

Transport Coefficients in the One-Fluid Approximation*

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Some comments of the justification of writing the viscosity and thermal conductivity coefficients of a mixture in the one-fluid approximation are presented. Anomalous behavior in the critical region is discussed.

Key words: Critical point; mixture; one-fluid theory; plait point; thermal conductivity coefficient; viscosity coefficient.

1. Introduction

In the one-fluid theory of mixtures, the thermodynamic properties of a mixture are equated to those of an equivalent but hypothetical pure substance [1].¹ The theory can be justified under well-defined assumptions and turns out to be a convenient practical tool. It is therefore logical to extend the one-fluid concept to the transport coefficients. For example if, as is usually done, a mixture is characterized by the density, ρ , the temperature, T , and by mass or mole fractions, x (or by P , T , and x , where P is the pressure) one might be expected to have for the viscosity (η_{mix}) and thermal conductivity (λ_{mix}),

$$\eta_{\text{mix}}(\rho, T, x) = \eta_x(\rho, T) \quad (1)$$

$$\lambda_{\text{mix}}(\rho, T, x) = \lambda_x(\rho, T) \quad (2)$$

where η_x and λ_x are the transport coefficients for the hypothetical pure substance.

In fact, eqs (1) and (2) have been used to calculate the transport coefficients of mixtures with some success [2, 3] yet, even assuming the one-fluid approximation is valid on statistical mechanical grounds, their justification is open to question. Three brief comments on this point are given here.

2. Thermal Diffusion Factor

For simplicity consider a binary isotropic mixture of species 1 and 2. The heat flux, \mathbf{J}_q , and the diffusion flux, \mathbf{J}_1 ($\mathbf{J}_1 = -\mathbf{J}_2$), can be given by

$$\mathbf{J}_q - \mathbf{J}_1 h' = -\delta^* \nabla_T \mu' - \gamma^* \nabla T \quad (3)$$

$$\mathbf{J}_1 = -\alpha^* \nabla_T \mu' - \beta^* \nabla T \quad (4)$$

Similarly for the flux of momentum, \mathbf{J} :

$$\mathbf{J} = \tau^* \nabla \mathbf{u} \quad (5)$$

In the above, μ' is the chemical potential, $\mu' = \mu_1 - \mu_2$; h' is the specific enthalpy, $h' = h_1 - h_2$; \mathbf{u} is the center of mass velocity; and δ^* , etc., are Onsager phenomenological coefficients with $\delta^* = \beta^* T$. Identifying these phenomenological coefficients with the usual definitions of the transport coefficients, η_{mix} and λ_{mix} , one has

$$\eta_{\text{mix}} \equiv \tau^* \quad ; \quad \lambda_{\text{mix}} \equiv \gamma^* - \frac{\beta^* \delta^*}{\alpha^*} \quad (6)$$

But the one-fluid model equates λ_{mix} with γ^* since $\lambda_{\text{mix}} \equiv \lambda_x$.

In practice, however, one can argue that the term $\beta^* \delta^* / \alpha^*$ of eq (6) is generally small. $\beta^* \delta^* / \alpha^*$ will vanish as the thermal diffusion factor, k_T^2 . It is straightforward to show that k_T^2 tends to zero as the term $\left(\Delta_1 + \frac{21}{8} \Delta_2\right)^2$ tends to zero in the special case of a dilute gas mixture of hard spheres. [Here we have characterized species 1 by size σ_1 and mass m_1 , and species 2 by $\sigma_2 = \sigma_1(1 + \Delta_1)$ and $m_2 = m_1(1 + \Delta_2)$]. Further, on the basis of the hard sphere Enskog theory of mixtures [4], it appears k_T^2 will vanish as the square of the mass difference and the square of the size difference to all orders in density. Hence, although k_T strictly is not known theoretically (or experimentally) for a realistic intermolecular interaction for all densities, it does seem reasonable to suppose that k_T^2 will generally be small, and that $\lambda_{\text{mix}} \approx \lambda_x$ as in eq (2) [2].

3. Critical Region

Our next comment concerns the critical region. An apparent difficulty arises if the mixture is close to a gas/liquid critical point (plait point) because limited experimental evidence [5] and the theoretical results of Mistura [6] suggest

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¹ Figures in brackets indicate the literature references at the end of this paper.

that the thermal conductivity coefficient is finite (an azeotropic critical point excepted), in contrast to the behavior of the coefficient of a pure fluid which is known to diverge [7]. At first sight, however, eq (2) leads to a divergent coefficient in the vicinity of the plait point (T^c , ρ^c , P^c) of a mixture.

It is perhaps interesting to note that this preliminary conclusion is incorrect. The reason is that the critical behavior of the thermal conductivity coefficient from eq (2) is determined by the conditions of mechanical stability, whereas the behavior of a true mixture is determined by the conditions of material stability. Thus, although λ_x would display a critical point enhancement as the critical temperature, T_x^c , and the critical density ρ_x^c (or critical pressure, P_x^c) of the hypothetical pure substance are approached, these variables are essentially inaccessible: the true critical temperature, T^c , is greater than T_x^c , and P^c is greater than P_x^c , for example. Hence λ_x cannot diverge [10].

To illustrate the type of behavior one would expect from eq (2) we have calculated the critical anomalous part of the thermal conductivity coefficient, $\Delta\lambda^c$, for a methane/propane mixture as a function of mole fraction along the plait point locus using the methods of references [2] and [3]. Estimates of this locus were obtained from data listed in reference [8].

Following eq (2), we set $\Delta\lambda^c = \Delta\lambda_x^c$. $\Delta\lambda_x^c$ was then determined from the thermal conductivity of methane (see references [3] and [9]). The result is shown in figure 1. It is seen that unless x_{CH_4} approaches one or zero, $\Delta\lambda^c$ is small.

4. Selection of Variables

Lastly, discussion of the critical region raises the comment on the variables chosen to describe the properties of a mixture in general. According to modern theory of the behavior of a fluid in the vicinity of a critical point [11], the variables selected are significant—especially if the properties of a mixture are to be equated with those of a pure fluid [12]; which is implied here. In our work, for instance, the transport coefficients, η_{mix} and λ_{mix} , have been characterized by the density (or pressure, P), the temperature, and a mass fraction. The theory of Griffiths and co-workers [11], and of Mistura [6], implies, however, that the coefficients should be considered with respect to the intensive variables, P , T , and μ . It is apparent, therefore, that eqs (1) and (2) should be reexamined in this coordinate system.

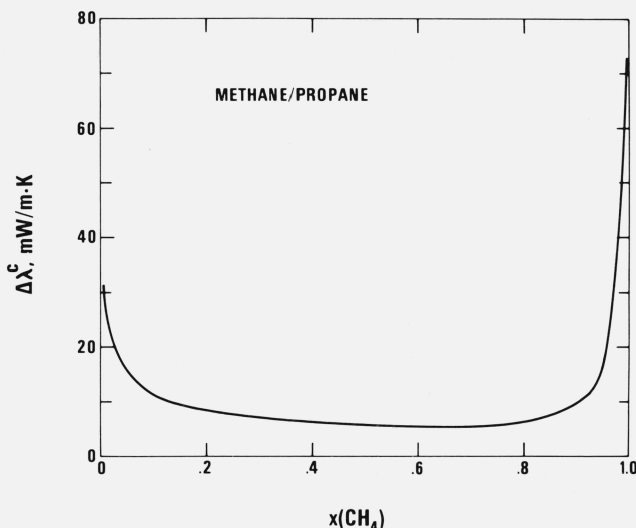


FIGURE 1. The critical excess thermal conductivity coefficient, $\Delta\lambda^c$; along the plait point curve for a methane/propane mixture, calculated by the method described in references [3] and [9].

An order-of-magnitude value for the thermal conductivity of this mixture in the absence of any critical point anomaly is ~ 50 mW/m·K.

5. References and Note

- [1] Rowlinson, J. S., *Liquids and Liquid Mixtures* (Butterworth, 1971). Second Edition; Byers Brown, W., *Phil. Trans.* **A250**, 175 (1957).
- [2] Mo, K. C., and Gubbins, K. E., *Chem. Eng. Commun.* **1**, 281 (1974); *Molecular Physics*, **31**, 825 (1976).
- [3] Hanley, H. J. M., *Cryogenics*, **16**, 643 (1976).
- [4] Van Beijeren, H., and Ernst, M. H., *Physica* **70**, 225 (1973).
- [5] Filippov, L. P., *Int. J. Heat Mass Transfer* **11**, 342 (1968).
- [6] Mistura, L., *Il Nuovo Cim.* **12**, 35 (1972); *J. Chem. Phys.* **62**, 4571 (1975).
- [7]engers, J. V., in *Transport Phenomena—1973* (AIP Press, 1973), Kestin, J., Editor.
- [8] Hicks, C. P., and Young, C. L., *Chem. Revs.* **75**, 119 (1975).
- [9] Hanley, H. J. M., *Proc. 7th Symp. on Thermophysical Properties* (ASME) (1977).
- [10] According to Mistura, $\Delta\lambda^c$ is zero for a mixture because of a cancellation between the critical parts of γ^* and $\beta^* \delta^* / \alpha^*$ of equation (6). In other words, k_T^* in the vicinity of a critical point is not negligible.
- [11] Griffiths, R. B., and Wheeler, J. C., *Phys. Rev.* **A2**, 1947 (1970); Leung, S. S., and Griffiths, R. B., *Phys. Rev.* **A8**, 2670 (1973); Saam, W. F., *Phys. Rev.* **A2**, 1461 (1970).