

VARIATIONAL THEORY OF MIXTURES

ESAM Z. HAMAD and G. ALI MANSOORI

Department of Chemical Engineering, University of Illinois
(Box 4348) Chicago, Illinois 60680

ABSTRACT

In the past the variational theory of mixtures due to Mansoori and Leland has been applied successfully to the calculation of excess properties of mixtures. In the present work the origin of the variational theory is discussed along with the important applications of the theory to pure fluid and mixture properties. The advances of the theory in performing mixture calculations are reviewed and analyzed. The review includes the area of simple fluid mixtures, for which the intermolecular potential energy function is well known, and the area of real fluid mixtures, where no explicit information about the potential function is available. The role of the reference fluid system and its effect on the predictive capability of the theory is also discussed. The use of the variational theory to obtain least upper and highest lower bounds to thermodynamic properties is described and some recent calculations involving infinite dilution thermodynamics are reported.

INTRODUCTION

In recent years a number of successful theories which deal with the problem of mixtures of simple fluids have been formulated. Almost all of these theories were first developed for pure fluids, and then later

extended to mixtures. The Integral-equation approximations such as Percus-Yevick theory (Percus and Yevick, 1958 ; Lebowitz, 1964 and Baxter, 1970), and the scaled-particle theory (Frisch, 1964 and Gibbons, 1970) represent a class of theories which are based on the distribution functions. Another approach is conformal solution theory which yields mixing rules for the intermolecular potential parameters of a hypothetical pure fluid. These parameters are then substituted in the reference fluid equation of state to calculate the mixture properties. The perturbation (Leonard, et al., 1970 and Weeks, et al., 1971) and variational theories (Mansoori and Leland, 1970) represent a class of successful theories which were tested for both pure fluids and mixtures. An advantage of using these theories in mixture calculations is the fact that no mixing rules are needed. In this work the advances in the variational theory of mixtures are reviewed, and new calculations for infinite dilution are reported.

ORIGIN OF THE VARIATIONAL THEORY

In the variational approach to the thermodynamic properties of fluids one attempts to find a relation between the properties of the system under study and a reference system with well known behavior. The basic relation in the variational approach is an inequality which gives an upper bound on the Helmholtz free energy. This relation, which is known as the Gibbs-Bogoliubov inequality, is given by:

$$A \leq A_0 + \langle U - U_0 \rangle_0 \quad (1)$$

where A is the Helmholtz free energy, U is the total configurational potential energy and $\langle \dots \rangle_0$ indicates the average or expectation value over the reference system configurations. The subscript "0" indicates the properties of the reference system. The inequality, eqn. (1) was first derived for the classical case by Gibbs (1902). His proof is based

essentially on the inequality

$$e^{-x} \geq 1 - x \quad \text{for all } x. \quad (2)$$

The above inequality can be verified by realizing that the function $f(x) = 1 - x - e^{-x}$ can not take negative values, because it has a negative derivative for $x < 0$, positive derivative for $x > 0$ and $f(0) = 0$. Later Bogoliubov extended eqn. (1) to the quantum case. Apparently he never published his work (Girardeau and Mazo, 1973), but it was given and attributed to him by Tolmachev (1960) and Girardeau (1964). In view of this history the inequality, eqn. (1) is called the Gibbs-Bogoliubov inequality. The same inequality was later rederived using a different method by Lukes and Jones (1968) and Mansoori and Canfield (1969a).

The Gibbs-Bogoliubov inequality gives an upper bound on the Helmholtz free energy. However, it can be modified to give the lower bound too. By interchanging the role of the original and reference systems one gets:

$$A_0 \leq A + \langle U_0 - U \rangle \quad (3)$$

where $\langle \dots \rangle$ indicates the expectation over the original system. The inequality, eqn. (3) can now be rearranged to read:

$$A \geq A_0 + \langle U - U_0 \rangle \quad (4)$$

The only difference between the inequalities, eqns. (1) and (4) is the expectation which is taken over the reference system in eqn. (1) and over the original system in eqn. (4). However, it is generally difficult to obtain the lower bound since the properties of the original system are usually not known.

Variational calculations based on the Gibbs-Bogoliubov inequality have found a large number of applications in the thermodynamic property

calculations of pure fluids and mixtures. For classical pure fluids the Gibbs-Bogoliubov inequality can be written in the following form:

$$A \leq A_0 + 2\pi N\rho \int_0^{\infty} (u - u_0)g_0 r^2 dr \quad (5)$$

where N is the number of molecules in the system, ρ is the density, u and u_0 are the binary interaction potential functions of the original and reference systems and g_0 is the radial distribution function of the reference system. The pair wise additivity assumption of the total potential function is necessary in deriving the above inequality.

Mansoori and Canfield (1969a) used eqn. (5) with the hard sphere fluid as the reference system to calculate the thermodynamic properties of Lennard-Jones fluids over a wide range of density and temperature. They used the average of the compressibility and the virial equations of state to get A_0 and the Wertheim (1963) expression for the Laplace transform of g_0 . To get the least upper bound they minimized the right hand side of eqn. (5) by varying the hard sphere diameter. This procedure gives very good agreement with the simulation data. A similar calculation was also done for the coexisting liquid and vapor phases (Mansoori and Canfield, 1970). Rosenfeld (1980) used the variational technique to calculate the equation of state for a number of simple fluids. He used the Lennard-Jones potential and included the quantum correction for light molecules such as hydrogen and deuterium.

Mansoori (1977), Rosenfeld (1980) and Rosenfeld and Baram (1981) applied the variational technique to pure soft-sphere ($u = \epsilon(\sigma/r)^n$) systems. Mansoori calculated the compressibility and Helmholtz free energy for soft-sphere fluid with $n=12$ for densities up to the freezing point. The variational theory results were in good agreement with the Monte Carlo simulation data of Hoover et al. (1970, 1971), especially at high densities. Rosenfeld and Baram (1981) used the Percus-Yevick virial entropy and g_0 to

arrive at a universal expression for the potential energy in the strong coupling regime. This expression is given by:

$$U_r/NkT = a_n \Gamma + b_n \Gamma^{1/4} - 1/2 \quad (6)$$

where $\Gamma = (4/3)(\pi\rho\sigma^3)^{n/3}/(kT/\epsilon)$, and a_n and b_n are constants which depend on the exponent n . Calculations based on eqn. (6) were compared to the Monte Carlo simulation data for $n=1,4,6,9,12$. It gives a good numerical accuracy especially for $n < 9$.

The variational technique has been shown to be very successful in the solid phase and the solid-liquid phase transition region. One of the early studies in this area was by Mansoori and Canfield (1969b). Rosenfeld et al. (1977) described the Mansoori-Canfield variational method as one of the simplest and easiest to apply in practice among similar theories. Young and Rogers (1984) described the variational procedure as the best theory for calculation of theoretical melting curves. Mansoori and Canfield (1969b) calculated the properties of the Lennard-Jones solid phase and the coexisting liquid and solid phases at different temperatures. Mansoori (1977) calculated the compressibility factor of a pure soft-sphere solid for $n=12$. Rosenfeld et al. (1977) incorporated the Kerley (1971) model in the Gibbs-Bogoliubov inequality to calculate the solid phase properties near the melting line. They obtained the densities of the liquid and solid phases and other thermodynamic properties near the phase transition of the Lennard-Jones and four soft-sphere potentials at four different temperatures. Their results agree very well with the Monte Carlo simulation data, except for the excess entropy which was about 8% too low. Additional studies in which the variational technique has been used in solid-liquid phase transition for pure components include those by Ross (1973), Buchanan (1974) and Rosenfeld (1975).

A number of investigators have used the variational technique to calculate the thermodynamic properties of liquid metals. A

pseudo-pair-potential is used to describe the net interactions in the system which are caused by the ions and the free electrons (Shimoji, 1977). For simple liquid metals, numerical evaluation of thermodynamic properties has been carried out by several investigators (Stroud and Ashcroft, 1972; Edward and Jarzynski, 1972; Watabe and Young, 1974 and others). In general the agreement with the experimental data is qualitatively reasonable. Mansoori et al. (1981) developed an analytic equation of state for liquid metals based on the variational theory.

Jedrzejek and Mansoori (1979) used the variational technique to develop analytic equations of state of a hard-core fluid with a Yukawa tail. The potential energy function for a hard-core fluid with one Yukawa tail is given by:

$$u(r^*) = \begin{cases} \infty, & r^* < 1 \\ -\epsilon/r^* \exp[-z(r^*-1)], & r^* > 1 \end{cases} \quad (7)$$

where $r^*=r/\sigma$ and σ is the hard-core diameter. Jedrzejek and Mansoori obtained an analytical form for the Helmholtz free energy when they used eqn. (7) and Wertheim's g_0 (1963) in eqn. (5). The minimization of the right-hand side of eqn. (5) yields an effective hard sphere diameter d , equal to the hard-core diameter σ . Comparison with the Monte Carlo simulation data of Henderson et al. (1978) for $z=1.8$ showed very good agreement. In a later paper Jedrzejek and Mansoori (1980) extended their work to a two-tail Yukawa potential. The working formulas are still analytic. The two-tail Yukawa parameters were chosen to give the best fit to the real argon potential. The results compared fairly well with the argon experimental data in light of the simplicity of the potential function.

Alem and Mansoori (1982) and Mansoori (1983) have used the variational theory to derive analytic equations of state for fluids with known and unknown intermolecular potentials. They started by minimizing the right hand side of the inequality, eqn. (5) for a hard sphere reference fluid. This

leads to:

$$[\partial(A_0 + \langle U - U_0 \rangle_0) / \partial d]_{T,\rho} = 0 \quad (8)$$

At the optimum diameter eqn. (5) can be written as:

$$A = A_0 + \langle U - U_0 \rangle_0 + \Delta \quad (9)$$

where Δ is the difference between the system Helmholtz free energy and the right-hand side of eqn. (5). Differentiating eqn. (9) with respect to temperature at constant density one gets:

$$[\partial A / \partial T]_{\rho} = [\partial(A_0 + \langle U - U_0 \rangle_0) / \partial T]_{\rho,d} + [\partial(A_0 + \langle U - U_0 \rangle_0) / \partial d]_{T,\rho} [\partial d / \partial T]_{\rho} + [\partial \Delta / \partial T]_{\rho} \quad (10)$$

Substituting eqn. (8) in eqn. (9) and realizing that $\langle U - U_0 \rangle_0$ does not depend on T for hard sphere fluid one arrives at:

$$-S_r = -S_{o,r} + [\partial \Delta / \partial T]_{\rho} \quad (11)$$

where S_r and $S_{o,r}$ are the residual entropies of the original system and the hard sphere fluid. If $[\partial \Delta / \partial T]_{\rho}$ is negligible, then eqn. (11) can be approximated as:

$$S_r \approx S_{o,r} \quad (12)$$

Eqn. (12) was also obtained as an inequality by Rosenfeld (1977). Alem and Mansoori used the Carnahan-Starling (1969) expression for $S_{o,r}$ in eqn. (12) and then solved for the effective hard sphere diameter d , in terms of S_r . They found that d can be accurately represented by a linear expression in ρ and $1/T$ which should minimize the right-hand side of eqn. (5). For polar fluids they used a potential function consisting of the Lennard-Jones,

dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interactions. For the non-additive part of the three body interactions they used the Axilrod-Teller expression. The resulting equation of state when tested in the liquid and vapor phases and in the critical region of methane and argon gives excellent agreement with the experimental data. Alem and Mansoori (1984b) also obtained very good agreement with the experimental data for a number of polar fluids. Alem and Mansoori (1981,1982) used a similar approach to derive an analytic equation of state based on the Yukawa potential function. This equation gives an accurate representation of the properties of methane in the liquid and vapor phases. Kerley (1980,1983) devised another technique to use the variational theory for real fluids where the potential energy function is usually unknown. Kerley (1983) used the zero-Kelvin isotherm of the solid to substitute for the missing information. He performed calculations for rare gases, for the hydrogen isotopes and other polyatomic molecules, and for liquid iron. His results agree well with experiment.

In addition to the hard-sphere, the soft-sphere fluid has been used as a reference system. Ross (1979) renormalized eqn. (5) to make the reference potential the inverse twelfth power; however, he continued using the hard sphere g_0 . Young and Rogers (1984) used the inverse twelfth power fluid as the reference system. For this purpose they used an accurate fit to the reference Helmholtz free energy, and tabulated accurate reference fluid radial distribution functions computed from a recent self consistent integral equation (Rogers and Young 1984). The results for Lennard-Jones, exponential-six, and $n=9,6$, and 4 inverse power potentials show good agreement in general, and excellent agreement at high pressure near the melting curve. Perturbation theories, such as Weeks-Chandler-Andersen, break down in this region.

Other applications of the variational theory to pure fluid properties include the areas of dielectric constant (Prager et al.,1970) and the self-diffusion coefficient and the shear viscosity (Rosenfeld, 1977)

VARIATIONAL THEORY OF MIXTURES

The Gibbs-Bogoljubov inequality was first applied to mixtures by Mansoori (1969) and Mansoori and Leland (1970). By assuming pair-wise additivity of the potential energy function they derived the following inequality for mixtures:

$$A \leq A_0 + 1/2 N\rho \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^{\infty} (u_{ij} - u_{ij,0}) g_{ij,0} 4\pi r^2 dr \quad (13)$$

In eqn. (13) c is the number of components in the system, x_i is the mole fraction of component i and $g_{ij,0}$ is the radial distribution function for the pair ij of the reference system.

In their work Mansoori and Leland (1970) calculated the excess properties of a mixture of Lennard-Jones fluids at zero pressure. The parameters of the Lennard-Jones potential were chosen to represent argon and krypton. They chose the binary mixture of hard spheres, with diameters d_{11} and d_{22} , as the reference system. For this system the Laplace transforms of the radial distribution functions $g_{ij,0}$ had been obtained by Lebowitz (1964). To obtain the least upper bound, and hence the best prediction of the excess properties of the original system (Lennard-Jones fluids mixture in this case) Mansoori and Leland minimized the right hand side of the inequality, eqn. (2) with respect to the diameters d_{11} and d_{22} . Their results showed excellent agreement with the Monte Carlo calculations of McDonald (1969).

Mansoori (1972a) made a more extensive comparison between the variational approach and the Monte Carlo data. He calculated the excess volume V^E , the excess enthalpy H^E and the excess Gibbs free energy G^E , for nine equimolar binary mixtures. The interactions between all molecules were taken to be of the Lennard-Jones type. The parameters of the

potential function were taken to simulate eight real pure fluids. Mansoori compared his results to the machine calculations, the average potential model, the van der Waals mixing rules, the perturbation theory, and the experimental measurements. The variational theory showed the best agreement with experimental and simulation data.

McDonald (1972, 1973) and Grundke et al. (1973) have also performed similar studies. They compared the excess properties predicted by the variational theory to the Monte Carlo data of a series of binary mixtures of Lennard-Jones fluid at zero pressure and three temperatures, 97, 115.8 and 117 K. Their comparison covered the following ranges of the energy and size parameters: $0.81 \leq \epsilon_{11}/\epsilon_{12} \leq 1.235$ and $0.88 \leq \sigma_{11}/\sigma_{12} \leq 1.12$. The variational theory showed excellent agreement with the machine calculations, especially for the excess enthalpy and the excess Gibbs free energy. Figs. 1-3 show the results of the perturbation and variational theories at $T = 115.8$ K. The variational theory is better for both H^E and G^E , but the perturbation theory gives a better prediction of V^E for $\epsilon_{11}/\epsilon_{12} = 0.663$. Nakanishi (1982) compared the variational theory prediction to his Monte Carlo data of Helmholtz free energy of mixing for a number of Lennard-Jones liquid mixtures. The variational theory again showed an excellent agreement. Mansoori (1977) used the variational theory to calculate the excess volume, enthalpy and Gibbs energy for equimolar mixtures of soft spheres. The calculation was done at $T = 100$ K and covers the pressure range of 0-10 MPa. In the light of the fact that variational theory produces least upper bound (or highest lower bound) for soft sphere thermodynamic properties this result is used to compare calculations based on other mixing rules.

Jedrzejek and Mansoori (1979) showed that for mixtures with molecules interacting by a hard-core potential with a two-Yukawa tail the variational theory gives analytic working formulas when the Lebowitz expressions for the radial distribution functions of a mixture of hard-spheres are used.

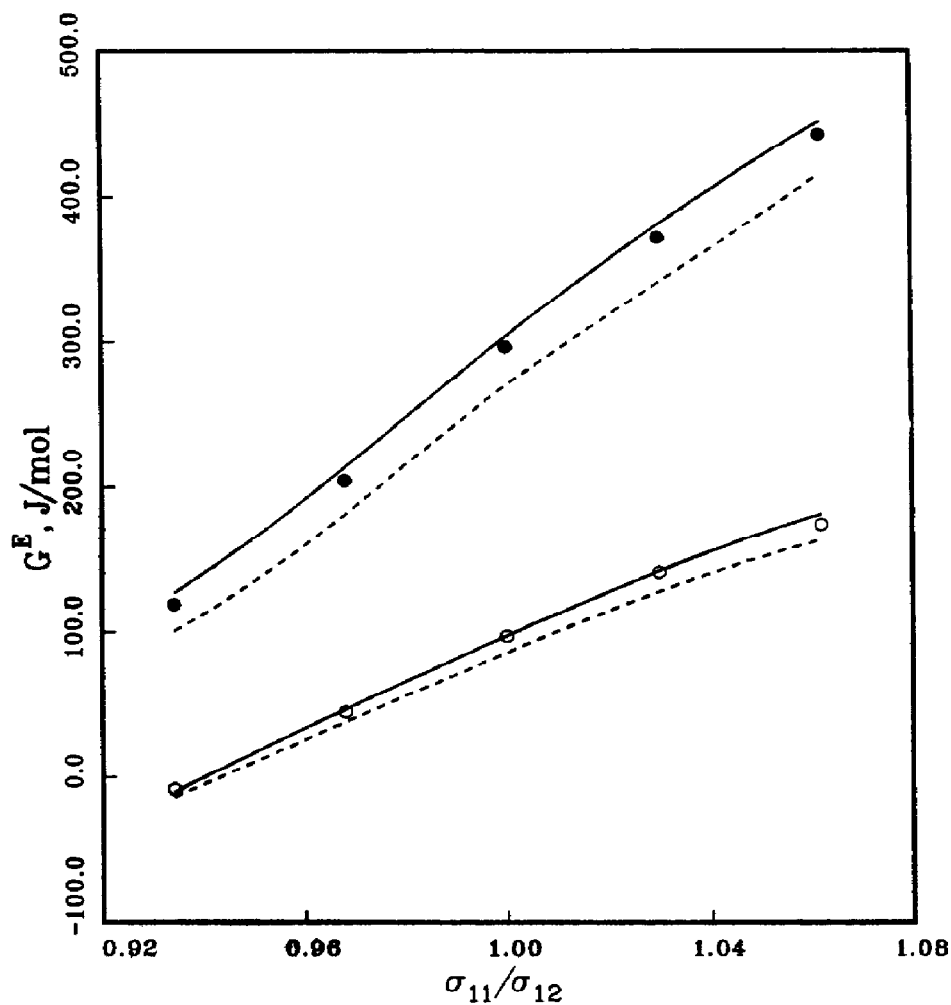


Figure 1 G^E as a function of σ_{11}/σ_{12} for an equimolar mixture of Lennard-Jones liquids at 115.8 K and zero pressure ($\epsilon_{12}/k=141.4$ K, $\sigma_{12}=35.19$ nm). The symbols ● and ○ represent the simulation results for $\epsilon_{11}/\epsilon_{12}=0.663$ and 0.819, respectively. The solid curves show the variational theory results and the dashed curves show the Barker-Henderson perturbation theory. Reproduced from McDonald (1973).

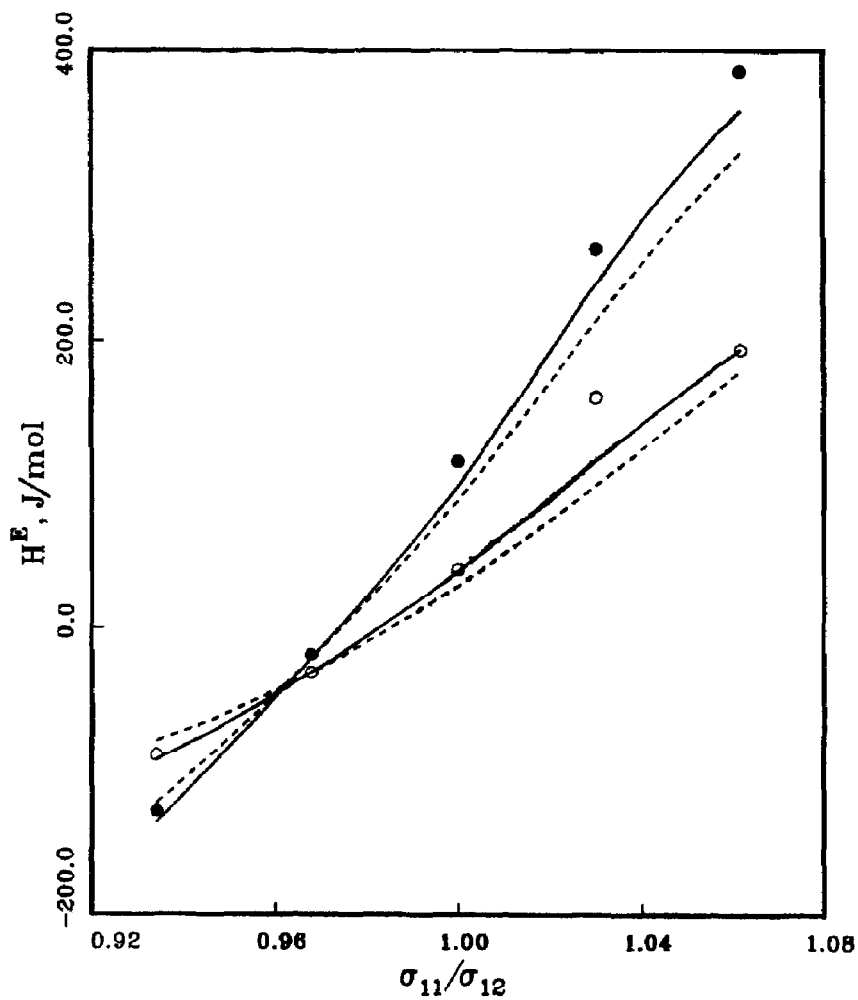


Figure 2 H^E as a function of σ_{11}/σ_{12} for an equimolar mixture of Lennard-Jones liquids at 115.8 K and zero pressure. For other details see caption to Fig.1. Reproduced from McDonald (1973).

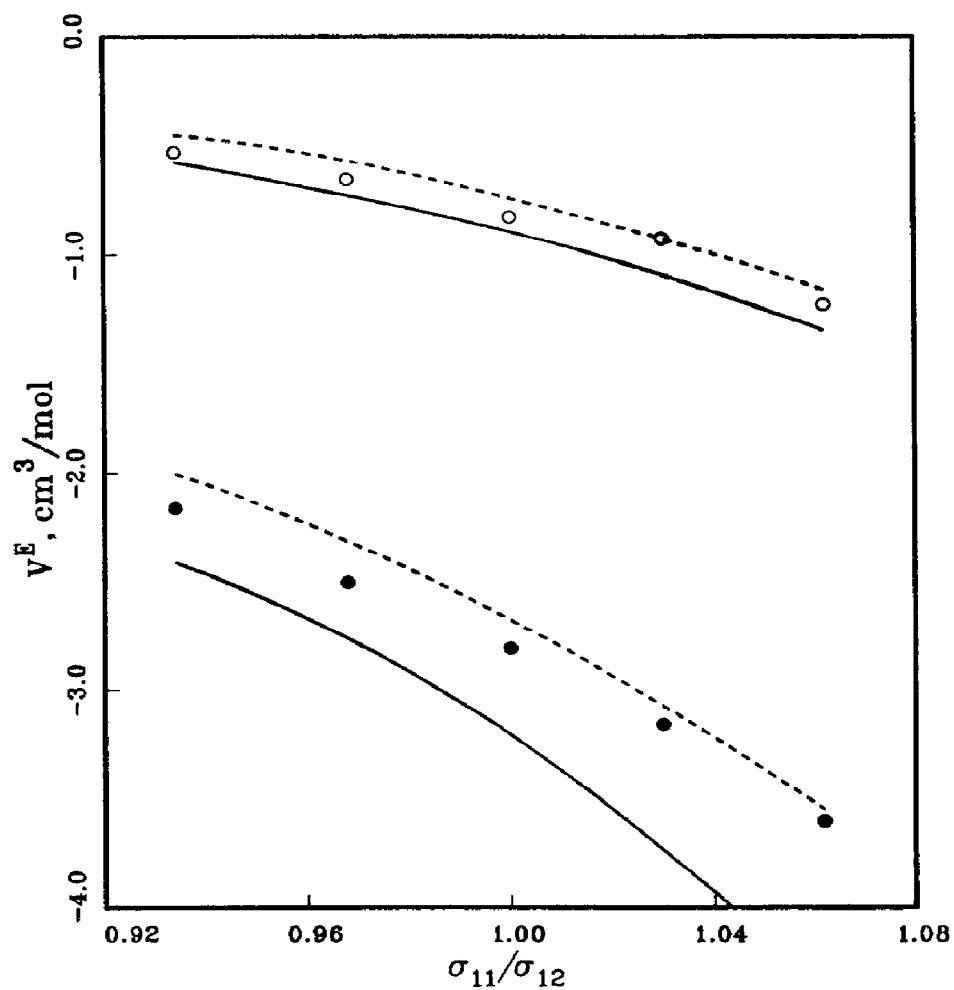


Figure 3 V^E as a function of σ_{11}/σ_{12} for an equimolar mixture of Lennard-Jones liquids at 115.8 K and zero pressure. For other details see caption to Fig.1. Reproduced from McDonald (1973).

Later Foiles and Ashcroft (1981) showed that the double Yukawa potential greatly simplifies the variational calculations when the mixture of hard spheres is taken as the reference system. In their work they used the virial hard-sphere equation of state to describe the reference system because it gives a better result than the semiempirical Carnahan-Starling expression. To demonstrate the computational simplifications resulting from the use of the double Yukawa potential, they calculated the phase diagram for Ar-Kr and Kr-Ne mixtures. They constructed the phase boundaries in the P - x plane for a number of different temperatures. Fig. 4 shows the phase boundaries for the Kr-Ne system at 178 and 133K. The qualitative agreement with experiment is excellent. The basic topology of the curves, and their pressure and temperature dependencies are correct. On the other hand there are quantitative discrepancies, but they are small compared to the characteristic pressures ϵ/σ^3 , of the calculation.

Hang and Leland (1986) used the variational theory in their study of the hard-sphere expansion (HSE) conformal solution theory of mixtures (Mansoori and Leland, 1972). In the HSE theory the repulsion contribution to mixture properties is obtained by using the optimum hard-core diameters for pure fluids in a hard-sphere mixture equation for which the composition dependence is known accurately. Hang and Leland (1986) showed that the variational theory can be used to obtain this optimum hard-core diameter. Since for real fluids the potential function is usually unknown, they used a procedure similar to that of Alem and Mansoori (1984) to develop a second order variational technique. This technique gives a properly optimized core diameter, but the reference fluid equation of state has to be capable of predicting accurate second order derivatives. A thirty-two constant modified Benedict-Webb-Rubin equation of state (Jacobsen and Stewart, 1973) was used for this purpose. The second order expansion was found to be important at low and moderate densities where the isochores show large deviation from linearity. Eqn. (12) is exact for fluids with linear isochores, and since at high density in the liquid region the isochores of real fluids

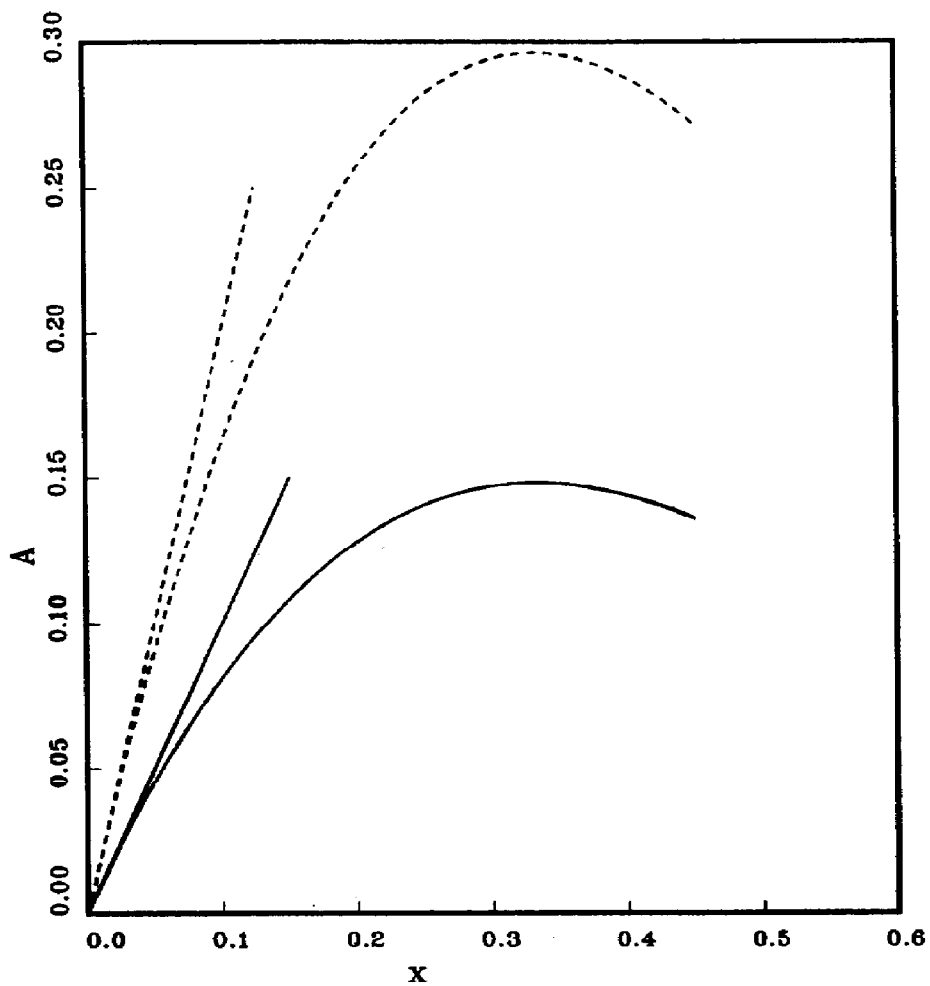


Figure 5 Illustration of the relation between the derivatives of the two sides of an inequality at a point where the two sides are equal.

approach linearity, it gives an accurate representation of fluids properties in this region. Hang and Leland compared the first and second order expansions by calculating the K-values of methane-propane system at 344 K from 2.76 to 6.89 MPa. The second order expansion showed an improvement in the average and in the maximum errors as shown in Table 1.

TABLE 1

Comparison of the first order and second order variational expansion. Vapor-liquid equilibria for CH₄-C₃H₈ at 344 K.

Hard-core from:	Component	Avg. abs. error, % in K-values	Max. error, % in K-values
First order theory with fitted k_{12} *	CH ₄	3.98	21.85
	C ₃ H ₈	1.35	-7.28
Second order theory with fitted k_{12}	CH ₄	1.37	-4.81
	C ₃ H ₈	0.66	-1.92

* k_{12} is the unlike pair interaction parameter.

Glyde (1971) used the variational theory to study the properties of solid phase mixtures. He calculated the interchange parameter ω , for a dilute solid mixture of argon in krypton in the temperature range 70 - 100 K. The interchange parameter is defined by

$$\omega = \mu_A - \mu_{A,0} - kT \ln x_A \quad (14)$$

where μ_A and $\mu_{A,0}$ are the chemical potentials of A in the mixture and in the pure state, respectively. The values of ω agree reasonably well with the experimental values.

Liquid alloys is another area where the variational theory has found applications. One of the existing studies in this field was conducted by

Hafner (1977). He used a pseudopotential to describe the interactions between the ions in liquid metals. He calculated the structure factor, the excess volume and the entropy and enthalpy of nine liquid alloys. For alloys with a nearly random distribution of components he got encouraging results. However, difficulties arise when nonrandomness has to be expected. Other studies have been done in this area too. They include the work of Stroud (1973), Umar et al. (1974), Lai et al. (1983) and others. When the calculations are compared to the experimental data, the results are not as good as the prediction of the variational theory in other areas. The reason behind this is the fact that in this case the variational results are compared to the experimental data, and the potential functions which are used in the calculations (pseudopotentials) do not accurately represent the real potentials.

Rudd and Frisch (1971) have applied the variational technique to derive sufficient conditions for the stability of binary mixtures relative to either pure components or to a two-phase mixture of the same composition. The first condition (stability relative to pure components) is given by:

$$2\pi N\rho \int_0^{\infty} [(x_1^2 - 1)u_{11} + 2x_1x_2 u_{12} + x_2^2 u_{22}] g_1 r^2 dr - \ln(\Theta) \leq 0 \quad (15)$$

where $\Theta = N! \lambda_1^{3N} / (N_1! N_2! \lambda_1^{3N_1} \lambda_2^{3N_2})$ and $\lambda_i = (h^2 / 2\pi m_i kT)^{1/2}$. They used the inequality, eqn. (15) to determine the stabilities of mixtures of hard spheres and molecules with hard-cores and "perturbing" square wells or steps ($u = \infty$, $r < \sigma_1$; $u = 2\epsilon$, $\sigma_1 \leq r < \sigma_2$; $u = 0$, $\sigma_2 \leq r$). They found that for square wells ($\epsilon < 0$) the mixture is always stable. For square steps ($\epsilon > 0$) they calculated the stability ranges as a function of reduced density, reduced temperature and composition.

Mazo (1964) and Mansoori (1972b, 1977) used the variational technique to compare and study the Scott and van der Waals one-fluid and two-fluid theories of mixtures. For the Lennard-Jones potential Mazo showed that the

Scott one-fluid theory gives the least upper bound to the Helmholtz energy for all temperature and density independent choices of the potential parameters of the pseudo pure fluid. Mansoori studied the upper bound to the entropy of a Lennard-Jones mixture. He found that the van der Waals theory of mixtures is an approximate solution to the equations which result from minimizing the upper bound to the entropy. For soft-sphere mixtures Mansoori (1977) showed that the Scott one-fluid and two-fluid theories give upper bounds to the Helmholtz free energy. The van der Waals one-fluid theory is a high temperature approximation to the upper bound for the entropy while no such conclusion could be drawn about the van der Waals two-fluid theory.

VARIATIONAL THEORY AT INFINITE DILUTION

The properties of dilute solutions are both important in practice and attractive for theoretical investigations. In practice the solubility of solids and liquids in compressed gases is an important quantity in supercritical extraction and in gas-liquid processes. From the theoretical point of view it is generally easier to apply theories to dilute solutions, and this provides a relatively simple way of testing mixture theories. Perhaps the most important property of dilute solutions is Henry's constant. It is defined as:

$$\ln(H_1/pkT) = \lim_{x_1 \rightarrow 0} \mu_{1r}/kT = \mu_{1r}^\infty/kT \quad (16)$$

where H_1 is Henry's constant of component one in the solvent, μ_{1r} is the residual chemical potential of component one and the superscript ' ∞ ' denotes infinite dilution ($x_1 \rightarrow 0$).

The first study to apply the variational technique in the infinite dilution region was done by Goldman (1977a). He calculated Henry's constant, the heat of solution and the partial molar volume of a number of binary mixtures containing hydrogen, helium and neon. Since he was dealing

with light molecules, he included the correction for translational quantum effect into the variational inequality. The comparison with the perturbation theory and the experimental measurements (Goldman, 1977b) showed that the variational theory is somewhat better for the helium-containing systems, and the perturbation theory is better for hydrogen-containing and neon-containing systems. Goldman explained this behavior in the light of previous studies (Mansoori, 1972a and Henderson et al., 1971) which suggested that for mixtures with $\epsilon_{11}/\epsilon_{22}$ and σ_{11}/σ_{22} close to unity the perturbation theory is more accurate. While the variational method deals more effectively than other first-order theories, with mixtures where these ratios deviate substantially from unity.

Goldman used the Lennard-Jones potential function to represent the interactions in the original system and selected the mixture of hard spheres as the reference system. Unfortunately, this procedure does not tell whether the prediction is an upper or lower bound. This was evident when he compared the results of the variational technique to the experimental data. The prediction was lower than the experimental data in some cases and higher in others. It is desirable if in addition to the good agreement with the experimental results one can tell whether the prediction is an upper or lower bound.

To reach this goal one should find when inequalities such as eqn. (1) would still hold even after differentiating both sides with respect to an independent variable such as the number of moles. From Fig. 5 it is clear that if at a given point the right hand side of eqn. (1) is equal to the left hand side, then at that point the inequality also holds for the slopes which are given by the derivatives. Accordingly, for Henry's constant one should choose the reference system such that as the mole fraction of the solute approaches zero, the inequality, eqn. (1) becomes strict equality. The obvious choice of the reference system is then the pure solvent.

Assuming pair-wise additivity of the total potential energy, the inequality, eqn. (1) takes the following form for binary mixtures:

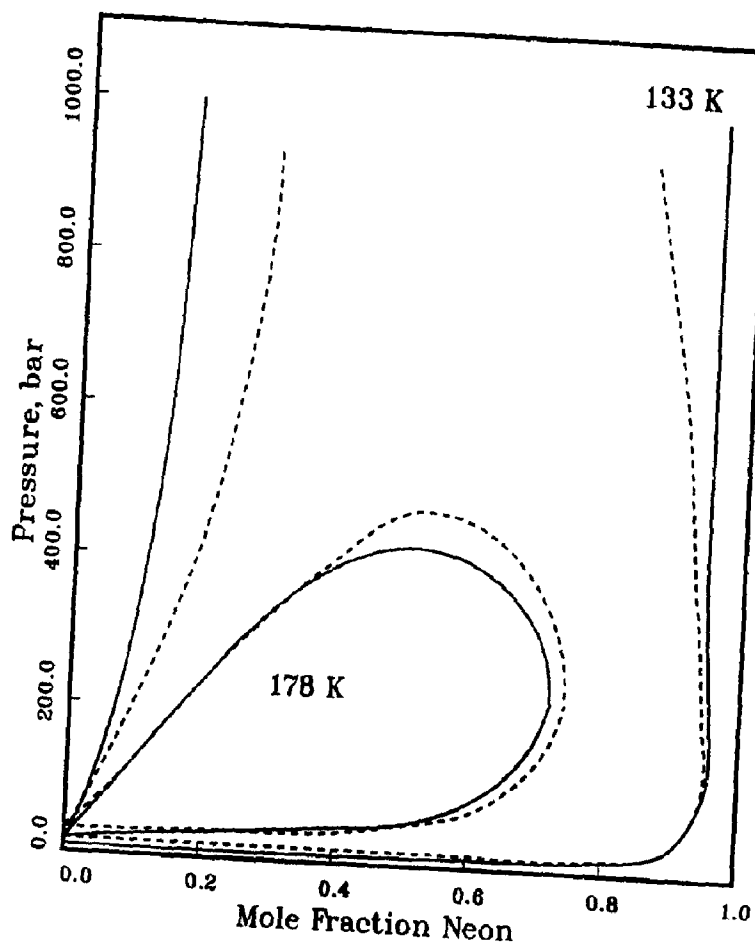


Figure 4 Comparison of experimental (solid curves) and variationally calculated (dashed curves) phase equilibria for neon-krypton mixtures at 133 and 178 K. Reproduced from Foiles and Ashcroft (1981).

$$A \leq A_2 + 1/2 N^2 \{x_1^2 \langle u_{11} \rangle_2 + 2 x_1 x_2 \langle u_{12} \rangle_2 + (x_2^2 - 1) \langle u_{22} \rangle_2\} \quad (17)$$

where from now on component one is the solute and component two is the solvent. Differentiating both sides of eqn. (17) with respect to n_1 and taking the limit as n_1 goes to zero, one gets:

$$\mu_{1r}^\infty \leq \mu_{2r,0} + N \langle u_{12} \rangle_2 - N \langle u_{22} \rangle_2 \quad (18)$$

where $\mu_{2r,0}$ is the residual chemical potential of the pure solvent at the same temperature and density of the mixture. The quantity $N \langle u_{22} \rangle_2$ is equal to twice the residual internal energy of the pure solvent $U_{2r,0}/N$. Upon Substitution of this in eqn. (18) one has:

$$\mu_{1r}^\infty \leq \mu_{2r,0} + N \langle u_{12} \rangle_2 - 2 U_{2r,0}/N \quad (19)$$

To obtain the lower limit one can write the inequality, eqn. (4) in the form:

$$A \geq A_2 + 1/2 \rho N \left\{ x_1^2 \int_0^\infty (u_{11} - u_{22}) g_{11} 4\pi r^2 dr + 2x_1 x_2 \int_0^\infty (u_{12} - u_{22}) g_{12} 4\pi r^2 dr \right\} \quad (20)$$

Following the same procedure as before one gets the lower bound on Henry's constant:

$$\mu_{1r}^\infty \geq \mu_{2r,0} + \rho \int_0^\infty (u_{12} - u_{22}) g_{12}^\infty 4\pi r^2 dr \quad (21)$$

where g_{12}^∞ is the radial distribution function at infinite dilution.

The inequalities, eqns.(19) and (21) will be compared to the simulation data of Shing and Gubbins (1982). This simulation was done for Lennard-Jones mixtures at $kT/\epsilon_{22} = 1.2$ and $\rho\sigma_{22}^3 = 0.7$. The simulation was

performed for a mixture of molecules with the same energy of interaction, but different sizes, and also molecules with the same size but different energies. The simulation covered a size ratio range of 0.3 - 2.0, and an energy ratio range of 0 - 4. The size ratio h is defined as $(\sigma_{12}/\sigma_{22})^3$, and the energy ratio f is defined as $\epsilon_{12}/\epsilon_{22}$.

For molecules which interact by the Lennard-Jones potential function the second term on the right hand side of the inequality, eqn. (19) can be written in the following form:

$$\begin{aligned} N\langle u_{12} \rangle_2 &= N \langle 4 \epsilon_{12} [(\sigma_{12}/r)^{12} - (\sigma_{12}/r)^6] \rangle_2 \\ &= 16\pi \epsilon_{12} \rho \sigma_{22}^3 \left\{ (\sigma_{12}/\sigma_{22})^{12} \int_0^{\infty} r^{*-10} g_0 dr^* - (\sigma_{12}/\sigma_{22})^6 \int_0^{\infty} r^{*-4} g_0 dr^* \right\} \end{aligned} \quad (22)$$

where g_0 is the radial distribution function of the pure solvent and $r^* = r/\sigma_{22}$. The integrals in eqn. (22) are two body integrals which are correlated in the literature (Nicolas et al. 1979). The expression for the upper bound is then:

$$\beta \mu_{1r}^{\infty} \leq \beta \mu_{2r,0} + 16\pi (\rho^*/T^*) r h^2 \{ h^2 J^{(12)} - J^{(6)} \} - 2 \beta U_{2r,0} / N \quad (23)$$

where $\beta = 1/kT$, and $J^{(n)}$ is given

$$J^{(n)} = \int_0^{\infty} r^{*-(n-2)} g_0 dr^* \quad (24)$$

For molecules with equal sizes the inequality, eqn. (23) reduces to the following form:

$$\mu_{1r}^{\infty} \leq \mu_{2r,0} + 2(f-1) U_{2r,0} / N \quad (25)$$

where $J_{12}^{(n)}$ is given by:

$$J_{12}^{(n)} = \int_0^{\infty} (\sigma_{12}/r)^{n-2} g_{12}^{\infty} d(r/\sigma_{12}) \quad (27)$$

The quantities $\mu_{2r,0}$ and $U_{2r,0}$ in the above inequalities can be calculated from Nicolas et al. (1979) equation of state for pure Lennard-Jones fluid.

The right hand side of the inequality, eqn. (25), which is the same expression as the one predicted by the van der Waals one fluid mixing rules, is plotted in Fig. 6. The Figure shows that all the simulation points lay below the curve except for the point at $\epsilon_{12}/\epsilon_{22} = 0.5$. This point is reported by Shing (1982) in her thesis, but it is not in a later paper (Shing and Gubbins, 1982). Apparently this point is not accurate and the variational theory confirms this. For the lower limit one has to have the radial distribution function g_{12} at infinite dilution for the Lennard-Jones mixture. Unfortunately it is not available for the above conditions.

The prediction of the variational theory when the mixture of hard spheres is the reference fluid is also shown in Fig. 6. In this case there is no guarantee that the variational theory will give an upper or lower bound. However, for the hard sphere reference fluid one has the advantage of minimizing the upper bound to the Helmholtz free energy before differentiating with respect to the number of moles. This, in a certain range, gives a better agreement with the simulation data as can be seen in Fig. 6 when f is less than about 0.3. For other values of f the pure solvent reference fluid gives better agreement with the simulation data.

The variation of Henry's constant with size is shown in Fig. 7. The upper bound is given by the right hand side of the inequality, eqn. (23). Except for a narrow region around $h=1$, the upper bound is too high. For the lower bound g_{12}^{∞} is available at the simulation conditions for $h = 2$ (Ely, 1986). The integrals $J_{12}^{(12)}$ and $J_{12}^{(6)}$ are evaluated and compared to those when

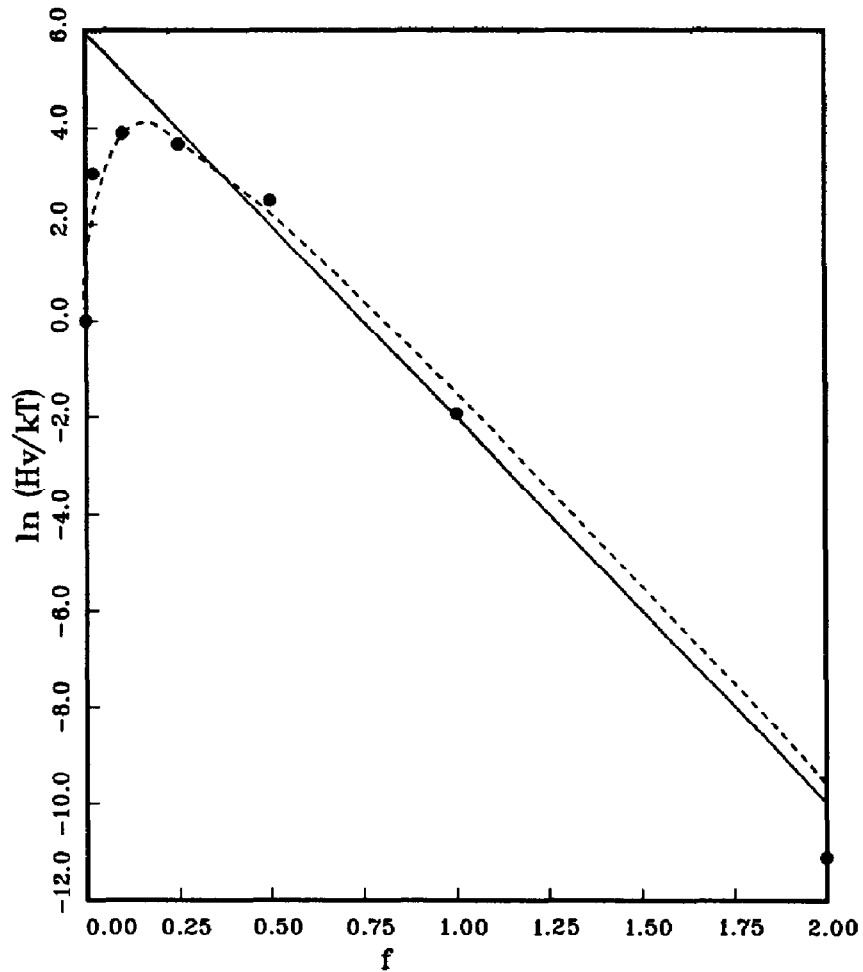


Figure 6 Henry's constant as a function of $f = \epsilon_{12}/\epsilon_{22}$ for Lennard-Jones fluid mixture at $kT/\epsilon_{22} = 1.2$ and $\rho\sigma_{22}^3 = 0.7$. The points are the simulation results of Shing and Gubbins (1982) and the solid curve is the upper bound as predicted by the variational theory. The dashed curve show the prediction of the variational theory with the hard sphere mixture as the reference system.

g_{12}^{∞} is that of the pure solvent ($h=1$). It is found that there is a little difference between the two. The error resulted from using the pure solvent integrals $J^{(12)}$ and $J^{(6)}$ to calculate $\beta\mu_{1r}$ at $h = 2$ is about four percent. Since this error is small compared to the accuracy of the simulation data, $J_{12}^{(12)}$ and $J_{12}^{(6)}$ at $h = 2$ are used to generate the lower bound for the entire h range. The resulting curve, according to the right hand side of the inequality, eqn. (26) is shown in Fig. 7. It has the same shape as the upper bound but in the negative direction of the pure solvent chemical potential.

For the hard spheres mixture reference fluid, the prediction of the variational theory is generally better. Except for the region close to $h=1$, the agreement with the simulation data is better than that of the upper or lower bounds. The agreement becomes very good for small values of h , (less than about 0.4).

CONCLUSIONS

Due to its generality the variational theory has been applied to a wide range of problems in pure fluid and mixture properties. In fact in some areas, such as the solid-liquid phase transition the variational theory is one of the simplest and best theories available. In applying the variational theory to mixtures, most of the work has been done for simple fluids, such as Lennard-Jones, because of the lack of information about the intermolecular potential energy function for real fluids. However, this difficulty is being overcome by the new techniques which are introduced recently to use the variational theory without the need of an explicit knowledge of the potential energy function. It is important to develop such techniques in order for the variational theory to find a wider range of applications in practice. In addition more studies are needed in the area of nonspherical and polar molecules.

The variational theory always predicts the correct qualitative behavior

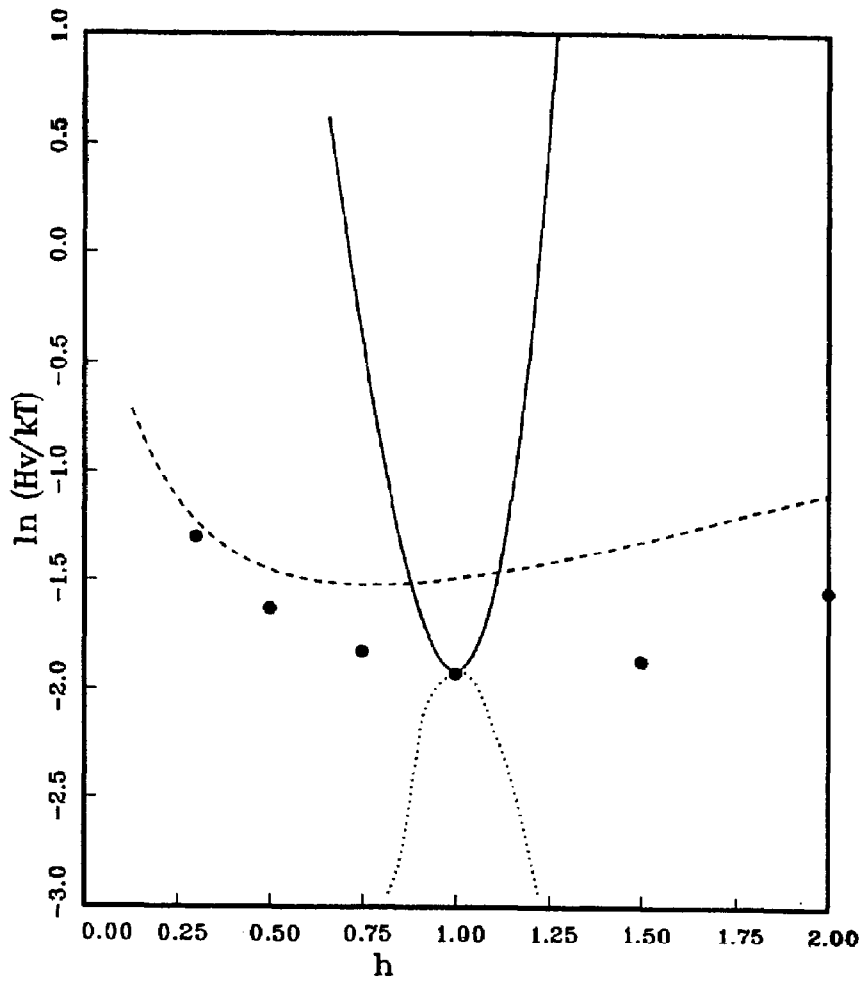


Figure 7 Henry's constant as a function of $h=(\sigma_{12}/\sigma_{22})^3$ for Lennard-Jones fluid mixture at $kT/\epsilon_{22}=1.2$ and $\rho\sigma_{22}^3=0.7$. The dotted curve is the lower bound. All other curves have the same meaning as in Fig. 6.

of mixtures, and when the proper choice and use of the reference system is made, it yields a very good quantitative agreement with the experimental or simulation data. For the time being the hard-sphere fluid is practically the only choice as the reference fluid for pure fluid calculations. However, in the few cases where a more realistic fluid is taken as the reference fluid (such as the inverse power potential) the prediction is improved. For mixtures the choice of the reference fluid becomes more important because one usually has more than one choice of the reference system. After choosing the reference system one has to correctly optimize the reference fluid parameters in order to get the best mixture prediction.

In this work it has been shown that the variational theory can give a least upper bound and a highest lower bound to chemical potential and other properties of mixtures which are related to the Helmholtz free energy derivatives. For Henry's constant the variational theory gives an upper bound which is in good agreement with the simulation data when the molecules do not differ much in size. This bound is close enough to the real values to detect, for example, an error in a simulation data. For large size differences between molecules of the mixture, the variational theory with a hard sphere mixture as the reference fluid gives better results than with a pure solvent reference fluid. However, in this case the variational theory prediction can no longer be identified as an upper or lower bound.

ACKNOWLEDGEMENTS

This research is supported by the Chemical Sciences Division of the Office of Basic Energy Sciences, the U.S. Department of Energy Grant # DE-FG02-84ER13229.

NOTATION

- A Helmholtz free energy
- a, b constants in eqn. (6)
- d hard sphere diameter

f	energy ratio
G	Gibbs free energy
g	radial distribution function
H	Henry's law constant
	enthalpy
h	size ratio
	Planck's constant
J	structure integral
k	Boltzmann constant
	unlike pair interaction parameter
m	molecular mass
N	number of molecules
n	constant in the soft sphere potential
r	position coordinate
S	entropy
T	absolute temperature
U	total configurational energy function
	internal energy
u	binary interaction potential energy function
V	volume
v	molar volume
x	arbitrary independent variable
	mole fraction
z	constant in Yukawa tail

- σ size parameter in potential functions
 ω interchange parameter

Subscripts

- o reference system
 pure component
 1,2,i,j species in a mixture
 r residual property

Superscripts

- * dimensionless quantity
 ∞ infinite dilution
 E excess property
 (n) power of position coordinate in the structure integrals

REFERENCES

- Alem, A. H. and Mansoori, G. A., 1981. Proceedings of the 2nd World Congress of Chemical Engineering, Vol. V, pp. 63.
 Alem, A. H. and Mansoori, G. A., 1982. In: S. A. Newman (editor), Chemical Engineering Thermodynamics. Ann Arbor Science Publishers, Ann Arbor, pp. 187.
 Alem, A. H. and Mansoori, G. A., 1984. AIChE J., 30: 468.
 Alem, A. H. and Mansoori, G. A., 1984. AIChE J., 30: 475.
 Baxter, R. J., 1970. J. Chem. Phys., 52: 4559.
 Buchanan, D. J., 1974. J. Chem. Phys., 60: 3727.
 Carnahan, N. F. and Starling, K. E., 1969. J. Chem. Phys., 51:635.
 Ely, J. F., personal communication, 1986.
 Foiles, S. M. and Ashcroft, N. W., 1981. J. Chem. Phys., 75: 3594.
 Frisch, H. L., 1964. Adv. Chem. Phys., 6: 229.
 Gibbons, R. M., 1970. Mol. Phys., 18: 809.
 Gibbs, J. W., 1902. Collected Works, Yale University Press, New Haven, Connecticut, pp 131.
 Girardeau, M. D., 1964. J. Chem. Phys., 40: 899.
 Girardeau, M. D. and Mazo, R. M., 1973. in Advances in Chemical Physics, ed. Prigogine, I. and Rice, S., John Wiley & sons, Inc., New York, Vol. XXIV.
 Glyde, H. R., 1971. Phys. Rev. B, 3: 3539.
 Goldman, S. 1977a. J. Sol. Chem., 6: 461.
 Goldman, S. 1977b. J. Chem. Phys., 67: 727.

Grundke, E. W., Henderson, D., Barker, J. A. and Leonard, P. J., 1973. *Mol.*

Phys. 25: 883.

Hang, T. and Leland, T. W., 1986. *Fluid Phase Equilibria*, 26: 251.

Henderson, D. and Leonard, P. J., 1971. In: H. Eyring, D. Henderson and W. Jost (Editors), *Physical Chemistry, an advanced Treatise*. Academic Press, New York, Vol. VIII, chap. 7.

Henderson, D., Waisman, E., Lebowitz, J. L. and Blum, L., 1978. *Mol. Phys.*, 35: 241.

Hoover, W. G., Ross, M., Johnson, K. W., Henderson, D., Barker, J. A. and Browns, B. C., 1970. *J. Chem. Phys.*, 52: 4931.

Hoover, W. G., Gray, S. G. and Johnson, K. W., 1971. *J. Chem. Phys.*, 55: 1128.

Jacobsen, R. T. and Stewart, R. J., 1973. *J. Phys. Chem. Reference Data*, 2: 757.

Jedrzejek, C. and Mansoori, G. A., 1979. *Acta Phys. Pol.*, A56:583.

Jedrzejek, C. and Mansoori, G. A., 1980. *Acta Phys. Pol.*, A57:107.

Kerley, G. I., 1971. *A New Model of Fluids*, Los Alamos Sci. Lab., Rept. LA-4760.

Kerley, G. I., 1980. *J. Chem. Phys.*, 73: 469.

Kerley, G. I., 1983. In: J. M. Halle and G. A. Mansoori (Editors), *Molecular-Based Study of Fluids*. American Chemical Society, Washington, D. C., pp.107.

Lai, S. K., Matsuura, M. and Wang, S., 1983. *J. Phys. F: Metal Phys.*, 13:2033.

Lebowitz, J. L., 1964. *Phys. Rev.*, 133: A895.

Leonard, P. J., Henderson, D. and Barker, J. A., 1970. *Trans. Faraday Soc.*, 66:

- Nakanishi, K., Okazaki, S., IKari, K. and Higuchi, J., 1982. *J. Chem. Phys.*, 76: 629.
- Nicolas, J. J., Gubbins, K. E., Streett, W. B. and Tildesley, D. J., 1979. *Mol. Phys.*, 37: 1429.
- Percus, J. K. and Yevick, G. J., 1958. *Phys. Rev.*, 110: 1.
- Prager, S., Kunkin, W. and Frisch, H. L., 1970. *J. Chem. Phys.*, 52: 4925.
- Rogers, F. J. and Young, D. A., 1984. *Pyhs. Rev. A*, 30: 999.
- Rosenfeld, Y., 1975. *J. Chem. Phys.*, 63: 2769.
- Rosenfeld, Y., 1977. *Phys. Rev. A*, 15: 2545.
- Rosenfeld, Y., 1980. *J. Chem. Phys.*, 73: 5760.
- Rosenfeld, Y. and Baram, A., 1981. *J. Chem. Phys.* 75: 427.
- Rosenfeld, Y., Avron, J. E., Goshen, S. and Thieberger R., 1977. *J. Chem. Phys.*, 66: 2758.
- Ross, M., 1973. *Phys. Rev. A*, 8: 1466.
- Rudd, W. G. and Frisch, H. L., 1971. *J. Chem. Phys.*, 54: 3479.
- Shimoji, M., 1977. *Liquid Metals*, Academic Press Inc., London, pp. 89.
- Shing, K. S., 1982. Ph. D. Thesis, Cornell University.
- Shing, K. S. and Gubbins, K. E., 1982. *Mol. Phys.*, 46: 1109.
- Stroud, D., 1973. *Phys. Rev. B*, 7:4405.
- Stroud, D., and Ashcroft, N. W., 1972. *Phys. Rev. B*, 5: 371.
- Tolmachev, V. V., 1960. *Dokl. Akad. Nauk. SSSR*, 134: 1324 [English trans.: 1961. *Soviet Phys. "Doklady"*, 5: 984]
- Umar, I. H., Meyer, A., Watabe, M. and Young, W., 1974. *J. Phys. F: Metal Pyhs.*, 4:1691.
- Weeks, J. D., Chandler, D. and Andersen, H. C., 1971. *J. Chem. Phys.*, 54, 5237.
- Wertheim, M. S., 1963. *Phys. Rev. Letters*, 10: 321.
- Young, D. A. and Rogers, F. J., 1984. *J. Chem. Phys.*, 81: 2789.