

$$dg = \dot{g}d\theta = [\alpha\dot{x} + \frac{1}{2}\beta\dot{y}] \dot{x}d\theta + [\frac{1}{2}\beta\dot{x} + \gamma\dot{y}] \dot{y}d\theta \quad (2.3)$$

Then by assuming that $dx \equiv \dot{x}d\theta$ and $dy \equiv \dot{y}d\theta$ may be regarded as independent differentials in (2.3), the square bracket coefficients of (2.3) are compared with (1.1) to conclude that

$$X = \alpha\dot{x} + \frac{1}{2}\beta\dot{y} \quad ; \quad Y = \frac{1}{2}\beta\dot{x} + \gamma\dot{y}$$

from which

$$\dot{x} = \frac{\gamma X - \frac{1}{2}\beta Y}{(\alpha\gamma - \frac{1}{4}\beta^2)} \quad ; \quad \dot{y} = \frac{-\frac{1}{2}\beta Y + \alpha X}{(\alpha\gamma - \frac{1}{4}\beta^2)}$$

obey the reciprocity relation. This procedure is, of course, equivalent to identifying the square bracket coefficients

of \dot{x} and \dot{y} in (2.2) **individually** with X and Y in (1.2), and is clearly invalid for one could just as well have written (2.2) as

$$\dot{g} = [\alpha\dot{x} - \beta\dot{y}] \dot{x} + [\gamma\dot{y}] \dot{y} \quad (2.4)$$

and concluded by the same argument the asymmetrical form

$$X = \alpha\dot{x} + \beta\dot{y} \quad ; \quad Y = \gamma\dot{y}$$

The difficulty with the procedure is that in (2.1) there is but one independent variation, that of the time parameter θ . The source of the difficulty may be traced

to the fact that (2.1) with \dot{g} positive definite is not a proper statement of the postulate of irreversible thermodynamics. Rather, it is necessary to proceed from (1.2)

with the postulate that the fluxes, \dot{x} and \dot{y} are linear in the affinities, X and Y , to deduce (2.1). Obviously the values of α, β, γ are determined by the symmetrical portion of the phenomenological matrix alone, and no amount

of manipulating the \dot{g} forms can yield conclusions about the remainder of the phenomenological matrix. Although

we have the restriction that \dot{g} is positive definite, there

is nothing to say that \dot{g} be an "even function" of \dot{x} and \dot{y} .

Finally, your authors seem not to have recognized that if molecular models are even conceivable which violate microscopic reversibility and yet are compatible with the phenomenological approach, one need go no further to conclude that the macroscopic theory per se has no more inherent capability of predicting reciprocal relations than it has of predicting numerical values of transport coefficients, short of direct measurement.

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