HIGH-PRESSURE TRANSPORT PROPERTIES OF FLUIDS: THEORY AND DATA FROM LEVITATED DROPS AT COMBUSTION-RELEVANT TEMPERATURES

Josette Bellan and Kenneth Harstad
Jet Propulsion Laboratory, California Institute of technology, Pasadena CA 91109

Kenichi Ohsaka
University of Southern California, Los Angeles, CA.

INTRODUCTION

Although the high pressure multicomponent fluid conservation equations have already been derived and approximately validated for binary mixtures by this PI, the validation of the multicomponent theory is hampered by the lack of existing mixing rules for property calculations. Classical gas dynamics theory can provide property mixing-rules at low pressures exclusively. While thermal conductivity and viscosity high-pressure mixing rules have been documented in the literature, there is no such equivalent for the diffusion coefficients and the thermal diffusion factors.

The primary goal of this investigation is to extend the low pressure mixing rule theory to high pressures and validate the new theory with experimental data from levitated single drops. The two properties that will be addressed are the diffusion coefficients and the thermal diffusion factors. To validate/determine the property calculations, ground-based experiments from levitated drops are being conducted.

ACCOMPLISHMENTS

During the last year, progress was made theoretically and experimentally, as follows:

1. Theoretical

The theoretical investigation was devoted both to enlarging the modeling of the high-pressure diffusion coefficients and to developing high-pressure mixing rules.

A. Enlargement of the diffusivity study

Previous high-pressure ($\rho_r \geq O(1)$) data was developed in the form of the function $w_D(\rho_r)$ which modifies known low pressure (kinetic theory) diffusivities. The latter requires values of the empirical normalization factor r_D. Some further data for solvent-aromatic solute (benzene, toluene, naphthalene, cumene) pairs with r_D values that are not known have been examined. Data for the solvent 2,3dimethylbutane [14] show a coincidence of plots of the variable $\omega^{1/4} r_D w_D$ versus ρ_r (Fig. 1); this holds for a generic w_D if $\omega^{1/4} r_D = $ constant, where ω is the solute acentric factor. Other data with CO_2 as the solvent is also available [1-13]. Since r_D for benzene in CO_2 has the value 0.90, the inference is made that $\omega^{1/4} r_D = 0.61$ for aromatics in CO_2. This results in estimates of r_D values of 0.85, 0.82 and 0.81 for toluene, naphthalene and cumene in CO_2, respectively. Using these values, plots of w_D data are shown in Figs. 2-4 together with $w_D = 1 + \delta_D$ and $\delta_D = 0.10\rho_r^2$.

B. Multicomponent fluid mixing rules

Generalized transport relations (fluxes in terms of thermodynamic forces) for arbitrary fluid mixtures at all pressures are best determined through the formalism of nonequilibrium

thermodynamics or statistical thermodynamics (fluctuation-dissipation theory). Although the proper forms for these relations are thus found, the transport coefficients themselves (viscosity, thermal conductivity, etc.) are not thereby determined. The coefficients, including their appropriate mixing rules, may be formulated for dilute, low-pressure mixtures through kinetic theory. Thus the conjunction of nonequilibrium thermodynamics and kinetic theory provides a needed starting point to the formulation of generalized mixing rules for fluid mixtures. The 13-moment approach to kinetic theory is utilized for this purpose.
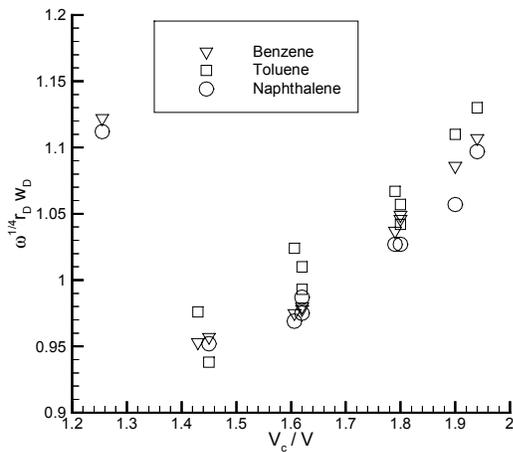

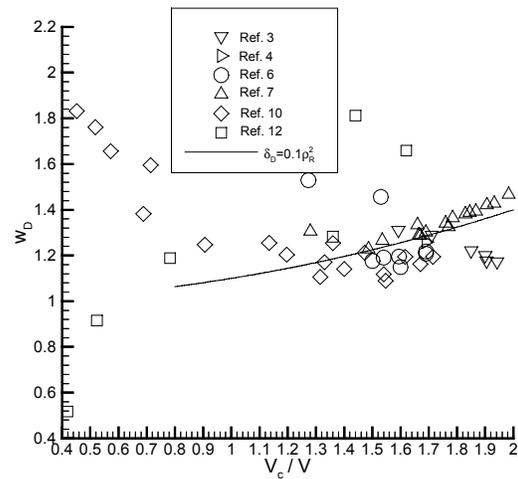**Figure 1 Scaled diffusivities of solutes benzene, toluene and naphtalene in solvent 2,3dimethylbutane.**

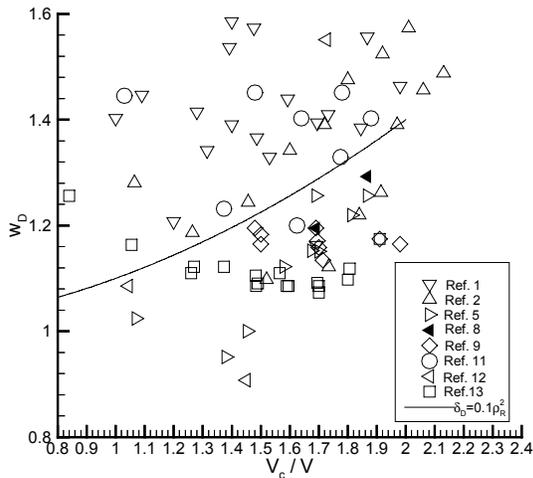**Figure 2 Scaled diffusivity of toluene in CO2: data and correlation.**

Figure 3 Scaled diffusivity of naphtalene in CO2: data and correlation.
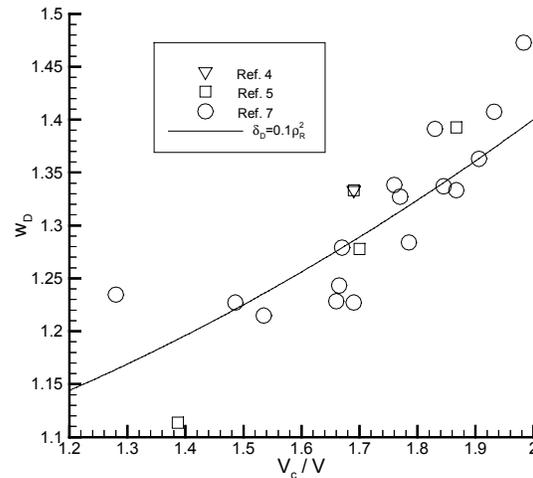

Figure 4 Scaled diffusivity of cumene in CO2: data and correlation.

This approach avoids many of the algebraic complications resulting from the expansions in inverse density (or mean free path) that are prominent in the Chapman-Enskog procedure. Substituting the 13-moment transport formulas into the nonequilibrium thermodynamic forms results in a coupled set of matrix equations that essentially determine the proper mixing rules.

These equations have been studied and manipulated; reduction to a single matrix equation that determines the mixture mass diffusion coefficients in terms of binary diffusion coefficients has been achieved. Then the mixing rules for the mixture thermal diffusion factors (flux cross-couplings) in terms of binary factors and the mixture thermal conductivity are found to be explicit in terms of the resulting mixture mass diffusion coefficients.

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2. Experimental

In the previous fiscal year, we built an electrostatic levitation apparatus. A difficult step of the electrostatic levitation is the deployment of a liquid drop. The original device worked well for water drops, but failed to deploy alcohol drops because the good wetting characteristics and small surface tension values of alcohol liquids make the detachment of a drop from the supporting rods difficult. We therefore needed to redesign the drop deployment device to overcome this difficulty. During this fiscal year, we assembled a new device and tested it. With the redesigned device we could levitate both water and ethyl alcohol drops whose diameters were initially approximately 2 mm. The drops could be charged either negatively (excess electrons) or positively (excess ions). We could keep the drops levitated as they gradually evaporated. Figure 5 shows a plot of the diameter squared of an ethyl alcohol drop as a function of the elapsed time. As seen in the figure, evaporation establishes a quasi steady state indicated by the straight line. The figure also shows the applied voltage which decreases as evaporation proceeds. As the diameter of the drop decreases but the charge remains constant, the charge density eventually reaches a limit called the Rayleigh limit. At this limit, some of the charge is discharged from the drop. In the figure, this happened first at around 32 minutes indicated by a kink in the voltage curve. When the drop loses the charge, the voltage must be increased to hold the drop at the same position. This discharge repeated as the drop evaporated further. We also tested the scheme to create a temperature gradient along the levitation axis. The scheme is to heat the top electrode and cool the bottom electrode. After waiting for the chamber to reach a steady state, we measured the temperature using a thermocouple. Figure 6 is a plot of the temperature variation along the levitation axis. The distance is measured from the surface of the bottom electrode. The highest temperature represents the temperature of the top electrode. We actually levitated a water drop, thus confirming that the drop could be levitated in a field where the temperature gradient was present. The drop was initially levitated at 10 mm from the bottom. Figure 7 shows a snapshot of the levitated drop.

We have installed a device which allows us to transport a levitated drop from the initial to final (supercritical temperature) positions. This procedure is necessary to quickly bring the drop in a supercritical state. This operation can be accomplished by moving the position of the drop position monitoring assembly (laser and detector) relative to the electrodes. When the assembly is moved along the axial direction, the levitated drop follows. We performed a demonstration in which a water drop was initially levitated at 10 mm from the bottom and then transported to 5 mm from the top electrode. Figure 8 shows a snapshot of the levitated drop at the final position. A white dot marks the initial position. The wires appear close to the drop, but they actually rest in the retracted position. If this mechanism is used in combination with the levitation field with the temperature gradient, we can quickly expose the levitated drop to different temperatures.
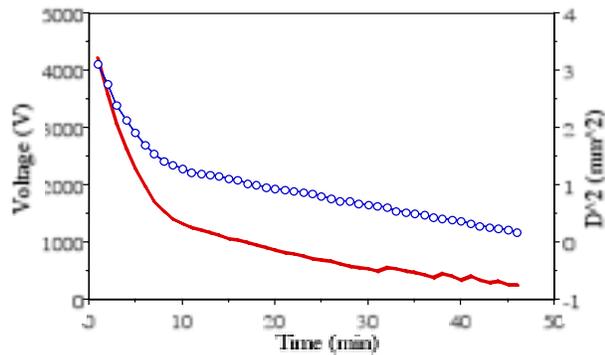

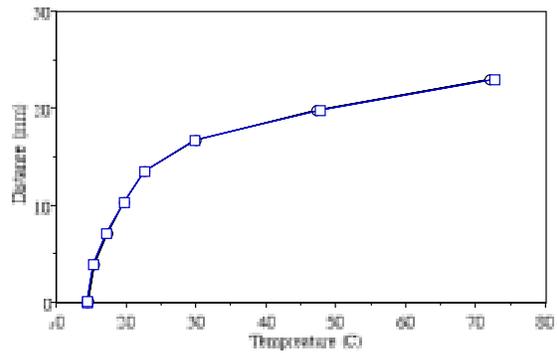**Figure 5 Drop diameter square (circles) and the applied voltage as a function of the elapsed time.**

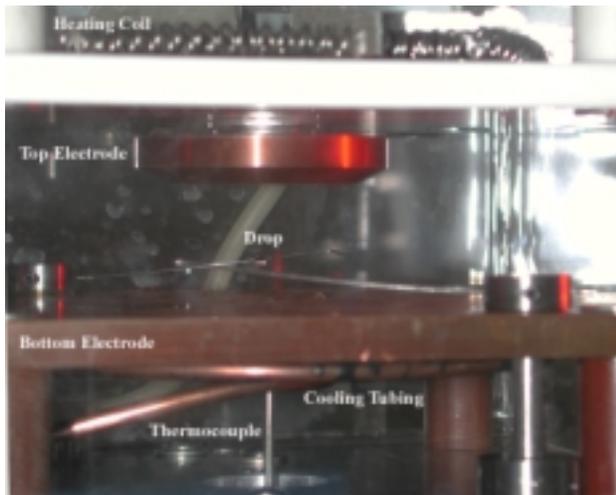**Figure 6 Temperature variation along the levitation axis.**

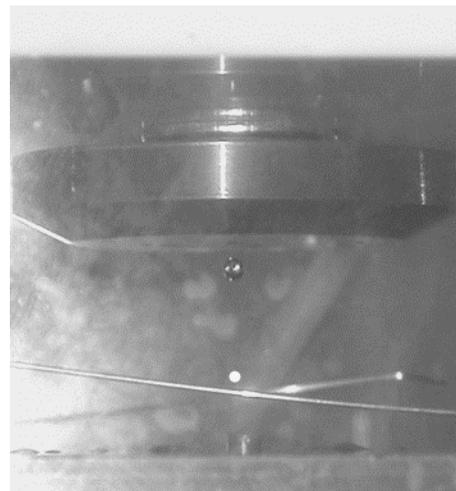**Figure 7 Drop levitated in the field with the temperature gradient.**

Figure 8 Photo showing a water drop transported to the final position from the initial position (white dot).