

This agrees with the relation analogous to (5), and the corresponding T variation, only if T is very low (it being only in this circumstance that the weak long range part of the interaction exercises a controlling influence). However the discrepancy is slight: a $T^{2/3}$ instead of a $T^{1/2}$ variation when T is high.

¹J. Troe, *J. Chem. Phys.* **66**, 4758 (1977).

²D. R. Bates, *J. Phys. B* **12**, 4135 (1979) and **13**, 2147 (1980).

³E. Herbst, *J. Chem. Phys.* **72**, 5284 (1980).

⁴A. Dalgarno in *Interactions between Ions and Molecules*, edited by P. Ausloos (Plenum, New York, 1974), p. 341.

⁵D. R. Bates, *Proc. Roy. Soc. London Ser. A* **360**, 1 (1978).

COMMENTS

The significance of Weinhold's length

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Weinhold¹ proposed that a metric for the space of thermodynamic states is $\eta_{ij} = \partial^2 U / \partial X_i \partial X_j$, where X_i and X_j are extensive variables. Here we present an interpretation of the physical significance of this quantity as a metric, and clarify the two different ways in which η_{ij} has been used. The usual interpretation² of η_{ij} is as a second fundamental form, giving the "distance" between the surface of energy U , a function of the extensive variables $X_1 = S, X_2, \dots, X_n$,

$$U = U(X_1, \dots, X_n), \quad (1)$$

and the plane tangent to this surface at U_0 , where η_{ij} is evaluated. Thus, for a displacement of the system from the state specified by X_1^0, \dots, X_n^0 to the state at X_1, \dots, X_n , the difference between U and the plane tangent to U at U_0 , is, to second order,

$$U - U_0 = \frac{1}{2} \sum_{i,j} \frac{\partial^2 U}{\partial X_i \partial X_j} (X_i - X_i^0)(X_j - X_j^0). \quad (2)$$

Because the value of this form is the "distance" between the point (X_1, \dots, X_n, U) and the tangent plane, it can be identified as the availability of the system that can come from its displaced state into equilibrium with an environment at (X_1^0, \dots, X_n^0) .³ In this regard, η_{ij} is a second fundamental form.

Weinhold showed¹ that the laws of thermodynamics assure that η_{ij} also has the positivity required of a metric or first fundamental form on the surface of thermodynamic states.⁴ This property enabled him to re-

derive thermodynamic relations using simple geometric arguments.

Equation (2) shows that the length computed with η_{ij} treated as a second fundamental form is the availability. More precisely, when the displacements $(X_i - X_i^0)$ are small enough for Eq. (2) to hold, *as they are for fluctuations*, $\frac{1}{2} \sum \eta_{ij} (X_i - X_i^0)(X_j - X_j^0)$ gives the availability. This is the well-established physical interpretation of η_{ij} taken locally, i.e., in the vicinity of a single point on the surface.

Next we examine the physical significance of the lengths of paths based on η_{ij} as a metric taken globally. This interpretation follows from the general relation between length and metric, and from using η_{ij} as Weinhold does, as a first fundamental form. We shall see that the result is a change of velocity characteristic of the type of path.

Consider for simplicity a system of one component so $X_1 = S$ and $X_2 = V$ are the only independent extensive variables. Suppose further that the trajectory of the system is given parametrically as $S = S(\xi)$, $V = V(\xi)$. Then the length of the path from the state p_0, V_0 to p_1, V_1 is

$$L = \int_0^1 \left[\eta_{11} \left(\frac{dS}{d\xi} \right)^2 + 2\eta_{12} \frac{dS}{d\xi} \frac{dV}{d\xi} + \eta_{22} \left(\frac{dV}{d\xi} \right)^2 \right]^{1/2} d\xi. \quad (3)$$

Dimensionally, L is the square root of energy, or, if U is given as specific energy (energy per unit mass), then L has the dimensions of velocity.

To illustrate what L is, consider an ideal gas, for which

$$\eta = \begin{bmatrix} T/C_v & -p/C_v \\ -p/C_v & \gamma p/V \end{bmatrix},$$

the heat capacities are constant, $C_p - C_v = R$ and $C_p/C_v = \gamma$. For convenience, we define $\theta = mC_v/R$, half the number of quadratic degrees of freedom apart from the particle mass scaling factor m . A reversible or endoreversible⁵ process at constant volume gives

$$L^{(v)} = \int_0^1 \left[\frac{T}{C_v} \right]^{1/2} dS \\ = 2\sqrt{C_v} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta}{3}} [v_1^2{}^{1/2} - v_0^2{}^{1/2}].$$

Note that v_1 and v_0 are gas-kinetic velocities at T_1 and T_0 , respectively. A reversible process at constant pressure gives

$$L^{(p)} = \int_0^1 \left[\frac{T}{C_v} \left[\frac{C_p}{V} \right]^2 \left(\frac{\partial V}{\partial \xi} \right)^2 - \frac{2p}{C_v} \frac{C_p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 + \frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi \\ = \int_0^1 \left(\frac{\gamma}{\gamma-1} \right)^{1/2} \sqrt{\frac{p}{V}} dV \\ = 2\sqrt{C_p} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta+1}{3}} [v_1^2{}^{1/2} - v_0^2{}^{1/2}],$$

where we assume $C_p = (\theta+1)R/m$.

A reversible process at constant temperature gives $L=0$, as expected because U is a function only of T .

A reversible adiabatic process gives

$$L^{(s)} = \int_0^1 \left[\frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi = \frac{2}{\gamma-1} \sqrt{\gamma p_0 V_0} \left[1 - \left(\frac{p_1}{p_0} \right)^{(\gamma-1)/2\gamma} \right],$$

which is the change in flow velocity of a gas undergoing

an isentropic expansion, e.g., in a rarefaction wave.⁶ In general, L is a change in a mean velocity, but characteristic of the constraints defining the path of the integral along which the length is measured. Incidentally for a solid whose equation of state is $V = V_0[1 + \alpha(T - T_0) - kp]$, $\eta_{11} = T/C_v$ as for the ideal gas, $\eta_{12} = \alpha T/kC_v$, and $\eta_{22} = (\alpha^2 T/kC_v) + 1/V_0 k$. The length L for an isochoric process is the same as for the gas; the length L for an isentropic process is of the form $L = \int [At + B]^{1/2} dV$.

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¹(a) F. Weinhold, *J. Chem. Phys.* **63**, 2479 (1975); (b) *ibid.* **65**, 559 (1976).

²P. Salamon, Doctoral Dissertation, The University of Chicago (1978) discusses this point specifically; standard texts on differential geometry, such as M. M. Lipschutz, *Differential Geometry* (McGraw-Hill, New York, 1969) or W. C. Graustein, *Differential Geometry* (Dover, New York, 1966), give general discussions of first and second fundamental forms. L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, Mass., 1966) discusses the subject and designates η_{ij} as the "stiffness" form.

³J. W. Gibbs, *Collected Works*, Vol. 1 (Yale Univ., New Haven, 1948); J. H. Keenan, *Thermodynamics* (MIT, Cambridge, Mass., 1970).

⁴The positivity of η fails at phase transitions; where these occur, there are lines along which η vanishes, which correspond to transformation of material from one phase to another without disrupting the equilibrium between system and environment. For further discussion see Ref. 1(b).

⁵"Endoreversible" is a term introduced by M. Rubin, *Phys. Rev. A* **19**, 1272 (1979) to characterize a thermodynamic system whose working substance undergoes reversible transformations, independent of whether the system is in equilibrium with its surroundings.

⁶E. F. Greene and J. P. Toennies, *Chemical Reactions in Shock Waves* (Edward Arnold, London, 1969), p. 109.

Comment on the structure of a simple liquid solvent near a n -butane solute molecule^{a)}

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The purpose of this comment is to discuss the distribution of solvent molecules around two different conformations of an n -butane solute molecule. In a recent pair of publications,^{1,2} we have reported computer sim-

ulation results for a fluid containing one model n -butane solute species and 123 Lennard-Jones solvent particles chosen to mimic liquid CCl_4 . The work presented here extends those studies by examining the distribution of