

Experimental evidence of a minimum in the thermal conductivity against composition curve for the He-HD mixture

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where the tensor $\mathbf{M}(\omega)$ is given in figure 1(d). This result compares with equation (11) of III. As in III each term contains the exponential factor which comes from (10); but now a heavy line represents $\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega)$ and the integrations are taken over all space. The combination of terms at order p is determined by equation (13). Note particularly that (16) contains the \mathcal{Y} functions and not the Ursell functions simply. Therefore the division, in III, of terms into surface-independent terms controlled by Ursell functions and 'surface terms' does not sufficiently categorize the terms: 'surface terms' remain at fourth and higher orders in (16). But these all converge because of the combination of Ursell functions and photon propagators. Thus the screening process is entirely due to all of the surface-dependent 'surface terms', which do not have this property. Then (16) is part of a translationally invariant theory with \mathbf{k}_0 and \mathbf{u} orthogonal but otherwise with arbitrary directions.

This analysis also enables us to report that the extended Einstein equation of IV is certainly valid up to $O(n^4\alpha^4(\omega))$ and removes the qualification beyond $O(n^3\alpha^3(\omega))$ noted in IV.

The details of this work will appear in the series of papers entitled 'Many-body optics' (see already I, II, Bullough 1970 to be published).

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4th February 1970

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Experimental evidence of a minimum in the thermal conductivity against composition curve for the He-HD mixture

Abstract. The thermal conductivity against composition curve for a He-HD mixture at 297 K shows a well-pronounced minimum giving a λ value for the equimolar mixture lower by about 4% than that of both the pure components. Although such behaviour is quite exceptional there is no reason to consider it as anomalous.

Recently several sets of experimental data have been published indicating that a slight minimum in the thermal conductivity against composition curve might occur for some binary gaseous mixtures. In this respect especially, the He-H₂ system has been investigated thoroughly (Barua 1960, Hansen *et al.* 1964, Neal *et al.* 1966, Mukhopadhyay and Barua 1967, Tondon *et al.* 1967, Minter 1968). The experimental data scatter considerably, leading to some confusion on the depth (Neal *et al.* 1966, Mukhopadhyay and Barua 1967), and even on the existence (Barua 1960, Tondon *et al.* 1967) of the dip. New measurements (Cauwenbergh and Van Dael to be published) indicate that the minimum is real but not larger than 0.5%: this result confirms the data obtained by Hansen *et al.* (1964) and by Minter (1968) and agrees also, within the error limits, with those of Tondon *et al.* (1967).

A similar very small minimum has been reported in Ar-N₂ and Ar-O₂ mixtures (Mukhopadhyay and Barua 1967): these data are so far not confirmed by other experiments.

A qualitative explanation of these so-called 'anomalous minima' has been given by invoking rotational-translational relaxation phenomena (Mukhopadhyay and Barua 1967).

We wish to point out that minima in λ_{mix} may occur owing to rather trivial reasons.

The thermal conductivity of a monatomic-diatomic mixture can be calculated using the Hirschfelder-Eucken expression

$$\lambda_{\text{mix}} = \lambda_{\text{monomix}} + (\lambda_2 - \lambda_{2\text{mono}}) \left(1 + \frac{x_1 D_{22}}{x_2 D_{12}} \right)^{-1} \quad (1)$$

with the usual meaning of the symbols (Hirschfelder *et al.* 1967).

Numerical results obtained using equation (1) have to be interpreted with some caution: the term λ_{monomix} can only be calculated in the first approximation, which is for the equimolar mixture in general too low by an amount of 1 or 2% (Van Dael and

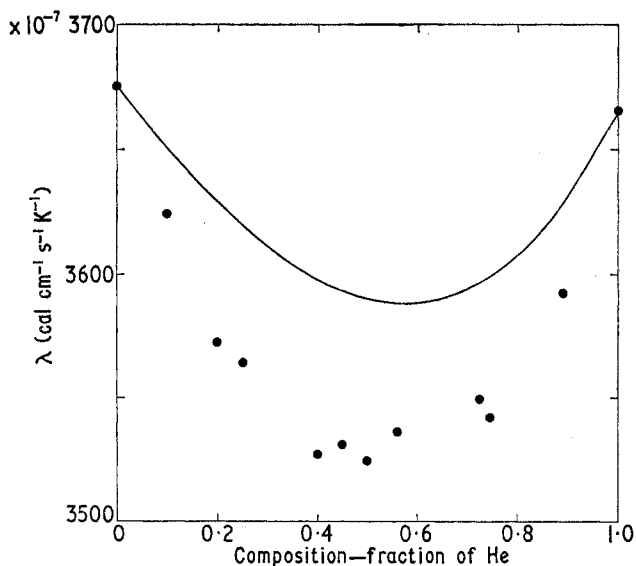


Figure 1. Experimental coefficients of thermal conductivity in He-HD at 297 K compared with the theoretical curve according to equation (1).

Cauwenbergh 1968). Part of this error can be due to the usual rather arbitrary choice of the combination rules for the potential-energy functions between non-identical molecules. Furthermore, the splitting up of the total heat transport into a separate translational and rotational part is only realistic if transitions between both energy forms are impossible.

More elaborate expressions obtained by Monchick *et al.* (1965) include the effect of a non-zero transition probability in terms of the collision number Z . For the hydrogen isotopes this Z is large and the corrections due to the relaxation effects are small compared with the uncertainties introduced in λ_{monomix} . A straightforward evaluation of both terms in the right-hand side of equation (1) suggests that a minimum could occur if the difference $\lambda_1 - \lambda_2$ is small compared with $\lambda_1 - \lambda_{2\text{mono}}$. The He-HD mixture fulfils this condition: it has been investigated in order to check this prediction.

Experimental data at 297 K are given in figure 1. The experimental technique has been described already (Van Dael and Cauwenbergh 1968). The purity of the gas HD is better than 99%. As expected, a well-pronounced dip occurs: the depth is about 3.9% of λ_{He} . Values of λ_{mix} calculated according to equation (1) agree qualitatively well and show anyway a clear minimum.

So there is no reason to consider the minimum itself as an anomalous effect: its appearance depends in the first place on a somewhat special and accidental relation between the absolute values of λ_1 , λ_2 and $\lambda_{2\text{mono}}$. For the He-H₂ mixture the same interpretation seems to be valid; at room temperature the minimum is so small that the approximations and the uncertainties involved in the calculations according to equation (1) may mask it partly or completely. However, this is probably not very relevant and not a sufficient reason to invoke anomalous effects.

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