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 exerts a controlling influence). However the discrepancy is slight: a $T^{2/3}$ instead of a $T^{1/2}$ variation when $T$ is high.


COMMENTS

The significance of Weinhold’s length

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Weinhold proposed that a metric for the space of thermodynamic states is $\eta_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j}$, 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 $\eta_{ij}$ has been used. The usual interpretation of $\eta_{ij}$ is as a second fundamental form, giving the “distance” between the surface of energy $U$, a function of the extensive variables $X = X_1, X_2, \ldots, X_n$,

$$U = U(X_1, \ldots, X_n),$$

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

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

Because the value of this form is the “distance” between the point $(X_1, \ldots, X_n, U)$ 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 $(X_1^0, \ldots, X_n^0)$. In this regard, $\eta_{ij}$ is a second fundamental form.

Weinhold showed that the laws of thermodynamics assure that $\eta_{ij}$ also has the positivity required of a metric or first fundamental form on the surface of thermodynamic states. This property enabled him to derive thermodynamic relations using simple geometric arguments.

Equation (2) shows that the length computed with $\eta_{ij}$ 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 $\eta_{ij}$ 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 $\eta_{ij}$ as a metric taken globally. This interpretation follows from the general relation between length and metric, and from using $\eta_{ij}$ 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 $p_0$ to $p_1$, $V_1$ is

$$L = \int_0^1 \left[ \eta_{11}(dS/d\xi)^2 + 2\eta_{12}(dS/d\xi)(dV/d\xi) + \eta_{22}(dV/d\xi)^2 \right]^{1/2} d\xi.$$  (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.
Comment on the structure of a simple liquid solvent near a n-butane solute molecule

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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, we have reported computer simulations results for a fluid containing one model n-butane solute species and 123 Lennard-Jones solvent particles chosen to mimic liquid CCl₄. The work presented here extends those studies by examining the distribution of