ABSTRACT

The Kirkwood-Eisenschitz and Rice-Allnatt theories of transport processes lead to the determination of the molecular distribution functions of a non-uniform liquid, and so to the evaluation of the coefficient of viscosity. Problems arising from these procedures are examined in the present thesis.

Numerical solutions of the equation determining the radial distortion $u(r)$ of the equilibrium distribution function are obtained using a mean pair potential curve for carbon tetrachloride.

The radial distortion must decrease with the intermolecular forces of the liquid, since the distortion is zero for a flowing gas. It is shown that the radial distortion selected by the 'strong' boundary condition of Eisenschitz ($r^3 u(r) \to 0$ as $r \to \infty$) fulfils this requirement. The 'weak' boundary condition of Kirkwood, Buff and Green ($r^2 e^{-\Psi} du/dr \to 0$ as $r \to 0$) is seen to select a distortion which does not satisfy the requirement, and it is concluded that the weak condition does not select the appropriate radial distortion.

The distortion selected by the boundary condition of Lowry, Rice and Gray ($r^2 e^{-\Psi} du/dr \to 0$ as $r \to \sigma$), appropriate to the Rice-Allnatt theory, is shown to be identical with the distortion selected by the strong boundary condition at all values of r greater than the rigid core diameter σ.

The hypothesis is made that the radial distortion changes sign at each of the points of vanishing of the mean pair

intermolecular force. This hypothesis is seen to eliminate the large negative contribution to the viscosity integral, and is shown to lead to the Kirkwood-Eisenshitz and Rice-Allnatt theories determining coefficients of viscosity of the same order of magnitude.

The value of the viscosity coefficient is seen to decrease with an increase of temperature. It is found that thermal expansion does not introduce any exponentially dependent factor into the temperature dependence of the coefficient of viscosity.