)\zeta_{lm}(x) \rangle\} \end{aligned} \quad (25)$$

and similarly

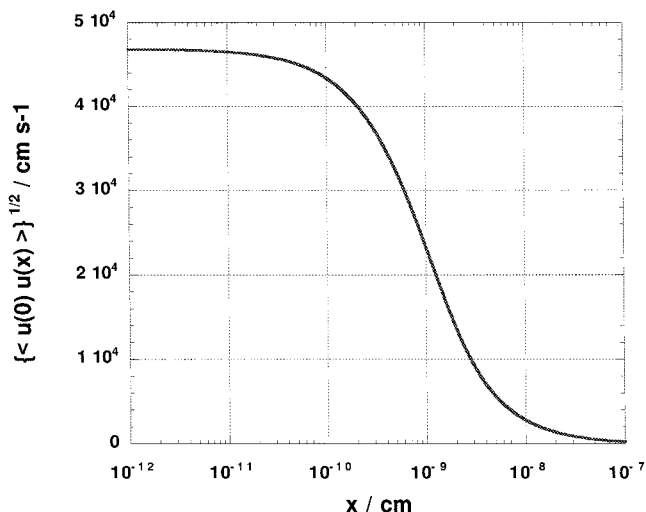
$$\begin{aligned} \langle \{u_{lm}(0) - u_{lm}(x)\}^2 \rangle &= \langle u_{lm}(0)^2 + u_{lm}(x)^2 - 2u_{lm}(0)u_{lm}(x) \rangle \\ &= 2\omega_{lm}^2\{\langle \zeta_{lm}^2 \rangle - \langle \zeta_{lm}(0)\zeta_{lm}(x) \rangle\} \end{aligned} \quad (26)$$

which can be integrated numerically over  $l$  as before to give  $\langle \{\zeta(0) - \zeta(x)\}^2 \rangle$  and  $\langle \{u(0) - u(x)\}^2 \rangle$ .

Calculated values of  $\langle \zeta(0) - \zeta(x) \rangle_{\text{rms}}$  for a water drop of radius 1 mm are plotted in Figure 3. Simpson and Rowlen<sup>6</sup> used the ansatz that  $\langle \zeta(0)\zeta(x) \rangle$  was set equal to the value of  $\langle \zeta^2 \rangle$  as calculated without any contribution from modes having wavelengths shorter than  $x$ ; results obtained by their method are also plotted in Figure 3. There is fair agreement between the two curves for large values of  $x$ , but the ansatz predicts a too rapid falloff at very small values of  $x$ .



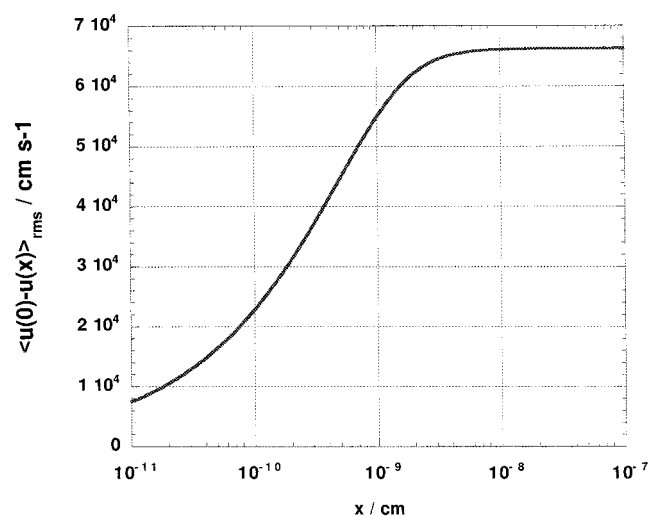
**Figure 3.** Comparison of  $\langle \zeta(0)\zeta(x) \rangle_{\text{rms}}$  values for a 1 mm radius water drop, as calculated from equations 19 and 21 and by the method of ref 6.



**Figure 4.** Values of  $\langle u(0)u(x) \rangle_{\text{rms}}$  plotted against distance for a drop of radius 1 mm.

The presence of the  $\omega_{lm}^2$  factor in eqs 23 and 26 causes values of  $\zeta_{lm}^2$  for large values of  $l$  to be weighted very heavily, so that the velocity correlation functions attain their final values at very short times or distances. This is shown in Figure 4, where  $\langle u(0) \cdot u(x) \rangle_{\text{rms}}$  is plotted against distance, and in Figure 5, where  $\langle u(0) - u(x) \rangle_{\text{rms}}$  is plotted against distance, for a drop of radius 1 mm. The value of  $\langle u(0) - u(t) \rangle_{\text{rms}}$  becomes constant for times  $t$  greater than about 10 ps, and  $\langle u(0) - u(x) \rangle_{\text{rms}}$  becomes constant for distances greater than about 0.1 nm. At such short distances the continuum model that we are using must break down, but the conclusion that  $\langle u(0) - u(x) \rangle_{\text{rms}}$  attains a constant, limiting value is unaffected by such a breakdown and is also unaffected by whether the cosine factor is included in eq 19. The magnitude of the limiting value, which is equal to the rms value of  $u(0)$  times  $2^{1/2}$  because  $\langle u(0)u(x) \rangle_{\text{rms}}$  goes to zero at large  $x$ , depends on the surface area per molecule but not on the drop radius. This can best be seen from the examples in Table 1, which includes values of the rms slope and displacement of a water surface for various combinations of  $r$  and  $\sigma$ . The rate at which the limiting value is attained is also independent of drop size. The striking inverse dependence of  $\langle u(0) - u(x) \rangle_{\text{rms}}$  on  $\sigma$ , shown in Table 1, is a consequence of the increasing roughness of the





**Figure 5.** Values of  $\langle u(0) - u(x) \rangle_{\text{rms}}$  plotted against distance for a drop of radius 1 mm.

**TABLE 1: Root-Mean-Square Displacement  $\zeta$ ,  $\alpha = \tan^{-1}(\text{rms slope})$ , and Limiting Value of the Root-Mean-Square Velocity Difference  $u(0) - u(x)$  at Large  $x$ , versus  $\sigma$  and  $r$**

$10^8 \sigma / \text{cm}$	$r / \text{cm}$	$10^8 \langle \zeta \rangle / \text{cm}$	$\alpha$ (degrees)	$\langle u(0) - u(x) \rangle / \text{ms}^{-1}$
1	1	4.06	43.5	1875
1	.1	3.79	43.5	1875
1	.01	3.58	43.5	1875
1	.001	3.20	43.5	1875
1	.0001	2.85	43.5	1875
2	1	3.98	25.4	663
2	.1	3.71	25.4	663
2	.01	3.42	25.4	663
2	.001	3.10	25.4	663
2	.0001	2.74	25.4	663
3	1	3.93	17.6	361
3	.1	3.66	17.6	361
3	.01	3.36	17.6	361
3	.001	3.04	17.6	361
3	.0001	2.67	17.6	361
4	1	3.90	13.4	234
4	.1	3.62	13.4	234
4	.01	3.32	13.4	234
4	.001	2.99	13.4	234
4	.0001	2.62	13.4	234

surface with decreasing  $\sigma$ . When  $\sigma$  is reduced, the waves become higher and steeper and  $\langle u(0) - u(x) \rangle_{\text{rms}}$  becomes correspondingly larger.

### Rate of Exchange between the Surface and Interior of a Drop

In an earlier paper<sup>4</sup> we presented a simple calculation of the rate at which a surface molecule would become engulfed by the bulk liquid as a consequence of concerted motions of the surface. We are now in a position to take this calculation a little further on the basis of the observation that the quantity  $\langle u(0) - u(x) \rangle$  rapidly attains a constant, nonzero value with increasing  $x$ , as shown in Figure 5.

In a well-known elementary derivation of the transition-state theory expression for the rate constant of a reaction, one degree of freedom of the reacting system is designated the reaction coordinate, and the rate of reaction is set equal to the concentration of an activated complex multiplied by the average velocity of its motion along this coordinate, divided by a distance  $\delta$  which is deemed to correspond to the critical region, or transition state. Subsequently, the quantity  $\delta$  cancels with a

factor in the translational partition function for the reaction coordinate, and the final outcome is that motion along the reaction coordinate contributes a factor  $k_B T/h$  to the rate constant. The rate constant of a unimolecular reaction is often written as  $(k_B T/h) \exp(-\Delta G^*/RT)$ , and the factor  $k_B T/h$  is then regarded as the actual frequency of decomposition of the activated complex into products.

More refined versions of transition-state theory obtain the  $k_B T/h$  factor by a procedure which avoids introducing the quantity  $\delta$ . Instead, the "transition state" is reduced to a limiting hyperplane in phase space, such that trajectories which cross this plane never return to the reactant side. Such a critical plane has zero thickness in the direction of the reaction coordinate. However, for a reaction in which an activation barrier has to be crossed, the top of the barrier is, by definition, flat, the Heisenberg uncertainty principle requires the top of the barrier to have a nonzero length, measured along the direction of the reaction coordinate, and we are free to call this length  $\delta$  if we wish. Then, if motion along some actual physical coordinate in ordinary space can be identified with motion along the reaction coordinate, a comparison of the physically observable velocity  $u^*$  with  $k_B T/h$  should provide an interesting estimate of the size of the region  $\delta$ . This is the approach that we shall follow here, setting  $k_B T/h$  equal to  $u^*/\delta$ , where  $u^*$  is the velocity with which a molecule penetrates below the surface layer. The quantities  $k_B T/h$  and  $u^*/\delta$  are not rigorously the same, but they probably differ only by a factor of order unity, and this procedure for estimating  $\delta$  should be just as valid and informative as the commonly accepted practice of discussing "abnormal" pre-exponential factors for unimolecular reactions in terms of unusual values of the entropy of activation  $\Delta S^*$ .

Extensive experimental work by Davidovitz and colleagues<sup>10</sup> has established the existence of a free energy barrier to accommodation of an adsorbed molecule into the interior of a liquid drop. Such a barrier also appears in the numerical simulations of the transfer of slightly soluble gases across the gas-liquid interface by Lyndon-Bell and co-workers.<sup>16</sup> The barrier can be visualized as arising because entropy decreases more rapidly than enthalpy as a molecule moves from the surface to the interior of the liquid.<sup>4</sup> Because a molecule's coordination number increases rapidly as the molecule moves below the surface, the location of the barrier is probably quite close to the surface. Therefore the speed of crossing the barrier can tentatively be identified with the difference in velocity  $\langle u(0) - u(x) \rangle_{\text{rms}}$  for a surface molecule, averaged over the locations of the surrounding surface molecules, and this speed can be divided by  $k_B T/h$  in order to estimate  $\delta$ . Note that this identification is not affected by the existence of any force arising from the free energy of interaction between the surface molecules and the bulk liquid, because the force of attraction or repulsion must go to zero at the top of the barrier, where the free-energy gradient is zero.

The sign of  $\langle u(0) - u(x) \rangle_{\text{rms}}$  can be positive or negative; this ensures detailed balance but does not affect the magnitude of  $\langle u(0) - u(x) \rangle_{\text{rms}}$ . When the velocity difference is averaged over the six surrounding molecules, the mean value of zero is unchanged but the quantity  $\langle \{u(0) - u(x)\}^2 \rangle$  is reduced by a factor of 6. Hence we obtain

$$u^* \approx \langle u(0) - u(x) \rangle_{\text{rms}} / (6)^{1/2} \quad (27)$$

Dividing this value of  $u^*$  by  $k_B T/h$  gives the values of  $\delta$  shown in Table 2. The general magnitude of the  $\delta$  values appears very reasonable, and their variation with  $\sigma$  is quite informative. The marked increase in  $\delta$  as  $\sigma$  decreases appears to be a further

**TABLE 2:  $\delta$  Values Calculated for Several Values of  $\sigma$** 

$\sigma / \text{\AA}$	$\delta / \text{\AA}$
1	1.23
2	0.433
3	0.236
4	0.153

consequence of the increased roughness of the surface when  $\sigma$  is small: when the surface becomes rougher, a molecule has to dive deeper in order to escape from the surface motion. This effect becomes even more striking when  $\delta$  is considered as a fraction of  $\sigma$ .

The random motion of the surface molecules of a liquid has much in common with the random motion of an ensemble of reactive systems on a potential energy surface, and in principle it should be possible to obtain an estimate of the physical size of the region  $\delta$  for any reactive system. Comparison of such estimates for different systems might provide interesting insight into the reaction dynamics.

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## Appendix: Derivation of Equation 19

We consider the local displacement  $\zeta(t)$ , due to an individual mode  $l, m$  of frequency  $\omega$ , as being the result of successive delta-function interactions with the subsurface heat bath at times  $t_i$  in the past, and write

$$\zeta(t) = \int_{-\infty}^t \zeta_i^0 e^{-(t-t_i)/\tau} \cos\{\omega(t-t_i) + \epsilon_i\} dt_i \quad (\text{A1})$$

where each impact contributes its own amplitude  $\zeta_i^0$  and phase shift  $\epsilon_i$ . The product  $\zeta(0)\zeta(t)$  can be written as

$$\zeta(0)\zeta(t) = e^{-t/\tau} \int_{-\infty}^0 \int_{-\infty}^t \zeta_j^0 \zeta_i^0 e^{(t_j+t_i)/\tau} x_j \{x_i \cos \omega t + y_i \sin \omega t\} dt_i dt_j \quad (\text{A2})$$

where  $x_i$  stands for  $\cos(\omega t_i - \epsilon_i)$  and  $y_i$  stands for  $-\sin(\omega t_i +$

$\epsilon_i)$ . At time  $t = 0$  eq A2 becomes

$$\zeta(0)^2 = \int_{-\infty}^0 \int_{-\infty}^0 \zeta_j^0 \zeta_i^0 e^{(t_j+t_i)/\tau} x_j x_i dt_i dt_j \quad (\text{A3})$$

which can, in principle, be averaged over the surface of the sphere to give  $\langle \zeta_{lm}^2 \rangle$ . At very short times we can ignore the  $\sin \omega t$  term in A2, and take the  $\cos \omega t$  term outside the integral, which gives eq 19. To obtain a more general result, we can divide the integral from minus infinity to  $t$  in A2 into two ranges, and so obtain

$$\zeta(0)\zeta(t) = e^{-t/\tau} [\zeta(0)^2 + \int_{-\infty}^0 \int_0^t \zeta_j^0 \zeta_i^0 e^{(t_j+t_i)/\tau} x_j \{x_i \cos \omega t + y_i \sin \omega t\} dt_i dt_j] \quad (\text{A4})$$

where the presence of the random quantities  $x_i$  and  $x_j$  in the integrals ensures that the second term in the bracket very quickly averages to zero.

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