Friction Coefficients and Self-Diffusivity Reduced State Correlations and Interrelationship

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Theoretical equations for the transport properties of dense gases and liquids require knowledge of the contact pair-correlation function $g_2(\sigma)$ and the friction coefficient ζ. Usually this latter quantity is made up of a hard-core contribution ζ^H and a soft-repulsion contribution ζ^S. Correlations are presented for the reduced friction coefficients $\zeta_r{}^H$, $\zeta_r{}^S$, and ζ_r in terms of reduced density ρ^* and reduced temperature T^*. These correlations were found to predict the dependence of self-diffusivity of several substances on temperatures and density in the dense gas region.

Equations for the transport properties of dense gases and liquids have been developed based on theory proposed by Rice and Allnatt (*1, 16*). Ikenberry and Rice (*7*) presented an equation for thermal conductivity consisting of three terms

$$k = k_k + k_v(\sigma) + k_v(r > \sigma) \qquad (1)$$

where k_k is the kinetic energy component and k_v is the potential energy contribution evaluated at $r = \sigma$ and $r > \sigma$. Equations for each of these contributions are given in terms of Lennard-Jones parameters σ, ϵ/κ, molecular mass m, temperature T, number density ρ_N, contact pair-correlation function $g_2(\sigma)$, and friction coefficient ζ.

In a similar manner Lowry, Rice, and Gray (*10*) developed an equation for shear viscosity

$$\mu = \mu_k + \mu_v(\sigma) + \mu_v(r > \sigma) \qquad (2)$$

where μ_k is the kinetic component arising from a net transfer of momentum across an arbitrary reference plane. The other components are the momentum contributions corresponding to the two regions of the intermolecular pair potential. As before evaluation of these components requires a knowledge of the friction coefficient.

Finally, the self-diffusivity is given by

$$D = \frac{\kappa T}{\zeta} \qquad (3)$$

where κ is the Boltzmann constant. Following earlier workers, Palyvos and Davis (*14*) defined the friction coefficient as the sum of two terms

$$\zeta = \zeta^H + \zeta^S \qquad (4)$$

where ζ^H is the friction coefficient arising from hard core collisions and ζ^S is that arising from soft interactions.

It is apparent that use of these equations for comparison of theoretical and experimental transport properties or for prediction of values where measurements are lacking depends on knowledge of $g_2(\sigma)$ and ζ over broad ranges of temperature and density. Ramanan presented such correlations for $g_2(\sigma)$ in terms of ρ^* and $1/T^*$ and also in terms of ρ_r and T_r (*15*). The purpose of this paper is to present correlations for the friction coefficient over comparable ranges of reduced conditions. These correlations are based on a combination of theoretical considerations and experimental self-diffusivities for argon. They were found to predict the self-diffusivities of several substances over a broad range of temperature and density.

FRICTION COEFFICIENTS

For convenience Equation (4) which defines the friction coefficient may be made dimensionless by dividing by ζ^*. This gives

$$\zeta_r = \zeta/\zeta^* = \zeta^H/\zeta^* + \zeta^S/\zeta^* \qquad (5)$$

$$= \zeta_r{}^H + \zeta_r{}^S \qquad (6)$$

where

$$\zeta^* = (8\rho_N \sigma^2/3)(\pi m \kappa T)^{1/2} \qquad (7)$$

Palyvos and Davis (*14*) have shown that

$$\zeta_r{}^H = g_2(\sigma) \qquad (8)$$

where $g_2(\sigma)$ is the contact pair-correlation function and

$$\zeta_r{}^S = f(g_2(r), \epsilon/\kappa, T) \qquad (9)$$

where $g_2(r)$ is the radial distribution function. These authors tabulated these quantities at three values of reduced density ($\rho^* = \rho_N \sigma^3$), 0.443, 0.674, and 0.818 over a range of reduced temperature $0.667 < T^* = T\kappa/\epsilon \leqq 10$. Calculations were based on the theoretical pair correlation function of Kirkwood, Lewinson, and Alder (*9*). Ramanan (*15*) included the results for $\rho^* = 0.276$ (*9*) and presented graphical correlations of $g_2(\sigma)$ over the range $0 \leqq \rho^* \leqq 1$. From Equation (8) such a correlation also represents the behavior of $\zeta_r{}^H$ as shown in Figure 1. The hard-core, reduced friction coefficient is seen to increase with density at constant temperature. It also increases with increasing temperature at a constant density.

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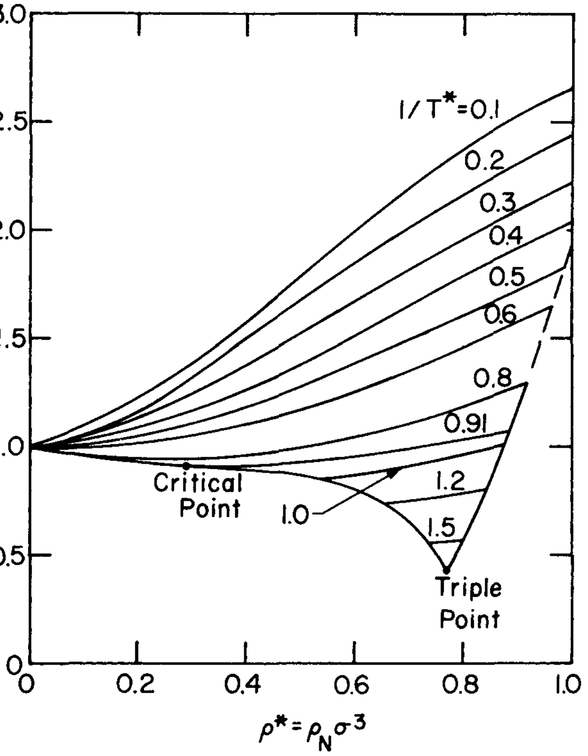

Fig. 1. Reduced, hard-core friction coefficient in terms of reduced molecular parameters.

TABLE 1. VALUES OF ADJUSTED LENNARD-JONES PARAMETERS (σ, ϵ/κ), δ, AND SOURCES OF EXPERIMENTAL SELF-DIFFUSIVITY DATA

Substance	σ, Å	ϵ/κ, °K	δ, sec./sq. cm.	Sources of data
Ar	3.300	137.2	0.293×10^5	(*13*)
Kr	3.377	166.0	0.377	(*13*)
Xe	3.683	265.0	0.343	(*13*)
N_2	3.490	116.9	0.252	(*18*)
CO_2	3.600	231.8	0.217	(3), (*17*)
CH_4	3.457	188.5	0.151	(*13*), (*20*)
C_3H_8	4.520	270.6	0.160	(*17*), (*20*)

At low densities approaching dilute gases a value of one is realized for all temperatures. Along the saturation curve representing vapor-liquid equilibrium, the value of the coefficient for the liquid decreases from 0.91 at the critical point to 0.44 at the triple point. Along the melting curve representing solid liquid equilibrium, the value for the saturated liquid increases rapidly with density. With the Lennard-Jones parameters determined previously for argon (*15*), and given in Table 1, the critical isotherm corresponds to a value of $T_c^* = 1.10$ and the critical density to $\rho_c^* = 0.290$. At the triple point, $T_t^* = 0.611$ and $\rho_t^* = 0.768$ (for the liquid).

The reduced friction coefficient based on soft interactions ζ_r^S was available from Palyvos and Davis over the range of $0.443 \leqq \rho^* \leqq 0.818$. To construct Figure 2, two additional pieces of information were used.

Self-diffusivity measurements for gaseous argon (1 atm.) were available in the literature (*6*, *19*) over a temperature range of 77° to 353°K. Combining Equations (3), (5), (6), and (7) gives

$$D = \frac{\kappa T}{(8\rho_N \sigma^2/3)(\pi m \kappa T)^{1/2}(\zeta_r^H + \zeta_r^S)} \qquad (10)$$

Rearranging and incorporating the definitions of ρ^*, T^*, and $M = m\,N$, one gets

$$\zeta_r^H + \zeta_r^S = \frac{T^{*1/2}}{(8/3)(\pi/N\kappa)^{1/2}} \left(\frac{\epsilon/\kappa}{M/\sigma^2}\right)^{1/2} \frac{1}{\rho^* D} \qquad (11)$$

Using Equation (11) and the experimental values for D at 1 atm. values of $\zeta_r^H + \zeta_r^S$ were calculated at $\rho^* \to 0$. As seen from Figure 1, under these conditions $\zeta_r^H = 1$, so ζ_r^S is readily calculated. These values were plotted at $\rho^* = 0$ and the curves between $0 \leqq \rho^* \leqq 0.443$ were estimated as shown by the dashed lines.

From PVT data for argon in the liquid and dense phase region (2) the isotherms were terminated at the corresponding saturated liquid densities. Values of ζ_r^S at the critical point and the triple point are 1.5 and 3.45.

From Equation (10) it is apparent that the sum $\zeta_r^H + \zeta_r^S$ is the quantity most useful for prediction of self-diffusivities based on the Rice-Allnatt theory. Such a correlation consistent with Figures 1 and 2 is shown in Figure 3. There is at least a two-fold variation in the reduced friction coefficient ζ_r along isotherms for which $1/T^* \leqq 0.91$ in going from a dilute gas to a dense liquid (Figure 3). It is also seen that this quantity decreases as temperature increases at constant density.

SELF-DIFFUSIVITY

Equation (11) relates the self-diffusivity to the molecular properties of a gas and shows the dependence on temperature, density, and reduced friction coefficient. If an analytical representation is used to relate $\zeta_r^H + \zeta_r^S$ to T^* and ρ^*, then the dependence of self-diffusivity on these variables can be found for any substance. The 87 values of Palyvos and Davis (*14*) were fitted by multiple regres-

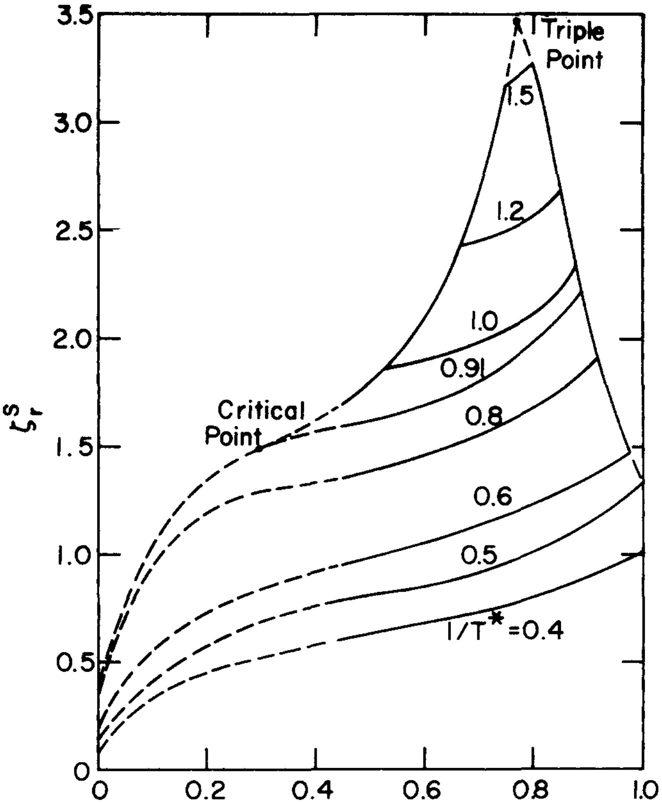

Fig. 2. Reduced soft-interaction friction coefficient in terms of reduced molecular parameters.

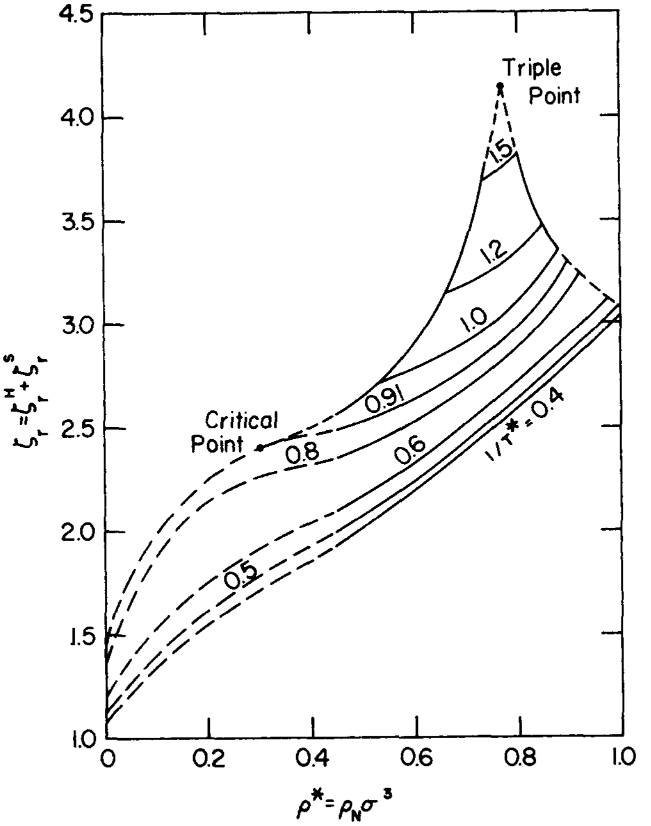

Fig. 3. Reduced friction coefficient in terms of reduced molecular parameters.

sion analysis to an equation of the form

$$\zeta_r^H + \zeta_r^S = a\,T^{*b}\,\rho^{*c} \tag{12}$$

using an IBM 360 computer. This form was chosen to give a simple equation for D in terms of T^* and ρ^*.

The constants were found to be $a = 3.46$, $b = -0.211$ and $c = 0.334$.[†] Substituting Equation (12) with these constants into Equation (11), and rearranging gives

$$\frac{D\delta}{T^{*0.711}} = (\rho^*)^{-1.334} \tag{13}$$

where

$$\delta(\text{sec./sq.cm.}) = 1.794 \times 10^5 \left(\frac{M/\sigma^2}{\epsilon/\kappa} \right)^{1/2} \tag{14}$$

Values of δ for seven substances were calculated from the Lennard-Jones parameters shown in Table 1. These parameters were evaluated from the equations given by Ramanan (*15*). Also shown in Table 1 are sources of experimental self-diffusivity data.

Since the fit of Equation (12) is unsatisfactory, it is recommended that Equation (11) be used in the following form to calculate self-diffusivities

$$D = \frac{3.46T^{*0.5}}{\delta\,\rho^*(\zeta_r^H + \zeta_r^S)} \tag{15}$$

This equation does not incorporate Equation (12); the factor 3.46 appears because it was included in the definition of δ.

In Figure 4 the quantity $D\delta/T^{*0.711}$ is plotted against ρ^* on a log-log scale. Again the liquid Lennard-Jones parameters were used to convert experimental temperatures and densities to the reduced values. Where experimental conditions were reported as temperature and pressure, the reduced-density plots of Thodos and coworkers for inert gases (*5*), carbon dioxide (*8*), and methane (*12*) were used to get the corresponding density. For propane the PVT chart by Edmister (*4*) was used and for nitrogen generalized compressibility relationships were utilized to obtain appropriate densities.

Two comparisons with the experimental data are also shown. First, Equation (13) is plotted as a straight line wth a slope of -1.334. At very low reduced densities ($\rho^* < 0.02$) and also at very high reduced densities ($\rho^* > 0.6$), this equation predicts self-diffusivity values that are too high. Better agreement with the experimental values was found by using Figure 3 in place of Equation (12) for representing the dependence of $\zeta_r^H + \zeta_r^S$ on reduced temperature and density. At each value of ρ^*, values of $\zeta_r^H + \zeta_r^S$ were read from each isotherm. Values of $D\delta/T^{*0.711}$ were calculated from Equation (15). The curved lines are drawn through the extreme values found at each ρ^*. Agreement between these calculated values and experimental data is shown in Table 2 up to a reduced density of 0.6. The substances listed are the only ones for which data were available in the dense gas region.

TABLE 2. COMPARISON OF EXPERIMENTAL AND CALCULATED DIFFUSIVITIES OBTAINED FROM FIGURE 4

Substance	ρ^* range	No. of pts.	Avg. $\frac{D_{\text{exp}} - D_{\text{calc}}}{D_{\text{exp}}} \times 100$, %
N_2	0.02-0.1	6	15.8
CO_2	0.02-0.6	15	−6.8
CH_4	0.06-0.22	9	14.0
C_3H_8	0.37-0.6	10	3.0

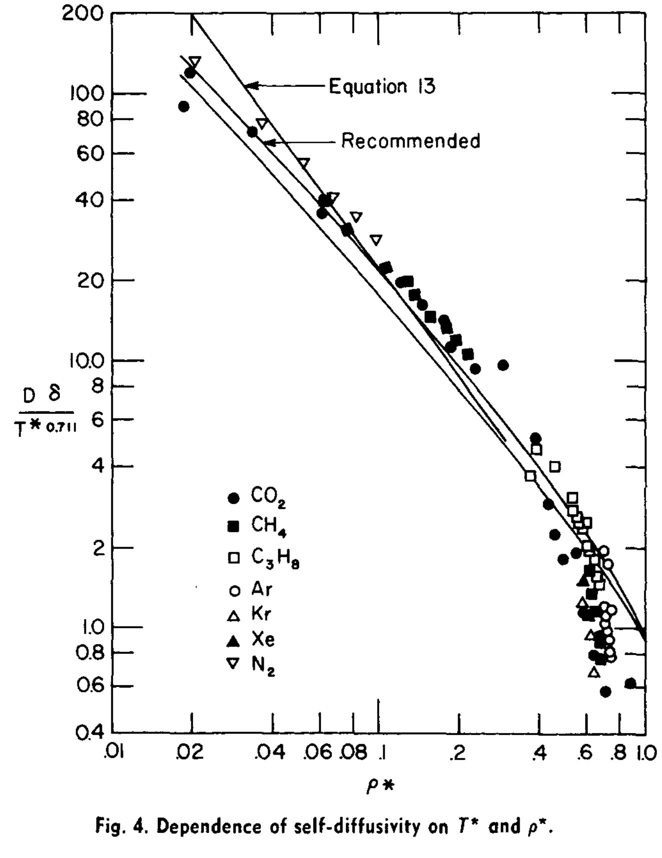

Fig. 4. Dependence of self-diffusivity on T^* and ρ^*.

[†] Correlation coefficient, $r = 0.740$

Using dimensional analysis Mathur and Thodos (*11*) found the following relationship for the self-diffusivity

$$D\beta = sT_r^{p}\rho_r^{q} \tag{16}$$

where β is a parameter for each substance dependent on its molecular weight, critical temperature, and critical pressure. Values for s, p, and q were determined from experimental data.

The form of Equation (16) found by these authors is the same as that based on theory as given in Equation (13). Mathur and Thodos used Equation (16) only to correlate diffusivities for gases at elevated pressures. Other equations were used at normal pressures and for the liquid state. The inadequacy of Equation (13) to predict the liquid state quantitatively is also shown in Figure 4. Further analysis appears necessary to account for the liquid behavior in the region of $0.6 \leqq \rho^* \leqq 1.0$.

In summary, correlations for the friction coefficient have been presented over wide ranges of ρ^* and T^* based on a Lennard-Jones potential function. These correlations were found to predict self-diffusivity data in the dense-gas region for several substances. Since the contact pair-correlation function is equal to ζ_r^H, all the information necessary is now available to test theoretical equations for viscosity and thermal conductivity and to compare the results with the numerous experimental values available in the literature.

ILLUSTRATIVE EXAMPLE

Calculate the self-diffusivity for propane at 196°F. and 2015 lb./sq.in.abs.

At these conditions the specific volume is evaluated from the PVT correlation of Edmister (*4*) as 0.0368 cu. ft./lb. (ρ = 0.435 g./cu.cm.). The molecular reduced properties are evaluated using the Lennard-Jones parameters listed in Table 1

$$T^* = T/(\epsilon/\kappa) = 364.2°\text{K.}/270.6°\text{K.} = 1.346$$

$$(M/N\sigma^3) = (44.11 \text{ g./g.-mole})/(6.023 \times 10^{23}/\text{g.-mole})(4.52 \times 10^{-8} \text{ cm.})^3$$

$$= 0.793 \text{ g./cu.cm.}$$

$$\rho^* = (0.435 \text{ g./cu.cm.})/(0.793 \text{ g./cu.cm.})$$

$$= 0.549$$

If the substance is not listed in Table 1, the following equations may be used to get appropriate Lennard-Jones parameters from tabulations of values based on gaseous viscosity data (*15*)

$$\sigma = 0.521 + 0.781\,\sigma_{\text{vis}}$$

$$\epsilon/\kappa = 50.6 + 0.928\,(\epsilon/\kappa)_{\text{vis}}$$

From Figure 3 a value of

$$\zeta_r^H + \zeta_r^S = 2.40$$

is read at $\rho^* = 0.549$ and $1/T^* = 0.743$.

These values are substituted into Equation (15) along with $\delta = 0.160 \times 10^5$

$$D = 3.46(1.346)^{0.5}/(0.16 \times 10^5 \text{ sec./sq.cm.})(0.549)(2.40)$$

$$= 19.0 \times 10^{-5} \text{ sq.cm./sec.}$$

$$D_{\text{exp}} = 16.8 \text{ sq.cm./day } (20)$$

$$= 19.4 \times 10^{-5} \text{ sq.cm./sec.}$$

An alternate method is to evaluate $D\delta/T^{*0.711}$ from the recommended curve of Figure 4.

NOTATION

a, b, c = constants in Equation (12)
D = self-diffusivity, sq.cm./sec.
$g_2(r)$ = radial distribution function
$g_2(\sigma)$ = contact pair correlation function
k = thermal conductivity, cal./(cm.)(sec.) °K.
m = mass per molecule, M/N
M = molecular weight
N = Avogadro's number, 6.023×10^{23} molecules/g.-mole
p, q, s = constants in Equation (16)
r = radial distance, cm.
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_r = reduced temperature, T/T_c
T_t = triple point temperature, °K.
T^* = reduced temperature, $T/(\epsilon/\kappa)$
T_c^* = reduced temperature at critical point, $T_c/(\epsilon/\kappa)$
T_t^* = reduced temperature at triple point, $T_t/(\epsilon/\kappa)$

Greek Letters

δ = self-diffusivity modulus, sec./sq.cm, Equation (14)
ϵ/κ = Lennard-Jones parameter, °K.
ζ = friction coefficient, g./sec.
ζ^H = hard-core friction coefficient, g./sec.
ζ^S = soft-interaction friction coefficient, g./sec.
ζ^* = reducing friction parameter, Equation (7), g./sec.
ζ_r = reduced friction coefficient, ζ/ζ^*
ζ_r^H = reduced hard-core friction coefficient, ζ^H/ζ^*
ζ_r^S = reduced soft-interaction friction coefficient, ζ^S/ζ^*
κ = Boltzmann constant, 1.380×10^{-16} erg/molecule, °K.
μ = shear viscosity, poise
ρ = density, g./cu.cm.
ρ_c = critical density, g./cu.cm.
ρ_N = number density, $\rho N/M$, molecules/cu.cm.
ρ_r = reduced density, ρ/ρ_c
ρ_t = triple-point density, g./cu.cm.
ρ^* = reduced density, $\rho/(M/N\sigma^3)$
ρ_c^* = reduced density at critical point, $\rho_c/(M/N\sigma^3)$
ρ_t^* = reduced density at triple point, $\rho_t/(M/N\sigma^3)$
σ = Lennard-Jones collision diameter, cm.

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The Peak Pool Boiling Heat Flux from a Sphere

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A hydrodynamic prediction is formulated for the peak nucleate boiling heat flux on spheres. It employs no empirical constants but it is justified by an experimental correlation of the vapor blanket thickness at the equator of the sphere. The prediction compares very favorably with 27 original data obtained by the transient calorimeter method in both water and N_2 on spheres of different sizes. It also compares well with the data of prior investigators for a large range of size, gravity, and boiled liquids. Assumptions as to the vapor removal configuration are supported with photographic observations of the boiling process.

The objective of this work is to provide a hydrodynamic prediction of the peak heat flux $q_{\max}$ on spheres and to support this theory with observations of both $q_{\max}$ and the dynamics of vapor removal. This study is part of an ongoing effort to predict the influence of gravity on the peak and minimum heat fluxes.

It is interesting that some of the earliest variable gravity studies [by Merte et al. (*1*, *2*)] used spherical heaters. These studies more-or-less demonstrated the one-quarter-power dependence of $q_{\max}$ on the gravity g predicted by Zuber (*3*) for flat-plate heaters,* that is,

$$q_{\max F} \simeq \frac{\pi}{24} \rho_g^{1/2} h_{fg} [\sigma g(\rho_f - \rho_g)]^{1/4} \qquad (1)$$

They also provided a variety of $q_{\max}$ data for nitrogen boiling on spheres of different size under a range of gravities.

Most studies of boiling from spheres have used the transient calorimeter technique. A heated sphere with a thermocouple mounted in the center has been quenched in the boiling liquid and allowed to cool. This involves making the tacit assumptions that the Biot Number $Bi = hR/k$ is small and that the process is quasi-static. Bergles and Thompson (*4*), quoting from earlier sources, suggest that Bi at $q_{\max}$ should not be much more than 0.4 for accuracy. But they also warn against the second possible source of error—namely that the boiling process might fail to accommodate rapidly enough to be quasi-static.

More recently Veres and Florschuetz (*5*) argued that Bergles and Thompson's accommodation discrepancy was in fact the result of a failure to use the same heaters in both the transient and steady state tests. But the heaters for the two situations differed little in shape and in surface condition. However, Veres and Florschuetz obtained results that were quite similar to steady state data when they quenched the same heaters, as long as the heaters were kept fairly clean during the quench. But sufficiently heavy oxide layers, accrued during the preheat prior to quenching, led to a deviation from steady state results. Veres and Florschuetz also provided additional $q_{\max}$ data for spheres.

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* This is the appropriate form of Zuber's prediction as long as the system pressure is not near the critical pressure.