

Numerical Methods Used in the Significant Structure Theory of Liquids

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A method for calculating thermodynamic properties of pure liquids according to the significant structure theory of liquids is presented. This involves an iterative method for finding a common tangent at two points on a complex surface. Also, a generalization of Gauss's *regula falsi* method is developed to solve sets of nonlinear equations.

I. INTRODUCTION

During the past decade the significant structure theory of liquids has been developed by Henry Eyring and his coworkers [1]. The same basic theory has been applied to a wide range of liquids, from the ideal gases [2] to water [3]. It has been successfully used to describe thermodynamic and transport properties of liquids [4] and mixtures [5].

Along with the development of the theories several specific numerical techniques have been developed, but have not been reported. In this paper we will present these methods.

II. VAPOR PRESSURE

The significant structure theory of liquids provides a description of the liquid state through use of a partition function f_ℓ .

The thermodynamic properties are based on the equation

$$A = -RT \ln f_\ell, \quad (1)$$

where A is the Helmholtz free energy. The partition function is dependent upon temperature and volume so that the helmholtz free energy can thus, be considered as a surface with temperature and volume as independent variables. The partial derivatives and curvature of this surface are the other thermodynamic variables.

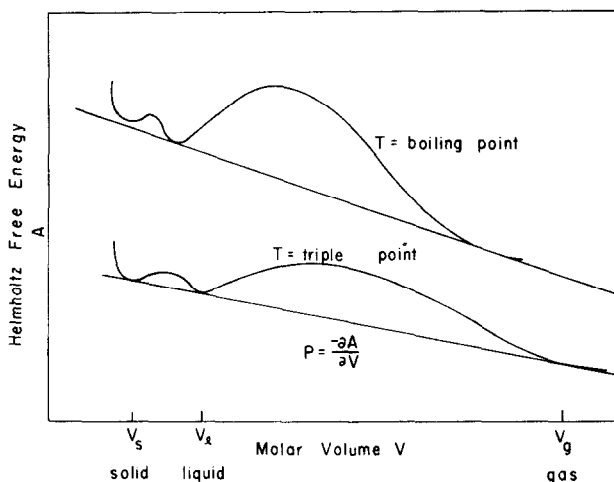


FIG. 1. Helmholtz free energy isotherms at melting and boiling points. Straight lines are the vapor pressure tangents.

The details of the significant structure theory need not concern us in this discussion. All we need to know is the general shape of the A surface. Figure 1 diagrammatically shows several isotherms as they cut the A surface. In general, there are three dips but only two minima. They occur at the solid volume V_s , the liquid volume V_l , and the gas volume V_g . The slope of these isotherms at any point is the pressure, since

$$(\partial A / \partial V) T = -p. \quad (2)$$

The equilibrium vapor pressure is represented by a common tangent between the liquid volume and the gas volume. At each point of tangency the pressure is necessarily equal. One of the major computational problems of significant structure theory is finding this tangent. Once the vapor pressure tangent is known, the molar volume is specified and so are all of the other thermodynamic variables since they are functions of temperature and volume.

Several numerical methods have been developed to find this tangent. We will describe a Newton's method of slope matching which has been the most widely used method. A successful trial and error hunting method has also been developed, but it is slower than the quadratic convergence of the Newton's method.

III. NEWTON'S METHOD FOR SLOPE MATCHING

To find the common tangent between the gas and liquid volumes (Fig. 1) the following iterative procedure is followed.

At the initial guesses of values of the gas and liquid volumes V_g^i and V_ℓ^i the helmholtz free energy is calculated A_g , A_ℓ . An approximate vapor pressure is calculated by

$$p_a^i = -(A_g^i - A_\ell^i)/(V_g^i - V_\ell^i), \quad (3)$$

which is the slope of a line connecting the initial points. Next the pressure P_c is calculated at each of these points by evaluating $-(\partial A/\partial V)_T$. If the calculated pressures are not the same as the approximate slope the line is not a common tangent.

Improved values of V_g and V_ℓ are found by finding the points at which the calculated pressure P_c is equal to the approximate vapor pressure P_a . This is done by a Newton's method iteration on the volume

$$V_2 = V_1 - (P_a - P_c)/(\partial P/\partial V)_T, \quad (4)$$

where $(\partial P/\partial V)_T$ is the second derivative of A with respect to volume. Usually less than 20 iterations are necessary in order to get a 5-6 significant figure matching of P_a and P_c .

With the improved values of V_g and V_ℓ the approximate vapor pressure is once again calculated [Eq. (3)], and the procedure repeated if the new line is not a tangent. Usually less than 10 iterations of this type are necessary to find a tangent that has 4-5 significant figures.

The region of convergence is bounded by the region where $(\partial P/\partial V)_T$ is negative. In the liquid volume region this may be rather small so a careful initial guess of V_ℓ is necessary. Usually the improved value of the volume V_2 is checked to be sure it remains within the region of convergence. The region of convergence for the gas volume is quite large. The only consideration is that V_g is large enough to insure that Eq. (3) has a positive result.

The calculation is performed on a UNIVAC 1108 computer and is written in double precision FORTRAN V [6]. This means the calculation is done with 64-bit or 16-decimal place accuracy. This is necessary because during the iteration of the volume [Eq. (4)] very small changes of the volume are necessary in order to match P_a and P_c . The pressure changes very rapidly in the region of the liquid minimum. So that a small change in the volume will change the pressure from positive to negative. Using this precision we have been able to converge to vapor pressures of 1.0×10^{-10} atm. When the approximate pressure P_a is smaller the increment of the volume is less than 10^{-14} cc and convergence is impossible.

IV. PARAMETER ADJUSTMENT

The second computational problem facing significant structure theory is the refinement of parameters. The properties of a liquid as described by the significant

structure model are dependent upon five parameters. Good estimations of these parameters can easily be made, but for complex liquids some refinement is necessary. In many cases these slight adjustments can be made by trial and error, but not in all cases.

The partition function for a simple liquid is written as follows:

$$f_l = f_s^{N(V_s/V)} \cdot f_g^{((V-V_s)/V)N}, \quad (5)$$

$$f_s = \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \left(\frac{V - V_s}{V_s} \right) \exp \left[\frac{-aE_s V_s}{(V - V_s)RT} \right] \right), \quad (6)$$

$$f_g = (2\pi mkT/h^2)^{3/2} (eN/V), \quad (7)$$

where V , T , N , R are, respectively, the molar volume, temperature, Avogadro's number, and the gas constant; m , h , k are, respectively, the mass of a molecule, Planck's constant, and Boltzmann's constant. The parameters are a , n , E_s , V_s , and θ .

The parameter a is a dimensionless constant that is a measure of the cooperative effect on the positional degeneracy. The parameter n is another dimensionless constant that is a measure of the amount of positional degeneracy possible. For spherical molecules it is approximately equal to the number of neighboring positions or about twelve. The parameters E_s , V_s , and θ are the energy of sublimation, molar volume of the solid at the melting point and the Einstein characteristic temperature.

Good estimates of E_s , V_s , and θ are the experimentally determined values for the solid state. Since the Debye characteristic θ_D is usually tabulated, the following rule of thumb is used.

$$\theta_E = \frac{2}{3}\theta_D \quad (8)$$

Estimates for a and n can be made by assuming that the liquid has the same degeneracy as a simple liquid such as argon. The parameters are then scaled for a difference in hole size and cooperative effect. Thus, the ratio n/V_s should be constant and in fact for the inert gases, methane and nitrogen the ratio is nearly constant with an average of 0.473. In a similar way the ratio $aE_s V_s / RT_{mp}$ is also a constant with an average of 1.55. Since the values of a and n have been calculated theoretically for argon [7], the values for argon are used.

If the melting point T_{mp} energy of sublimation E_s and volume of the solid V_s are known, the parameters a and n can be estimated.

$$n_{cpd} = \left(\frac{n}{V_s} \right)_{\text{Argon}} V_s(cpd) = 0.432 \times V_s(cpd) \quad (9)$$

$$a_{cpd} = \left(\frac{aT_{mp}V_s}{RT} \right)_{\text{Argon}} \cdot \left(\frac{RT_{mp}}{E_s V_s} \right)_{cpd} = 1.472 \left(\frac{RT_{mp}}{E_s V_s} \right)_{cpd} \quad (10)$$

There are a number of other methods that give an estimated set of parameters. They are the benzene technique [8], two-temperature technique [8], Seoul method [3], and the simplified method [9]. They are all similar in that they start with several equilibrium conditions expressed in terms of the significant structure model partition function. The resulting equations are nonlinear and various approximations are made in order to extract the solutions. All of these methods provide good approximate parameter sets, but they suffer from the necessary approximation and are usually applicable to certain types of liquids using fixed equilibrium conditions. We will describe a more general method that gives a refined parameter set.

V. REGULA FALSI

Any thermodynamic property at a fixed temperature and volume is a function of the parameters.

$$R_{ki} = F_k(\mathbf{Y}_i) \quad (11)$$

$$\mathbf{Y}_i = \begin{pmatrix} y_{i1} \\ y_{i2} \\ \vdots \\ y_{in} \end{pmatrix} \quad (12)$$

where R_{ki} is an observable property, F_k is the significant structure model expression for the property and \mathbf{Y}_i is a column vector of the parameters y_{ij} . If P_k is the experimentally observed value of the property we want the following conditions to hold:

$$D_k(\mathbf{Y}_i) = P_k - F_k(\mathbf{Y}_i) = 0. \quad (13)$$

There will always be enough thermodynamic properties so that a set of n equations (Eq. 13) in n unknowns can be formed. The solution of this set of equations will be the desired parameters.

As stated previously, this set of equations (13) is nonlinear and cannot be solved analytically. We are forced to use a numerical method. A generalization of Newton's method would work, but a Jacobi matrix of the partial derivatives must be formed. Because the expressions F_k are themselves derivatives of complex functions these derivatives with respect to the parameters are quite formidable. Also, any change in the partition function would require these to be reformed.

Another method known as the regula falsi or secant method is available [10]. It has not, as far as the authors could determine, been generalized for more than one variable. The criterion for convergence and other mathematical questions also have not been thoroughly investigated. Kawalik and Osborne [11] present a discussion for the *Gauss Algorithm* which is similar to this approach.

For the cases we have studied there have been no convergence problems.

The regula falsi method is based on a linear approximation to the function. The solution of the equation set (13) is a minimum of the D_k surface. To find the minimum a plane approximation in Y_i space is formed through the $n + 1$ points Y_i . Where this plane crosses zero is the improved point. One of the old points is discarded and a new plane formed. The procedure is repeated until the minimum is found.

Assume that $n + 1$ approximate solutions to equation set (13) are known:

$$\mathbf{X} = \{\mathbf{Y}_1 \mathbf{Y}_2 \cdots \mathbf{Y}_{n+1}\}, \quad (14)$$

\mathbf{X} is the n by $n + 1$ matrix of these approximate points. Then make a linear approximation to each function D_k .

$$D_k(\mathbf{Y}_i) = \sum_{j=0}^{n+1} Q_{ij} a_{jk}, \quad (15)$$

where

$$Q = \begin{pmatrix} 1 & y_{11} & y_{12} & \cdots \\ 1 & y_{21} & y_{22} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} = \begin{pmatrix} 1 & \mathbf{Y}_1^+ \\ 1 & \mathbf{Y}_2^+ \\ \vdots & \vdots \\ 1 & \mathbf{Y}_{n+1}^+ \end{pmatrix}.$$

There are $n + 1$ linear equations of the form $\mathbf{D}_k = \mathbf{Q}\mathbf{a}_k$ or $\mathbf{D} = \mathbf{Q}\mathbf{A}$ with $\mathbf{D} = (\mathbf{D}_1, \mathbf{D}_2, \dots, \mathbf{D}_{n+1})$ and $\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_{n+1})$. The function D_k must be evaluated for each approximate point Y_i . Since this is a linear set of equations, it is easily solved.

To find the next approximate set of parameters Y_{n+2} , the set of linear equations

$$\sum_{i=0}^n y_i' a_{ik} = 0 \quad \text{or} \quad \mathbf{X}\mathbf{a} = 0 \quad (16)$$

is where $\mathbf{X} = \mathbf{Y}_{n+2}$ solved for the new parameters y_i' . The point farthest away from the new point is discarded and the procedure repeated. Distance is measured as

$$d = \left(\sum_{i=1}^n (y_i' - y_{ki})^2 \right)^{1/2}. \quad (17)$$

Since this method involves only linear equations a general program can easily be written [6]. Only the functions D_k need to be changed if a different set of equations were to be solved.

In applying this method we have found that the best thermodynamic property set is vapor pressure P , molar volume V , and the entropy. This set is used to adjust E_s , V_s , and θ . The parameters a and n do not strongly affect the thermodynamic properties and are adjusted by finding the minimum values necessary for convergence in the vapor pressure calculation at the melting point. The three parameters may be considered simultaneously or independently solved. Somewhat better results are found if each parameter is solved for independently keeping the other parameters constant. The procedure is repeated until a self-consistent set is found. It is necessary to perform a vapor pressure convergence to calculate the thermodynamic functions, F_k .

TABLE I
Two-Dimensional Case Showing Convergence of E_s for Liquid Toluene

Iteration	E_s (cal/mole)	D^a (atm $\times 10^{-2}$)	$D/P^b(\%)$
1	11009.5	1.97	52.1
	11011.0	1.95	51.6
2	11011.0	1.95	51.6
	11161.7	0.329	8.7
3	11161.7	0.329	8.7
	11192.3	0.0597	1.58
4	11199.1	0.0019	0.05

^a See Eq. (13). The vapor pressure is used to adjust E_s .

^b This is the percentage error.

TABLE II
Example of Approach to Self-Consistent Set of Parameters for Toluene

Pass	θ (deg)	E_s (cal/mole)	V_s (cc)	C^a
initial	38.561	11009.5	92.068	—
1	39.701	11199.1	91.278	109.5
2	39.123	11097.6	91.212	58.6
3	39.415	11122.1	91.218	14.2
4	39.345	11116.2	91.217	3.45
5	39.362	11117.6	91.217	0.86
6	39.357	11117.3	91.217	0.22
7	39.359	11117.4	91.217	0.056
8	39.359	11117.3	91.217	0.014

^a Root mean square change defined as

$$C = \left[\sum_j \left(\frac{y_j^i - y_j^{i+1}}{y_j^{i+1}} \right)^2 \right]^{1/2}$$

An example of the *regula falsi* convergence is given in Table I. The parameter E_s for liquid toluene was adjusted to give the experimentally observed vapor pressure at a specified temperature and volume. The results of the complete calculation are summarized in Table II. During each pass each of the parameters was adjusted independently using the *regula falsi* iteration.

The procedure we have described is quite general and could be applied to other systems. We have not used any optimization such as least squares to refine the parameters. This is a parameter fixing method and should not be misunderstood to be a curve fitting procedure since the minimum number of experimental properties are used.

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