Effect of Ultrasonic Waves on Mass Transfer Rates of Selected Fluids

H. SCOTT FOGLER and KLAUS D. TIMMERHAUS
University of Colorado, Boulder, Colorado

The application of ultrasonic energy to a fluid in a capillary has resulted in greatly increased rates of mass transfer (of the order of 800 to 2,000% above that without insonation) to occur at specific heights in the capillary. Reproducible results with several selected fluids (carbon tetrachloride, acetone, ethanol, and methanol) have shown that these specific heights are always at the half wavelengths of the particular fluid investigated. The mathematical model developed herein predicts that at these half wavelengths, the fluid particle displacement of the ultrasonic wave becomes quite large, exceeds the threshold value necessary for the stability of the surface waves, and causes droplets to be ejected into the vapor above the surface in the form of a fog. The resulting decrease in the diffusional path length of the ejected fluid provides the final mechanism for an increased mass transfer from the capillary tube.

The application of ultrasonics to chemical processes has received considerable attention in recent years. Such applications include precipitation of corrosive aerosols, drying of heat-sensitive materials, increasing of chemical reaction rates of certain chemical reactions, and increasing of heat transfer coefficients in specific gas-solid systems. In most of these examples, the ultrasonic waves were applied to the gas phase; however, in the work reported here, the ultrasonic waves were applied directly to the liquid phase in an attempt to determine their effects on the rate of mass transfer.

Preliminary investigations were carried out with an ultrasonic cleaner as the wave source. These waves were transmitted from the cleaner through a coupling fluid to a constant temperature bath that contained a vertical capillary. The liquids studied were placed in the capillary and their rate of mass transfer was obtained by measuring the height of the gas-liquid interface with a cathetometer as a function of time. The ultrasonic cleaner could not be varied in frequency or output power. This deficiency was rectified ultimately by the design and construction of an ultrasonic wave generator that could be varied in both frequency and intensity.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The basic electrical circuit is shown in Figure 1. The oscillator transmits a signal of between 0 and 20 v. to the amplifier. Here the signal is amplified and the proper phase relationship between the current and voltage is obtained by a careful adjustment of the bias, frequency, and liquid level in the crystal tray. Probes are attached to the cable which leads directly to the crystal. This permits monitoring of the voltage, current, and phase relationship between the voltage and current quantities on an oscilloscope. The maximum output power of the crystal in this arrangement is about 12 w. The lead zirconate piezoelectric crystal used in this research operates at a frequency of about 100 kilocycles/sec. The crystal is epoxied to the lower surface of a thin 0.008-in. stainless steel tray that supports the coupling fluid. The lower side of the crystal is exposed to the atmosphere to avoid unnecessary constraints on the crystal. The tray to which the crystal is cemented is ¼-in. × 4-in. × 6-in. A wooden box gives support around the edges.

Figure 2 shows the arrangement of the glass capillary tube and the associated measuring equipment with respect to the crystal. The liquid to be studied is placed in the bottom segment of the capillary tube, 1.5 mm. I.D. and 5 cm. in length; the latter is attached to a horizontal section of glass capillary tubing of the same dimensions as the vertical tube. Dry air is blown through this horizontal glass tubing and across the capillary junction to maintain essentially a zero concentration of the evaporating liquid at this junction. A small vertical tube extends 2 cm. above the junction of the bottom capillary tube and the horizontal glass tubing. This extension permits filling the capillary tube with the fluid under investigation by inserting a 0.5 mm. O.D. intramedic tubing, which is attached to a hypodermic syringe, into the capillary tube.

The seal at the lower end of the capillary tube was ground to a thin flat membrane. During experimental runs, this flat portion of the capillary was positioned within 1 mm. of the stainless steel tray surface. Operating characteristics of the crystal were impaired whenever the bottom of the capillary accidentally touched the tray surface. The micrometer with the needle point, shown to the left of the figure, was used to measure the liquid level of the coupling fluid, which was water in all cases. This coupling fluid level was maintained at a constant height during the course of a run by spreading a layer of dodecyl alcohol on the surface of the coupling fluid to cut down on evaporation losses. Since the height of the coupling fluid in the tray seriously affects the electrical impedance of the crystal, careful adjustments were necessary—simultaneously with the frequency adjustment—until the proper phase relationship between voltage and current was obtained.

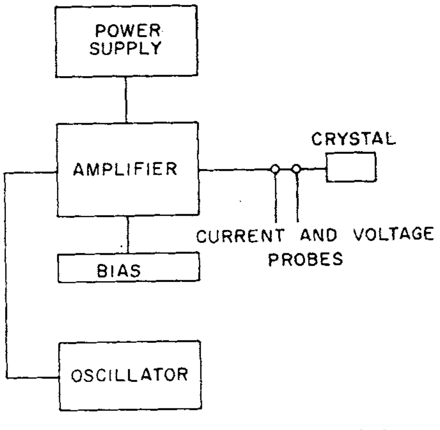

Fig. 1. Schematic diagram of electrical circuit.

H. Scott Fogler is with the University of Michigan, Ann Arbor, Michigan.

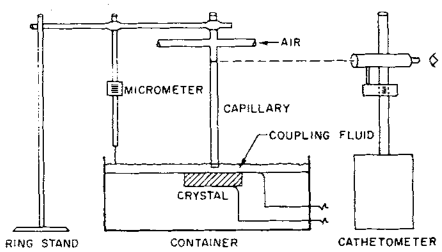

Fig. 2. Schematic diagram of apparatus.

EXPERIMENTAL RESULTS

The rate of mass transfer was determined by measuring the rate of fall of the gas-liquid interface in the capillary. This was done with a cathetometer and an electric timer. The height of the interface, voltage, current, and phase relationship between the voltage and current were recorded at various time increments. The frequency of the ultrasonic wave was fixed at 99 kilocycles/sec. When no insonation was applied to the experimental system, normal diffusion occurred in the capillary and the interface level receded at a rate predicted by the well-known diffusion equations. When insonation was applied to the system, however, the interface level first fell at a rate approximately equal to that when no insonation was applied. Then a point was reached at which a sudden surge in evaporation occurred and the level dropped very rapidly during an approximate time interval of 5 to 30 sec. After this, the level again decreased to a rate approximately equal to that when no insonation was applied, until the next point of sudden increase was reached. These points of sudden increase occurred at regularly spaced intervals down the capillary tube. When the distance between these intervals was evaluated, it was found to be equal to one-half the wavelength of the standing wave in the capillary column. That is, as the height of the liquid level fell in the capillary, sudden increases in the rate of mass transfer occurred at integral half wavelengths, while no apparent increase in rate was observed between these half nodes. The term half-node refers to the point corresponding to the half wavelength distance in the capillary and also where the sudden evaporation takes place. Various liquids such as benzene, ethanol, methanol, carbon tetrachloride, and acetone were studied; all yielded the same result. The results of these studies are shown in Table 1. The experimental values of the half wavelength were determined by measuring the distances between the large increases in mass transfer. The first value indicates the experimental value obtained for the first pair of points of rapid mass transfer, while the second value represents the experimental value as determined from the next successive pair of points in the capillary. At the half-nodes, it was difficult to measure the mass transfer rate precisely, since the interface level fell so rapidly. The rate of mass transfer observed at these half-nodes showed an increase of 800 to 2,000% over the rate observed between the nodes. Figures 3 and 4 show a plot of the rate of fall of the gas-liquid interface (mm./unit time) vs. the depth of the interface in the capillary measured from the junction of the capillary tube and the horizontal glass tubing for carbon tetrachloride and acetone, respectively. The distance between the peaks was equal to the half wavelength in the liquid. At the half-nodes where the surges in mass transfer occurred, violent fogging was noted and small droplets of the fluid under investigation could be observed shooting up in a fountain effect above the surface.

SOLUTION TO THE ONE-DIMENSIONAL WAVE EQUATION

The fact that the increase in mass transfer occurs at integral half wavelengths suggests some sort of resonance phenomena. The wave reinforces itself at these half-nodes and large particle displacements and particle velocities are obtained at the gas-liquid interface. This can be shown by solving the wave equation for the particle displacement at the gas-liquid interface. Since the thickness of the ground

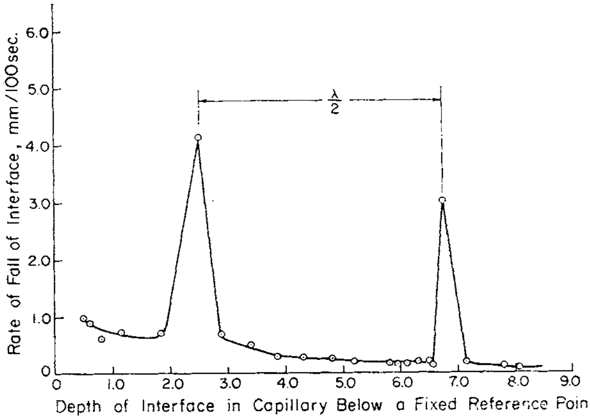

Fig. 3. Rate of mass transfer with insonation as a function of liquid level in the capillary tube for carbon tetrachloride.

TABLE 1. EXPERIMENTAL VALUES OF HALF WAVELENGTHS

Liquid	Run	Theoretical values of the half wavelength in the fluid λ/2, cm.	Experimentally determined values of the half wavelength in the fluid λ/2, cm.	λ/2, cm.	Voltage, v.	Current, amp.	Maximum % error
Methanol	1	0.562	0.555		250	0.0270	1.2
	2		0.565		225	0.0265	0.5
	3		0.535		325	0.0230	5.0
	4		0.555		430	0.0180	1.2
Benzene	5	0.625	0.630		400	0.0120	0.8
Carbon tetrachloride	6	0.468	0.465	0.465	270	0.0210	0.6
			0.460				1.7
	7		0.455		128	0.0530	3.0
	8		0.468		220	0.0690	0.0
Acetone	9	0.593	0.600	0.600	375	0.0840	1.2
	10		0.605		160	0.0420	2.0

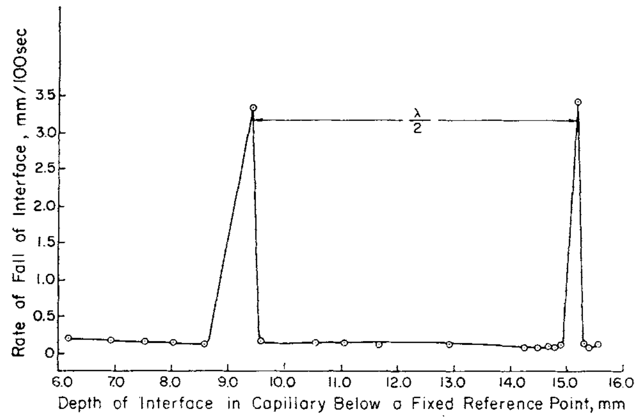

Fig. 4. Rate of mass transfer with insonation as a function of liquid level in the capillary tube for acetone.

bottom surface of the glass capillary and the distance between the bottom of the glass capillary and the oscillating surface of the crystal are quite small (on the order of 0.8 mm.), the equations can be derived by assuming that the crystal transmits directly to the liquid in the capillary. In the liquids studied, the attenuation coefficient for the ultrasonic wave in the liquid is extremely small (for example, for acetone $\alpha = 3 \times 10^{-5}$ nepers/cm.). The liquid is regarded therefore to be nonabsorbing and the ultrasonic wave is assumed to be undamped. Under these conditions the wave equation takes the form (*1*)

$$\frac{\partial^2\epsilon}{\partial t^2} = c^2\frac{\partial^2\epsilon}{\partial y^2} \tag{1}$$

The boundary conditions of this second-order partial differential equation are given in terms of the excess pressure, as defined by (2)

$$P = -c^2\rho_o\frac{\partial\epsilon}{\partial y} \tag{2}$$

P is the excess pressure produced by compression of fluid particles. At the gas-liquid interface, this excess pressure is zero. The crystal is oscillating at a frequency of 99 kilocycles/sec. and the particle displacement at the liquid-crystal surface varies as the cosine of ωt.

At zero time the fluid particle velocity will be taken as zero, and the fluid particle displacement at the crystal surface will be ϵ^*. These boundary conditions can be expressed in the following manner:

$$\begin{aligned} &t = 0, \ \frac{\partial\epsilon}{\partial t} = 0 \ \text{for}\ y > 0 \\ &t = 0, \ \epsilon = \epsilon^* \ \ y = 0 \\ &y = 0 \ \ \epsilon = \epsilon^* \cos\omega t \ \text{for}\ t > 0 \\ &y = l \ \ P = 0 \ \text{for}\ t > 0 \end{aligned} \tag{3}$$

The wave equation can be solved by the separation of variables technique. Let

$$\epsilon(y, t) = Y(y)\,\hat{T}(t) \tag{4}$$

$$c^2 Y''\hat{T} = Y\hat{T}'' \tag{5}$$

$$\epsilon = \left(E\sin\frac{\bar{\mu}}{c}y + N\cos\frac{\bar{\mu}}{c}y\right)(F\cos\bar{\mu}t + D\sin\bar{\mu}t) \tag{6}$$

The velocity can be obtained from Equation (6) by differentiating ϵ with respect to time.

$$\frac{\partial\epsilon}{\partial t} = \bar{\mu}\left(E\sin\frac{\bar{\mu}}{c}y + N\cos\frac{\bar{\mu}}{c}y\right)(-F\sin\bar{\mu}t + D\cos\bar{\mu}t) \tag{7}$$

At $t = 0$, $\partial\epsilon/\partial t = 0$ for all y; thus, $D = 0$. Now let $A = E \cdot F$ and $B = N \cdot F$; then from Equation (6)

$$\epsilon = \left(A\sin\frac{\bar{\mu}}{c}y + B\cos\frac{\bar{\mu}}{c}y\right)\cos\bar{\mu}t \tag{8}$$

At the crystal surface, $y = 0$.

$$\epsilon^*\cos\omega t = B\cos\bar{\mu}t \tag{9}$$

Therefore

$$B = \epsilon^*, \bar{\mu} = \omega, k_u = \omega/c = 2\pi/\lambda_u$$

The excess pressure is found by differentiating ϵ with respect to y, and multiplying the resulting expression by $-\rho_o c^2$ as indicated by Equation (2).

$$P = -\rho_o c^2\frac{\partial\epsilon}{\partial y} = -\rho c^2(A\cos k_u y - \epsilon^*\sin k_u y)k_u\cos\omega t \tag{10}$$

At the gas-liquid interface, $y = l$

$$P = 0 = -\rho_o c^2 k_u\,(A\cos k_u l - \epsilon^*\sin k_u l)\cos\omega t \tag{11}$$

Since Equation (11) must be true at any time, the expression enclosed in the parenthesis must be equal to zero. Therefore

$$A = \epsilon^*\frac{\sin k_u l}{\cos k_u l} \tag{12}$$

The following equation thus gives the fluid particle displacement as a function of time and vertical distance above the crystal surface.

$$\epsilon = \epsilon^*\left[\frac{\sin k_u l\sin k_u y + \cos k_u l\cos k_u y}{\cos k_u l}\right]\cos\omega t \tag{13}$$

Let $\epsilon_o = \epsilon^*\cos\omega t$ where ϵ_o represents the oscillatory fluid particle at the crystal surface.

$$\epsilon = \epsilon_o\left[\frac{\sin k_u l\sin k_u y + \cos k_u l\cos k_u y}{\cos k_u l}\right] \tag{14}$$

At the gas-liquid interface, that is, at $y = l$

$$\frac{\epsilon}{\epsilon_o} = \frac{1}{\cos k_u l} \tag{15}$$

As the liquid in the capillary evaporates, the height of the interface l above the crystal is continually changing. The absolute value of the ratio ϵ/ϵ_o is plotted as a function of the ratio l/λ_u in Figure 5. The height of the interface is divided by the wavelength on this plot so that it may apply to any, rather than to one specific, liquid studied. As $\cos k_u l$ approaches zero, the ratio ϵ/ϵ_o tends toward infinity. This occurs when

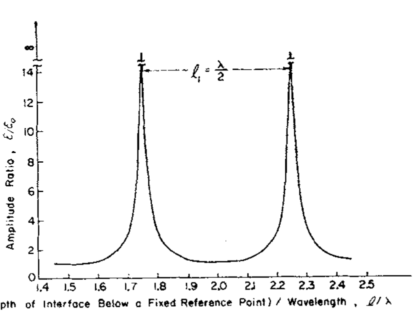

Fig. 5. Theoretical values of particle displacement amplitude ratio as a function of depth of gas-liquid interface in capillary.

$$k_u l = \left[\frac{2n+1}{2} \right] \pi \quad n = 1, 2, 3, \ldots \tag{16}$$

or

$$l = \frac{n}{2} \lambda_u + \frac{\lambda_u}{4} \tag{17}$$

Thus at integral half wavelengths, the fluid particle displacement at the gas-liquid interface becomes infinite for the case of the undamped wave. For the damped wave the fluid particle displacement can be shown to be finite but quite large. A comparison of Figures 3 and 4 with Figure 5 shows that the large experimental increase in mass transfer with observed acoustical fogging occur at integral half wavelengths in the same manner as that predicted by the above theory for the particle displacements at the interface.

EQUATION FOR THE SURFACE WAVES

A mechanism for this acoustical fogging at integral half wavelengths can be described by considering the hydrodynamics of a free surface. Faraday was one of the first to observe that horizontal waves were produced on the liquid surface in a cylindrical vessel by applying vertical oscillations to the bottom of the vessel (3). In discussing the equations describing these waves, we assume that the fluid is incompressible, that the flow is irrotational, and that a rough approximation to small viscous dissipative forces can be made. Euler's equation for an inviscid fluid, which is developed in numerous texts, can be expressed in the form (*4, 5*)

$$\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = \sum F_i \tag{18}$$

By applying this momentum balance to the forces involved here, the following expression is obtained:

$$\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = -\frac{1}{\rho} \frac{\partial p}{\partial x_i} + X_i - \epsilon_i \omega^2 \cos \omega t \tag{19}$$

The last term of Equation (19) represents the oscillatory force on the surface layer produced by the ultrasonic waves. Since the flow is irrotational and incompressible

$$u_i = -\frac{\partial \phi}{\partial x_i} \tag{20}$$

and

$$\nabla^2 \phi = 0 \tag{21}$$

The small viscous forces involved will be incorporated in the term representing the body forces.

$$X_i = \frac{f_i}{\rho} - g \tag{22}$$

If it is assumed that the deviation of any fluid particle from the state of uniform flow is resisted by a force proportional to the velocity and viscosity, then

$$f_i = -C_o \mu u_i \tag{23}$$

This was first proposed by Lamb (*6*) and later modified by Eisenmenger (*7*). The latter indicated that this approximation for viscous damping for surface waves is obeyed best when

$$C_o \cong (2k)^2 \tag{24}$$

This law is not an altogether natural one, but it serves to represent approximately the effect of small dissipative forces, without interfering with the irrotational character of the motion. By replacing the velocities with the gradients of the velocity potential and combining Equations (19) through (24), we obtain the following expression.

$$-\frac{\partial}{\partial x_i}\left(\frac{\partial \phi}{\partial t}\right) + \frac{1}{2}\frac{\partial}{\partial x_i}(u_j u_j) = -\frac{\partial}{\partial x_i}\left(\frac{p}{\rho}\right) - \frac{\partial}{\partial x_i}(x_2 g) + \frac{4k^2\mu}{\rho}\frac{\partial \phi}{\partial x_i} - \frac{\partial}{\partial x_i}(x_2 \epsilon_i \omega^2 \cos \omega t) \tag{25}$$

This expression can be integrated with respect to x_i and the constant of integration (which can be a function of time) set equal to zero (*8*). The fluid particle velocities are indeed quite small, estimated to be the order of 0.13 ft./sec. (*9*), in comparison with the other terms; therefore the square of these terms can be neglected. The effect of gravity on low-amplitude high-frequency surface also is quite small (*7*) and can be neglected. With these operations and modifications Equation (25) reduces to

$$-\frac{\partial \phi}{\partial t} - \frac{4k^2\mu\phi}{\rho} + y\, \epsilon_i \omega^2 \cos \omega t + \frac{p}{\rho} = 0 \tag{26}$$

The solution to Equation (26) is aided by the following conditions, definitions, and substitutions. Once a particle is on the surface it remains on the surface. For this particle on the surface one can write

$$y = \eta(x, t) \tag{27}$$

The inside pressure on the surface is the negative product of the surface tension and the reciprocal curvature of the surface

$$p = -T \frac{\partial^2 \eta}{\partial x^2} \tag{28}$$

Equation (26) now takes the form

$$-\frac{\partial \phi}{\partial t} - \frac{4k^2\mu\phi}{\rho} + \eta\, \epsilon_i \omega^2 \cos \omega t - \frac{T}{\rho}\frac{\partial^2 \eta}{\partial x^2} = 0 \tag{29}$$

Since the velocity amplitude of the surface wave should decrease in the liquid as one moves away from the interface and as surface waves are produced in the x coordinate direction, the following start is made for the solutions to Equations (21) and (29). The amplitude of the surface wave consists of a time-dependent part and a coordinate part, while the velocity potential consists of a time-dependent part and two coordinate dependent parts.

$$\phi = R\phi^*(t)\, e^{k(y-l)} \cos kx \tag{30}$$

$$\eta = b\, \eta^*(t) \cos kx \tag{31}$$

By substituting Equations (30) and (31) into Equation (29), along with the condition at the liquid surface that the time rate of change of the amplitude of the surface wave is equal to the vertical component of velocity, that is

$$\frac{\partial \eta}{\partial t} = v = -\frac{\partial \phi}{\partial y} = -\phi k \tag{32}$$

we obtain

$$\frac{\partial^2 \eta^*}{\partial t^2} + \frac{4k^2\mu}{\rho}\frac{\partial \eta^*}{\partial t} + \left(\frac{Tk^3}{\rho} + \epsilon_i \omega^2 k \cos \omega \mathrm{t} \right) \eta^* = 0 \tag{33}$$

If we let $\eta^* = M(t)\, e^{-2k^2\mu t/\rho}$ and $\theta = \omega t/2$ be a dimensionless time then Equation (33) reduces to Mathieu's differential equation (*10, 11*).

$$\frac{d^2 M}{d\theta^2} + (a - 2q \cos 2\theta)\, M = 0 \tag{34}$$

where

$$a = 4\left(\frac{Tk^3}{\rho\omega^2} - \frac{4k^4\mu^2}{\rho^2\omega^2} \right) \quad \text{and} \quad q = -2k\epsilon_i$$

The general solution for small values of q is of the form

$$M(\theta) = e^{\gamma\theta} H(\theta) \tag{35}$$

$H(\theta)$ is a series of sine-elliptic and cosine-elliptic Mathieu functions. For the model presented here

$$H(\theta) = S_1 \sin(\theta - \sigma) + S_3 \sin(3\theta - \sigma) + S_5 \sin(5\theta - \sigma) + \ldots\ldots + C_3 \cos(3\theta - \sigma) + C_5 \cos(5\theta - \sigma) + \ldots\ldots \tag{36}$$

The prefixes $S_1, S_3, \ldots\ldots$ and $C_3, C_5, \ldots\ldots$ are dependent on the Mathieu parameter q. For small values of q, the characteristic index γ takes the form

$$\gamma = -\frac{1}{2} q = k\,\epsilon_l \tag{37}$$

The final form of the solution is expressed in terms of the amplitude of the surface wave

$$\eta = b \exp\left[\left(\gamma - \frac{4k^2\mu}{\rho\omega}\right)\frac{\omega t}{2}\right] H\left(\frac{\omega t}{2}\right) \cos kx \tag{38}$$

DISCUSSION

From Equation (38) which expresses the amplitude of the capillary wave, it is evident that, since time is always increasing, the amplitude of the surface wave grows quite large whenever the exponent is positive. From this, one can obtain a critical value of γ as

$$\gamma_o = \frac{4k^2\mu}{\rho\omega} \tag{39}$$

The only parameter in γ that varies is the fluid particle displacement ϵ_l, since the frequency is fixed. The critical or threshold value of the fluid particle displacement is

$$\epsilon_c = \frac{4k\mu}{\rho\omega} \tag{40}$$

Equation (15), which expresses the ratio of the fluid particle at the interface to the fluid particle displacement at the crystal surface, can be written in the form

$$\epsilon_l = \frac{\epsilon_o}{\cos k_u l} = M_o\,\epsilon_o \tag{41}$$

where M_o is a magnification factor depending upon the height of the interface above the crystal surface in the capillary. This equation shows that M_o goes to infinity at integral half wavelengths for the case of no wave damping. When damping of the ultrasonic wave in the fluid is considered, the result is essentially the same, except that a finite limit is placed on M_o at the antinodes (*9*). For the liquids considered, the damping coefficients yield a value of M_o of the order of 10^4 at the integral half wavelength. Thus the fluid particle displacement at the gas liquid interface becomes very large at these integral half wavelengths.

This mathematical model predicts that as the liquid level in the capillary recedes and passes through integral half wavelengths of the standing wave, the fluid particle displacement at the gas-liquid interface exceeds the critical value ϵ_c necessary for the stability of the surface waves. This permits the amplitude of the surface waves η to become large, unstable, and to cap, causing their crests to be ejected into the air as droplets. The diameter of these droplets is estimated to be the order of 20 microns (*12*). Once these droplets are in the gas phase above the interface, evaporation takes place at an increased rate due to the increased surface area. The evaporation from these droplets then saturates the gas phase above the interface. This essentially moves the saturation plane closer to the top of the capillary T and shortens the diffusional path length, so that the rate of diffusion is increased, and sudden increases in the mass transfer are possible. The predicted points of atomization of the droplets in the capillary coincide with the observed points of fogging.

Another mechanism of interest concerns cavitation near the interface; this is also under investigation as a possible explanation of ultrasonic fogging. However, this mechanism appears to come into play only at high acoustical powers. At lower powers, which were applied in this research, the surface wave mechanism appears to be the correct mechanism. Lang's experimental correlation relating the droplet diameter to the wavelength of the surface wave indicates the strong plausibility of this mechanism at low acoustical powers (*12*).

SUMMARY

As the gas-liquid interface in the capillary tube recedes because of evaporation, certain points are reached at which large increases in the rate of mass transfer are observed. The distance between these points is equal to one-half the wavelength of the ultrasonic wave in the liquid. The mathematical model presented in this study predicts that at these half wavelengths the fluid particle displacement of the ultrasonic wave will become quite large and exceed the threshold value necessary for the stability of the surface waves. The large amplitude of these waves causes the resulting crests to cap and to eject their peaks into the air as droplets. These droplets then saturate the air column above the gas-liquid interface and allow the evaporated liquid to diffuse out at an increased rate due to the reduced diffusional path length. The predicted levels of acoustical fogging coincide with the observed levels of fogging.

ACKNOWLEDGMENT

The authors express their appreciation to both the National Aeronautics and Space Administration and to the National Science Foundation for financial assistance during the course of this work. Fellowship support has been provided by NASA, while specific research equipment has been obtained through NSF assistance.

NOTATION

A = constant
a = constant in Mathieu's equation
b = maximal capillary wave amplitude, cm.
B = constant
c = velocity of sound in the fluid, cm./sec.
C_o = proportionality constant, sq. cm.
D = constant
E = constant
f_i = i component of viscous force, dynes/cc.
F = constant
F_i = i component of force, dynes/g.
g = gravitational constant, cm./sec.^{2}
H = solution to Mathieu's equation
k_u = wave number of ultrasonic wave, cm.$^{-1}$
k = wave number of surface wave, cm.$^{-1}$
l = height of gas-liquid interface in capillary tube, cm.
M = solution to Mathieu's equation
M_o = magnification factor
n = integer 1, 2, 3, ...
N = constant
P = excess pressure produced by the ultrasonic wave, dynes/sq. cm.
p = fluid pressure, dynes/sq. cm.
q = parameter in Mathieu's equation

R = constant
T = surface tension, dynes/cm.
$\hat{T}$ = separation of variables parameter, only a function of t
t = time, sec.
u_i = i component of velocity, cm./sec.
u_j = j component of velocity, cm./sec.
v = y component of velocity, cm./sec.
x_i = i coordinate distance
x_j = j coordinate distance
x_2 = y coordinate distance
X_i = i component of body force
y = y coordinate distance
Y = separation of variables parameter, only a function of y

Greek Letters

α = ultrasonic wave attenuation coefficient, neper/cm.
γ = characteristic Mathieu function index
γ_c = critical value of Mathieu function index
ϵ = fluid particle displacement, cm.
ϵ^* = maximal value of fluid particle displacement at the crystal surface, cm.
ϵ_o = particle displacement caused by the crystal at the crystal surface, cm.
ϵ_l = particle displacement at gas-liquid interface, cm.
η = capillary wave amplitude
η^* = time dependent part of capillary wave amplitude
θ = dimensionless time
λ = wavelength of surface wave cm.$^{-1}$
λ_u = wavelength of ultrasonic wave, cm.$^{-1}$
μ = surface viscosity
$\bar{\mu}$ = constant defined by Equation (6)
ρ = density of fluid, g./cc.
ρ_o = constant equilibrium density, g./cc.
σ = phase angle in solution to Mathieu's equation = $\pi/4$
ϕ = velocity potential
ϕ^* = time dependent part of velocity potential

LITERATURE CITED

1. Kinsler, L. F., and A. R. Frey, "Fundamentals of Acoustics," p. 133, Wiley, New York (1962).
2. *Ibid.*, p. 112.
3. Rayleigh, Baron, "Theory of Sound," Vol. II, p. 343, Dover, New York (1945).
4. Kuethe, A. M., and J. D. Schetzer, "Foundations of Aerodynamics," 2 ed., p. 46, Wiley, New York (1959).
5. Jeffreys, Harold, "Cartesian Tensors," p. 57, Cambridge Univ. Press, Cambridge (1963).
6. Lamb, Horace, "Hydrodynamics," 6 ed., p. 399, Dover, New York (1945).
7. Eisenmenger, W., *Acustica*, 9, 327 (1959).
8. Stoker, J. J., "Water Waves," p. 9, Interscience, New York (1957).
9. Fogler, H. S., Ph.D. dissertation, Univ. Colorado, Boulder (1965).
10. McLachlan, N. W., "Theory and Application of Mathieu Functions," Dover, New York (1946).
11. Hayashi, C. H., "Forced Oscillations in Non Linear Systems," Nippon, Osaka, Japan (1953).
12. Lang, R. J., *J. Acous. Soc. Am.*, 34, 6 (1962).

Manuscript received March 9, 1965; revision received July 19, 1965; paper accepted July 26, 1965. Paper presented at A.I.Ch.E. San Francisco meeting.

A Generalized Equation for Computer Calculation of Liquid Densities

LEWIS C. YEN and S. S. WOODS
Phillips Petroleum Company, Bartlesville, Oklahoma

A generalized equation explicitly relating reduced density to reduced temperature and reduced pressure has been developed for calculating liquid densities of pure compounds on a digital computer. The analytical formulation is based mainly on a modified corresponding states principle and the graphical correlation of Lydersen, Greenkorn, and Hougen. The calculated densities from the equation reproduce the literature data within 2% for sixty-two saturated liquids and nineteen compressed liquids.

With the aid of a pseudocritical method and a generalized equation of vapor pressure, the same equation is readily applied to the estimation of liquid mixture densities. The method of Prausnitz and Gunn is chosen for the evaluation of pseudocritical constants. For fifteen binary systems, one ternary system, and one quinary system, the one hundred fifty-nine calculated densities agree with the literature data to within 3%. This method is limited to pseudoreduced temperatures less than 1.0.

The principle of corresponding states has been used extensively in correlating and predicting volumetric properties and thermodynamic functions. Based on a modified form of the principle which contains a third parameter, z_c, Lydersen, Greenkorn, and Hougen (9) have developed a generalized correlation for liquid densities of pure compounds over a wide range of temperatures and pressures. This correlation, presented in both graphical and tabular form, has been thoroughly reviewed and found to be accurate to about 2 to 5% (*13*). When experimental data for liquid densities are not available, the generalized correlation has been widely used for the prediction of liquid densities in engineering work. However, this use has been limited to manual calculations. While digital computers are increasingly used in process calculations throughout the industry, the adoption of the Lydersen–Greenkorn–Hougen correlation for computer work would require a storage for a large number of points and exten-