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1972 J. Phys. A: Gen. Phys. 5 L37

(http://iopscience.iop.org/0022-3689/5/3/002)

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Comments on the theoretical derivation of Wada's and Rao's relations

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MS received 20 October 1971, in revised form 31 January 1972

Abstract. It is pointed out that the derivation made by Mathur *et al* leading to the relations of Wada and Rao, in effect, employs only the repulsive term of the Lennard–Jones potential. An alternative derivation due to Schuyer, also leading to the relations of Wada and Rao, duly makes use of both terms.

In a recent publication, Mathur *et al* (1971) have derived expressions relating the sound velocity C, density ρ, adiabatic compressibility χ_s and molecular weight M of a liquid, starting from the equation of state

$$p = \frac{kT}{v} - \frac{\partial\phi}{\partial v} \tag{1}$$

where v is the volume per molecule, and

$$\phi = -\alpha v^{-\mu} + \beta v^{-\nu}. \tag{2}$$

From this it follows at once that:

$$\frac{v}{\chi_T} = \frac{v}{\gamma\chi_s} = kT + \beta\nu(\nu+1)v^{-\nu} - \alpha\mu(\mu+1)v^{-\mu} \tag{3}$$

(their equation (5)), where χ_T is the isothermal compressibility and $\gamma = \chi_T/\chi_s = C_P/C_V$. They show that in this expression kT may be neglected, and then proceed to derive a complicated relation between $d\chi_s/dT$ (assuming γ constant) and dv/dT. Integrating this expression again, they find

$$\frac{1}{\chi_s} \propto v^{-\lambda} \qquad \text{that is} \qquad \frac{1}{\chi_s} \propto \rho^{\lambda} \tag{4}$$

where λ is a constant, and they then compare this result with Wada's relation, $M\chi_s{}^{-1/7}/\rho$ = constant. However, their derivation of (4) is erroneous, because the equation to be integrated contains a function $K(v)$ which they have treated as a constant. The actual relationship between χ_s and v is of course given on this model by (3). In particular, they find that if $K = 1$, $\lambda = \nu+1$, but it is easily seen that setting $K = 1$ is equivalent to neglecting completely the last term in (3), and in this case the result (4) with $\lambda = \nu+1$ follows at once.

They also discuss Rao's relation, $MC^{1/3}/\rho$ = constant, but this is not independent of Wada's relation: if

$$\frac{M\chi_s{}^{-1/7}}{\rho} = A$$

say, it follows at once that:

$$\frac{MC^{1/3}}{\rho} = \frac{A^{7/6}}{M^{1/6}}.$$

It may also be useful to point out that similar relations albeit differently derived, have been obtained by Schuyer (1959) from the L–J (6:n) potential. These results are

$$\frac{M\chi_s{}^{-3/m+n+4}}{\rho} = \text{constant} \tag{5}$$

$$\frac{MC^{6/m+n+1}}{\rho} = \text{constant} \tag{6}$$

which promptly reduce to Wada's and Rao's empirical relations for $n = 11$. Whereas in this derivation both the attractive and repulsive terms find their due place, the value of the exponent of the repulsive term is 11 in comparison to 18 ($\nu = 6$) taken by Mathur *et al.* The more commonly used values of n are around 12.

One of us (OS) wishes to thank the University Grants Commission, New Delhi for the award of a fellowship.

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