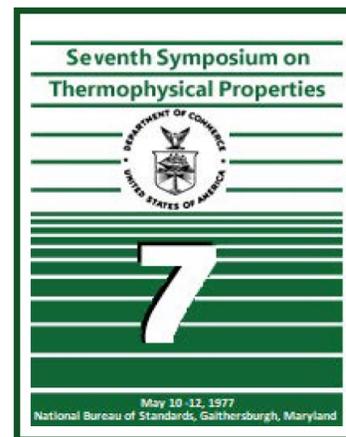


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## STATISTICAL THERMODYNAMICS OF SOFT-SPHERE SYSTEMS

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### ABSTRACT

The Gibbs-Bogoliubov inequality is used to produce inequalities for the variational calculations of thermodynamic properties of pure-fluid, pure-solid, and mixture of soft-spheres. For the pure-fluid and pure-solid soft spheres it is shown that the results of the variational theory are in agreement with the Monte Carlo data for steep soft-sphere systems. Through Gibbs-Bogoliubov inequality it is shown that in addition to the variational theory of mixture, the Scott (1f) and Scott (2f) theories also give upper bounds to the Helmholtz free energy of soft-sphere mixture. It is also shown that vdW (1f) theory gives an approximation to an upper bound of the entropy of mixture while the case for vdW (2f) is not clear. Over all it is shown that vdW (1f) and the variational theories are superior to vdW (2f), Scott (1f), and Scott (2f) theories in predicting the thermodynamic properties of soft-sphere mixture.

### NOMENCLATURE

A	Helmholtz free energy function
d	reference hard-sphere diameter
g	radial distribution function
G	Laplace transform of radial distribution function
k	Boltzmann's constant
n	soft-sphere exponent
N	number of molecules
r	intermolecular distance
S	entropy
T	absolute temperature
u	pair intermolecular potential energy function
U	total intermolecular potential energy function
ubA	upper bound of A
ubS	upper bound of S
V	total volume
x	mole fraction

### Greek Letters

$$\eta = (\pi/6)pd^3$$

$\epsilon$	intermolecular energy parameter
$\rho$	number density
$\sigma$	intermolecular length parameter

### Superscripts

\* excess property over ideal gas

### bscripts

o	reference system
i,j	molecules i,j

### INTRODUCTION

The pair intermolecular potential energy function of realistic molecules contains both attractive and repulsive parts. The repulsive part of the potential function contributes mainly to the structure, or the distribution of the molecules, in a macroscopic many body thermodynamic system in equilibrium, and the attractive part of the potential energy function contributes to the internal pressure of the system<sup>(1)</sup>. This has lead research on the equilibrium theories of liquids, solids, and mixtures to the direction of perturbation techniques with the repulsive part of the potential taken as the reference or the "unperturbed" part<sup>(2)</sup>. Accordingly, if a statistical theory considers only the repulsive part of the potential energy function, it could only reproduce the structural characteristics of a realistic many body system which has the same kind of repulsive forces plus additional attractive forces. Perturbation of the attractive forces around this repulsive statistical model would effectively converge to satisfactory relations for the thermodynamic functions of the realistic many body systems. Another application of the repulsive models is in the prediction of thermodynamic properties of substances at high temperatures and under shock wave or detonation conditions.

For the above mentioned applications of repulsive models, the common practice is the use of the hard-sphere model for which the analytic thermodynamic functions are available. The repulsive part of the potential energy function of realistic molecules is not infinitely steep like hard-spheres. Consequently, the hard-sphere model cannot effectively take care of the repulsive characteristics of substances. For this reason, the thermodynamic functions of the soft-sphere fluid models, when available, will be preferred. As exemplified in later parts of this report, there is another advantage in the study of statistical thermodynamics of soft-sphere molecules; the possibility of analytic comparison of mixture theories through this potential model which is generally impossible in the case of other intermolecular potential functions<sup>(3)</sup>. This can be done by the application of Gibbs-Bogoliubov inequality<sup>(4)</sup>.

### PURE SOFT-SPHERE SYSTEMS

The potential energy function for soft-spheres could be shown by the following relation

$$u(r) = \epsilon(\sigma/r)^n ; n > 3 \quad (1)$$

This indicates that the soft-sphere potential function could be characterized by two independent parameters, n and  $\epsilon\sigma^n$ . As n goes toward infinity, relation (1) reduces to the potential function of hard-spheres with

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diameter  $\sigma$ .

The Gibbs-Bogoliubov inequality was introduced as follows<sup>(4)</sup>

$$A \leq A_0 + \langle U - U_0 \rangle \quad (2)$$

where  $A_0$  and  $U_0$  are the Helmholtz free energy and the internal energy of a reference system, respectively, while  $A$  and  $U$  are the properties of a desired system of molecules called the original system. The angled brackets indicate the expectation value of  $U - U_0$  over the reference system. In the case where the original system consists of molecules in fluid state with soft-sphere intermolecular potential function as given by Equation (1) and the reference system consists of molecules in fluid state with hard-sphere intermolecular potential function, with diameters  $d$ , the above inequality will be as follows<sup>(5)</sup>

$$A \leq A_0 + \frac{2\pi N^2}{V} (\epsilon \sigma^n) \int_d^\infty r^{-n} g^0(r) r^2 dr \quad (3)$$

where  $g^0$  is the radial distribution function of the hard-sphere system. By using the reformulation procedure, presented before,<sup>(5)</sup> the above inequality will take the following form

$$\frac{A - A^{id}}{NkT} \leq A_0^*(n) + \left[ \left( \frac{\epsilon}{kT} \right) (\rho \sigma^3)^{\frac{n}{3}} \right] \cdot A_1^*(n, n) \quad (4)$$

where

$$A_0^* = \frac{A_0 - A^{id}}{NkT}$$

is the excess Helmholtz free energy of the hard-sphere pure reference system over ideal gas and

$$A_1^* = \frac{2}{(n-2)} \left( \frac{6\eta}{\pi} \right)^{\frac{1}{3}} \cdot \int_0^\infty s^{(n-2)} \cdot G(S, n) dS \quad (4a)$$

where

$$\eta = \frac{\pi}{6} \rho d^3, \text{ and } G(S, n)$$

is the Laplace transform of  $rg^0(r)$ . For  $G(S, n)$  we use the analytic form already available<sup>(5,6)</sup>. It should be pointed out that exact computer calculated results for radial distribution function of hard-sphere fluid is available also<sup>(6)</sup>. For the kind of computations which are reported here the analytical Percus-Yevick solution is satisfactory. For  $A_0^*$  we use the relation due to Carnahan and Starling,<sup>(7)</sup> that is,

$$\frac{A_0 - A^{id}}{NkT} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (5)$$

Inequality (4) can be used to calculate a least upper bound for the Helmholtz free energy of pure soft-sphere fluid by a variational calculation based on the minimization of the right-hand side of Inequality (4) with respect to  $\eta$ , the hard-sphere reduced density, as the variational parameter<sup>(5)</sup>. Equation (5), although accurate enough, is an approximate relation and one may get more reliable results by using the "exact" machine-calculated hard-sphere results for Helmholtz free energy.

Similarly, the Gibbs-Bogoliubov inequality can be used to produce another inequality for the Helmholtz free energy of a system consisting of soft-spheres in

solid state. The procedure will be the same as in the case of solid Lennard-Jones molecules shown before<sup>(5,8)</sup>. In this case for the reference system the Einstein model (molecules in solid state with harmonic oscillator potential energy functions) will be used. For the analytical calculation of the thermodynamic properties of the Einstein model, the cell theory of Lennard-Jones is used. The inequality for the Helmholtz free energy of soft-sphere, in solid phase, will be as follows

$$\frac{A - A^{id}}{NkT} \leq \frac{3}{2} \ln(\Delta) + \left[ \left( \frac{\epsilon}{kT} \right) (\rho \sigma^3)^{\frac{n}{3}} \right] \cdot A_2^*(\Delta, n) \quad (6)$$

with

$$A_2^*(\Delta, n) = \left( \frac{\Delta}{\sqrt{2}} \right)^{\frac{-n}{3}} \cdot \left( \frac{\Delta}{8\pi} \right)^{\frac{1}{2}} \sum_{i=1}^m \frac{N_i}{Z_i^*} \int_{\alpha_i^*}^{\beta_i^*} y^{(1-n)} \cdot \exp \left[ -\frac{\Delta}{2} (Z_i^* - y)^2 \right] dy \quad (6a)$$

where  $\Delta$  is the coefficient of harmonic-oscillator potential energy function

$$W(r) = kT \left( \frac{r}{a_0} \right)^2 \Delta; \quad a_0^* = \frac{a_0}{\sigma}, \quad a_0 = (\sqrt{2}/\rho)^{\frac{1}{3}}, \quad y = \frac{r}{a},$$

$$Z_i^* = \frac{Z_i}{a_0}, \quad Z_i$$

is the distance of the  $i^{\text{th}}$  shell of neighbors from the central molecule, and  $N_i$  is the number of molecules in the  $i^{\text{th}}$  shell<sup>(8)</sup>. Also

$$\alpha_i^* = \left( Z_i^* - \frac{1}{\sqrt{2}} \right); \quad \beta_i^* = \left( Z_i^* + \frac{1}{\sqrt{2}} \right) \quad (7)$$

Relations (7) for the limits of integrals in (6a) are different from what was reported before<sup>(5,8)</sup>. This is due to the fact that terms smaller than or equal to  $\exp(-\frac{\Delta}{4})$  can be neglected in the evaluation of the radial distribution function for the cell model of molecules having harmonic-oscillator potential energy function as suggested by Corner and Lennard-Jones<sup>(10)</sup>. This will end up with the following inequality as derived by Buchanan:<sup>(9)</sup>

$$\frac{1}{2} \left( \frac{Z_i^* - r}{a_0} \right)^2 \geq \frac{1}{4} \quad (7a)$$

Thus we obtain relations (7) for the limits of the integrals appearing in (6a).

The choice of limits, as given by Equation (7), is required, also, to avoid divergence of the lower limits; it amounts to a (valid) cut-off procedure especially for  $i = 1$ . An alternative choice of lower limits, for example, would be the value of  $y$  for which

$$y^{1-n} \exp \left[ -\frac{\Delta}{2} (Z_i^* - y)^2 \right]$$

is a minimum.

Based on Inequality (7a), it can be shown that<sup>(9)</sup> in the case of Lennard-Jones solid the value of  $m$  (the number of effective shells) has to be at least equal to 2 (instead of 3 as was previously suggested<sup>(5,8)</sup>). In the case of soft-sphere solids, because of the positive (repulsive) form of the potential function,  $m$  can have

any value, as small as  $m = 1$ .

There are some Monte Carlo data available for the thermodynamic properties of pure soft-sphere fluid and solid systems (11,12). The data available are for  $n = 4, 6, 9, 12$ , with  $n$  being the power in Equation (1). The smaller the value of  $n$  is, the greater will be the deviation of Equation (1) from the hard-sphere potential function.

With the understanding that inequality (4) gives only a least upper bound for the Helmholtz free energy of soft-sphere fluid, based on the minimization of its right-hand side, and the fact that the reference system for this inequality is the hard-sphere fluid, the variational calculations upon inequality (4) will give satisfactory results for only large values of  $n$ . On Table I the Monte Carlo calculations on compressibility,

$$\frac{PV}{NkT}$$

and Helmholtz free energy

$$\left( \frac{A - A_{id}}{NkT} \right)$$

for pure soft-sphere fluid (11) with  $n = 12$ , are compared with the results of variational calculations on inequality (4) versus

$$\left( \frac{\epsilon}{kT} \right)^{\frac{1}{4}} (\rho\sigma^3) / \sqrt{2} .$$

Also shown on Table I, are the results of perturbation theory (11) for soft-spheres. The comparison indicates that the results of the variational theory are in good agreement with the Monte Carlo calculations, specifically at high densities. Figures I, II, and III show the changes in compressibility, Helmholtz free energy, and entropy, respectively, of soft-sphere fluid with respect to  $n$ , calculated by inequality (4) for different values of

$$\left( \frac{\epsilon}{kT} \right)^{\frac{3}{n}} (\rho\sigma^3) .$$

The dashed lines are the asymptotic (hard-sphere) values as  $n$  goes toward infinity. As illustrated, the thermodynamic properties of soft-spheres converge faster to hard-sphere results at lower densities.

Similar to inequality (4), variational calculations upon inequality (6) will give satisfactory results for the soft-sphere solid system only at large values of  $n$ . This is also because of the nature of the reference system in inequality (6) which is a solid single-occupancy Einstein cell model (harmonic-oscillator potential function inside each cell, and the infinity value of the potential at the walls of the cells). In Table II the Monte Carlo calculations on compressibilities (11) of pure soft-sphere solids are compared with the results of variational calculations for inequality (6), cell model, (11) and correlated-cell model (11). For the variational calculations three cases are considered:  $m = 1$  or shell,  $m = 2$  or 2 shells, a  $d_n$   $m = 3$  or 3 shells in inequality (6). The results of these calculations are in agreement with the Monte Carlo calculations, specifically at high densities.

**SOFT-SPHERE MIXTURE**

Aside from the variational theory of mixtures, (13,14)  $\langle r^{-2n} \rangle_0 - \langle r^{-n} \rangle_0^2 > 0$

there are other theories which actually give upper bounds to the thermodynamic properties of soft-sphere mixtures. These are the van der Waals' (vdW) and Scott's one- and two- fluid theories of mixture.

**Variational Theory For Soft-Sphere Mixture**

Inequality (2) will be in the following form for a system of soft-sphere fluid mixtures, with the hard-sphere fluid mixture taken as the reference system: (13)

$$A \leq A_0 + \frac{2\pi N^2}{V} \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^n \int_{d_{ij}}^{\infty} r^{-n} g_{ij}^0(r) r^2 dr \quad (8)$$

In the above inequality  $g_{ij}^0$ 's are the radial distribution functions of the reference hard-sphere mixture  $x_i$ ,  $x_j$  are the mole fractions of components  $i$  and  $j$ , and  $\epsilon_{ij}$ ,  $\sigma_{ij}$  are the intermolecular interaction parameters for the components  $i$  and  $j$ . This inequality, like inequality (3) for pure soft-sphere fluid, can also be reformulated with respect to the available Laplace transforms of  $rg_{ij}^0$ 's as given before (13). Minimization of the right-hand side (rhs) of inequality (8) with respect to  $d_{ij}$ 's will produce a least upper bound (lub) for the Helmholtz free energy of the soft-sphere fluid mixture.

**The Scott's "One-Fluid" Theory of Mixtures**

In the case where the original system consists of a mixture of molecules of different species and the reference system consists of a pure system of molecules, both with the same number of molecules and with soft-sphere intermolecular potential functions, we will have

$$U = \frac{1}{2} \sum_{i,j} \sum_{k,l} (\epsilon_{ij} \sigma_{ij}^n) r_{kl}^{-n} \quad (k \neq l) \quad (9)$$

and

$$U_0 = \frac{1}{2} \sum_{k,l} (\epsilon \sigma^n) r_{kl}^{-n} \quad (k \neq l) \quad (10)$$

In equation (9), the first summation is over the components and the second summation is over the interactions.  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the intermolecular interaction parameters for the components  $i$  and  $j$ , while  $r_{kl}$  is the intermolecular distance between molecules  $k$  and  $l$ . In equation (10) the summation is over the interactions.

Considering inequality (3) and relations (9) and (10) for  $U$  and  $U_0$ , in calculating the lub for  $A$  (the Helmholtz free energy of the soft-sphere mixture) it is necessary for the first derivative of the rhs of inequality (2) with respect to  $\epsilon \sigma^n$  to vanish (3,15). This will produce the following relation between  $\epsilon \sigma^n$  and  $\epsilon_{ij} \sigma_{ij}^n$ 's of the components of the mixture: (3,15)

$$\epsilon \sigma^n = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^n \quad (11)$$

Equation (11) is the condition necessary for the rhs of inequality (2) to be minimum with respect of  $\epsilon \sigma^n$ . The sufficient condition is when its second derivative is positive. That is, the following inequality must be valid:

$$\langle r^{-2n} \rangle_0 - \langle r^{-n} \rangle_0^2 > 0 \quad (12)$$

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The left-hand side of Inequality (12) is always positive and consequently Equation (11) for  $\epsilon\sigma^n$  will give a lub for the Helmholtz free energy of soft-sphere mixture. Equation (11) is actually the mixing rule for the Scott's "one-fluid" theory of soft-sphere mixture (16).

The Scott's "Two-Fluid" Theory Of Mixture

Consider the case where the original system consists of a soft-sphere mixture with total potential energy function given by Equation (9) and the reference system with the following total potential energy function:

$$U_0 = \frac{1}{2} \sum_i \sum_{k,l} (\epsilon_{ikl} \sigma_{ikl}^n) r_{kl}^{-n} \quad (13)$$

(k≠l)

In this case, to find the lub for A, it is necessary for the first derivatives of the rhs of inequality (2) to vanish, with respect to  $\epsilon_{ij} \sigma_{ij}^n$ 's. This will produce the following relations for  $\epsilon_{ij} \sigma_{ij}^n$ 's

$$\epsilon_{ij} \sigma_{ij}^n = \sum_j x_j \epsilon_{ij} \sigma_{ij}^n \quad (14)$$

To find the sufficient conditions for lub of A, we must look at the second derivatives of the rhs of inequality (2) with respect to  $\epsilon_{ij} \sigma_{ij}^n$ 's. In the case when i,j = 1,2, the sufficient conditions are

$$\frac{\partial^2(\text{ubA})}{\partial \Delta_1^2} > 0 \quad (15a)$$

$$\frac{\partial^2(\text{ubA})}{\partial \Delta_2^2} > 0 \quad (15b)$$

$$\frac{\partial^2(\text{ubA})}{\partial \Delta_1^2} \cdot \frac{\partial^2(\text{ubA})}{\partial \Delta_2^2} - \left( \frac{\partial^2(\text{ubA})}{\partial \Delta_1 \partial \Delta_2} \right)^2 < 0 \quad (15c)$$

where  $\Delta_1 = \epsilon_{ij} \sigma_{ij}^n$  and ubA = upper bound of A (the rhs of inequality (2)). Calculations show that conditions (15a) and (15b) are satisfied, but condition (15c) is not (the rhs of inequality (15c) vanishes). Consequently, it is not clear whether we can get to a lub for A in this case. Equation (14) is actually the mixing rule for the Scott's "two-fluid" theory of soft-sphere mixture (16).

The van der Waals' "One-Fluid" Theory of Mixture

By exchanging the places of the original and reference systems, inequality (2) can be written as follows:(3)

$$A_0 \leq A + \langle U_0 - U \rangle \quad (16)$$

In this inequality the angled brackets indicate the expectation value of  $U_0 - U$  over the original system. By consideration of the definition of entropy

$$TS = -A + \langle U \rangle \quad (17)$$

inequality (16) can be written with respect to entropies

$$TS \leq TS_0 + [\langle U_0 \rangle - \langle U_0 \rangle_0] \quad (18)$$

Considering inequality (18) and relations (9) and (10) for U and  $U_0$ , in order to find the lub for S, the entropy of the soft-sphere mixture, it is necessary for the first derivative of the rhs of inequality (18) with

respect to  $\epsilon\sigma^n$  to vanish, and the second derivative to be positive. That is, for the first and the second derivatives, relations (19) and (20), given below, should satisfy, (3) respectively

$$\langle r^{-n} \rangle_0 - \langle r^{-n} \rangle = 0 \quad (19)$$

$$\langle r^{-2n} \rangle_0 - \langle r^{-n^2} \rangle > 0 > 0 \quad (20)$$

Inequality (20) is always satisfied. Insertion of relation (19) in (18) will give

$$S \leq S_0 \quad (21)$$

Consequently  $S_0$  is the lub for S.  $S_0$  is the entropy of a reference pure soft-sphere which its molecular parameters ( $\epsilon, \sigma$ ) should satisfy relation (19). Analytic solution of Equation (19) for  $\epsilon$  and  $\sigma$ , with respect to  $\epsilon_{ij}, \sigma_{ij}$  is not generally possible, but it could be solved at high temperature (3,17) which gives the following results:

$$\sigma^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (22)$$

$$\epsilon\sigma^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3$$

Relations (22) are the mixing rules for van der Waals' "one-fluid" theory of mixture. This indicates that vdW (1f) theory of mixture gives an approximation to a lub for the entropy of mixture of soft-spheres (1,12).

The van der Waals' "Two-Fluid Theory of Mixture

In the case where U is given by Equation (9) and  $U_0$  is given by Equation (13) we investigate the possibilities of minimizing the rhs of inequality (18) with respect to  $\epsilon_{ij} \sigma_{ij}^n$ 's in order to derive a lub for the entropy of soft-sphere mixture. For this, the first derivatives of the rhs of inequality (18) with respect to  $\epsilon_{ij} \sigma_{ij}^n$ 's should vanish yielding the following relation

$$\langle r^{-n} \rangle_0 - \langle r^{-n} \rangle = 0 \quad (23)$$

For the second derivatives, where i,j = 1,2, it is necessary to satisfy the following relations in order to have a lub for S.

$$\frac{\partial^2(\text{ubS})}{\partial \Delta_1^2} > 0 \quad (24a)$$

$$\frac{\partial^2(\text{ubS})}{\partial \Delta_2^2} > 0 \quad (24b)$$

$$\frac{\partial^2(\text{ubS})}{\partial \Delta_1^2} \cdot \frac{\partial^2(\text{ubS})}{\partial \Delta_2^2} - \left( \frac{\partial^2(\text{ubS})}{\partial \Delta_1 \partial \Delta_2} \right)^2 < 0 \quad (24c)$$

with ubS the "upper bound of S" and  $\Delta_1 = \epsilon_{ij} \sigma_{ij}^n$ . Algebraic calculations show that conditions (24a) and (24b) are satisfied but condition (24c) is not (the left-hand side of condition (24c) vanishes). This indicates that we cannot be sure whether relation (23), substituted in the rhs of inequality (18) will minimize it or not. At high enough temperatures, and by a similar process as in the case of vdW (1f) theory, we can solve Equation (23) for  $\epsilon_1$  and  $\sigma_1$  with the following results(17)

$$\left\{ \begin{aligned} \sigma_i^3 &= \sum_j x_j \sigma_{ij}^3 \\ \epsilon_i \sigma_i^3 &= \sum_j x_j \epsilon_{ij} \sigma_{ij}^3 \end{aligned} \right. \quad (25)$$

Relations (25) are the mixing rules for the van der Waals' "two-fluid" theory, vdW (2f), of mixture (17,18).

#### Comparison Of The Theories of Mixtures

For calculation of the thermodynamic properties of soft-sphere fluid mixtures through the variational theory, inequality (8) is used. For the properties of reference hard-sphere mixture systems, the results of the Percus-Yevick theory is used (19,20) as in the case of variational theory for Lennard-Jones mixture (13,14). While the variational theory will produce a lub for the Helmholtz free energy based on inequality (8), it is shown in the case of Lennard-Jones mixture that the excess thermodynamic properties of mixture calculated through the variational theory are in agreement with the machine-calculated and experimental data (14,21). This is because the errors on total properties correct each other in the calculation of excess properties. In Figures IV-VI excess Gibbs free energy, excess enthalpy and excess volume calculated by variational theory, for binary soft-sphere mixture are compared with the results of binary hard-sphere mixture (20) and binary Lennard-Jones mixture, (13,14) all equimolar, at different constant pressures and at  $T = 100^\circ\text{K}$ . The molecular diameters of the components for all the three potential models (hard-sphere, soft-sphere, and Lennard-Jones) in these figures are chosen equal. For the soft-sphere potential in these figures it is assumed that  $u(r) = 4\epsilon(\sigma/r)^{12}$ , consistent with the Lennard-Jones potential function. Also for unlike interaction parameters in the three potential models it is assumed that

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 = 3.596 \text{ \AA}$$

and

$$\epsilon_{12}/k = \epsilon_{11}/k = \epsilon_{22}/k = 133.5^\circ\text{K}$$

As shown in these figures, the excess Gibbs and excess enthalpy of Lennard-Jones mixture are not very sensitive, while its excess volume is more sensitive to changes of pressure. In the case of soft-sphere and hard-sphere excess properties, it is shown that sensitivities with respect to pressure are much more than in the case of Lennard-Jones excess properties. There is a peculiarity in the excess volume of soft-sphere mixture and that is its very strong sensitivity to pressure change.

For calculation of the properties of soft-sphere fluid mixture through the Scott and van der Waals theories of mixture, besides the mixing rules for these theories we need a reference pure soft-sphere equation of state (1,18). For the purpose of comparison of the results of these mixture theories with the results of the variational theory of soft-sphere mixture, we use the variational equation of state for pure-soft-spheres, Equation (4), as the reference equation.

By joining Equation (11) with inequality (4) we get the following inequality

$$\frac{A - A_{1d}}{NkT} \leq A_0^*(\eta) + \left[ \sum_i \sum_j x_i x_j \left( \frac{\epsilon_{ij}}{kT} \right) (\rho \sigma_{ij}^3)^{\frac{n}{3}} \right] A_1^*(\eta, n) \quad (26)$$

Minimization of the rhs of inequality (26) with respect to  $\eta$  will give the Helmholtz free energy of soft-sphere

mixture through the Scott's "one-fluid" theory of mixture with the pure soft-sphere variational equation of state as the reference equation.

In the case of the Scott's "two-fluid" theory of mixture with the pure soft-sphere variational equation of state as the reference equation, the working inequality will be as follows

$$\frac{A}{NkT} \leq A_0^*(\eta) + \left[ \sum_i x_i \left( \frac{\epsilon_i}{kT} \right) (\rho \sigma_i^3)^{\frac{n}{3}} \right] \cdot A_1^*(\eta, n) \quad (27)$$

where  $\epsilon_i \sigma_i^n$  appearing in the above inequality is given by Equation (14). Joining Equation (14) with inequality (27) will produce inequality (26) and consequently the results of the Scott (1f) and Scott (2f) theories of mixture will be equivalent.

By joining Equation (22) with inequality (4) we get the following inequality

$$\frac{A}{NkT} \leq A_0^*(\eta) + \left[ \sum_{i,j} x_i x_j \left( \frac{\epsilon_{ij}}{kT} \right) \frac{\sigma_{ij}^3}{\sum_{m,n} x_m x_n \sigma_{mn}^3} \right] \cdot \left( \sum_{i,j} x_i x_j \rho \sigma_{ij}^3 \right)^{\frac{n}{3}} A_1^*(\eta, n) \quad (28)$$

Minimization of the rhs of inequality (28) with respect to  $\eta$  will give the Helmholtz free energy of soft-sphere mixture through the vdW (1f) theory of mixture with the pure soft-sphere variational equation of state as the reference equation.

In the case of the vdW (2f) theory of mixture with the pure soft-sphere variational equation of state as the reference equation, the working inequality will be the same as inequality (27), with  $\epsilon_i, \sigma_i$  appearing in this inequality given by Equation (25). By joining Equation (25) with inequality (27) we get the following inequality

$$\frac{A}{NkT} \leq A_0^*(\eta) + \sum_i x_i \left\{ \left[ \sum_j x_j \left( \frac{\epsilon_{ij}}{kT} \right) \frac{\sigma_{ij}^3}{\sum_i x_i \sigma_{ij}^3} \right] \cdot \left( \sum_j x_j \rho \sigma_{ij}^3 \right)^{\frac{n}{3}} \right\} \cdot A_1^*(\eta, n) \quad (29)$$

Minimization of the rhs of inequality (29) with respect to  $\eta$  will give the Helmholtz free energy of soft-sphere mixture through the vdW (2f) theory of mixture with the pure soft-sphere variational equation of state as the reference equation.

In Figures VII and VIII Helmholtz free energy and entropy of equimolar binary soft-sphere mixture calculated by different mixture theories for  $n = 12$  are compared. For these figures  $T = 100^\circ\text{K}$ , specific volume = 30cc/mole,  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 = 3.596 \text{ \AA}$  and  $\epsilon_{11}/k = \epsilon_{22}/k = \epsilon_{12}/k = 133.5^\circ\text{K}$ .

As it is proved here, the variational and Scott (1f) theories both give least upper bounds for the Helmholtz free energy of soft-sphere mixture based on their respective inequalities. In Figure VII it is shown that for the system chosen the upper bound due to the variational theory is much lower than the upper bound due to the Scott (1f) theory. This indicates that the results of the variational theory for Helmholtz free energy of soft-sphere mixture is much closer to reality than the results of the Scott (1f) theory.

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The results of the Scott (1f) theory for Helmholtz free energy is equivalent to the Scott (2f) theory as indicated above.

It was also proved that for soft-sphere mixture the vdW (1f) theory gives an approximation for a lub of entropy of the mixture based on its respective inequality and that it is not certain whether the vdW (2f) theory gives a least upper bound to entropy. On Figure VIII entropies calculated by the vdW (1f) and vdW (2f) theories are compared with the results of other theories. The values of entropies calculated by vdW (1f) are higher than those of the vdW (2f) theory. Of course, this does not mean that vdW (2f) is closer to reality, due to the fact that it is not certain whether the vdW (2f) theory gives an upper bound to entropy. Even if we accept that the vdW (2f) theory gives an upper bound (lower than the upper bound due to vdW (1f) theory) for entropy, we can see from Figure VII that the Helmholtz free energy by vdW (2f) is much farther from the lowest upper bound of Helmholtz free energy (the results of variational theory) than the result of the vdW (2f) theory. Similarly, we can compare the variational and Scott (1f,2f) theories with the vdW (1f) theory (which gives a lub for entropy) on Figure VIII and conclude that the variational theory gives a better estimate of entropy of soft-sphere mixture than the Scott (1f,2f) theories. Of course, it should be remembered that the vdW (1f) theory gives only an approximation to an upper bound of entropy of mixture which it is accurate at high temperatures. Overall, results of the variational and vdW (1f) theories are very close to each other and they are expected to be closer to the real thermodynamic properties of soft-sphere mixture than the other theories. The superiority of the vdW (1f) and variational theories over the vdW (2f) and Scott (1f,2f) theories have already been demonstrated by many investigators for hard-sphere and Lennard-Jones mixtures (1,2,13,20-22).

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**Table I:**

Pure Soft-Sphere Compressibility and Helmholtz Free Energy  
 Versus Density with  $u(r)=\epsilon(\sigma/r)^{12}$   
 (Fluid Phase)

$\rho^* / \sqrt{2}$	PV/NkT				$(A-A^{id})/NkT$			
	M.C.	Var.	Pert. (1)	Pert. (2)	M.C.	Var.	Pert. (1)	Pert. (2)
0.10	1.45	1.49	1.47	1.36	0.40	0.44	0.42	0.39
0.20	2.12	2.22	2.15	2.11	0.91	0.99	0.94	0.89
0.30	3.10	3.29	3.16	3.18	1.53	1.67	1.58	1.54
0.40	4.56	4.82	4.65	4.72	2.32	2.53	2.40	2.37
0.50	6.64	6.97	6.89	6.93	3.33	3.60	3.43	3.43
0.60	9.46	9.94	10.31	9.98	4.60	4.93	4.79	4.77
0.65	11.36	11.81	12.70	11.88	5.35	5.72	5.62	5.57
0.70	13.47	13.98	15.73	14.13	6.20	6.59	6.60	6.46
0.75	15.91	16.48	19.63	16.61	7.14	7.58	7.74	7.45
0.80	18.76	19.36	24.74	19.57	8.19	8.67	9.10	8.55

$\rho^* = (\epsilon/kT)^{1/4} (\rho\sigma^3)$

**Table II:**

Pure Soft-Sphere Compressibility versus Density with  $u(r)=\epsilon(\sigma/r)^{12}$   
 (Solid Phase)

$\rho^* / \sqrt{2}$	PV/NkT					Cell	Corr. Cell
	Monte Carlo	Variational					
		1 shell	2 shells	3 shells			
0.80	16.51	15.42	15.50	15.53	16.12	16.53	
0.90	22.55	21.71	21.83	21.88	22.34	22.56	
1.00	30.99	30.23	30.42	30.49	30.85	30.98	
1.20	56.16	56.34	56.73	56.87	57.09	57.15	

$\rho^* = (\epsilon/kT)^{1/4} (\rho\sigma^3)$

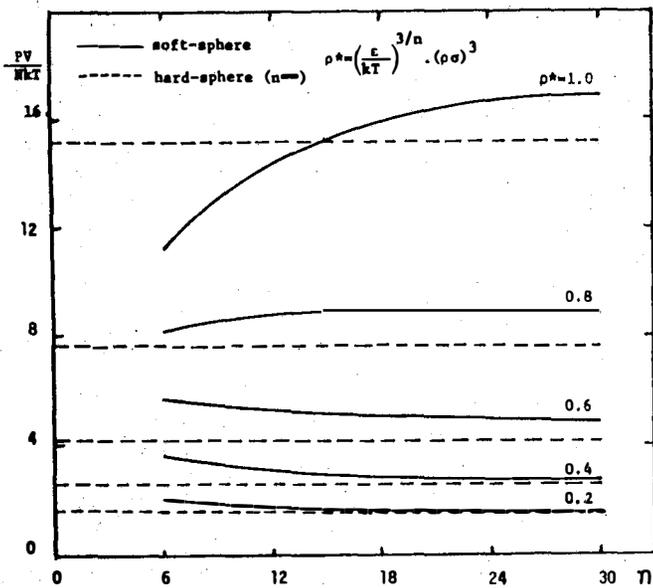


Figure I: Compressibility versus  $n$ , the exponent in Eq. (1) for pure systems calculated by the variational theory.

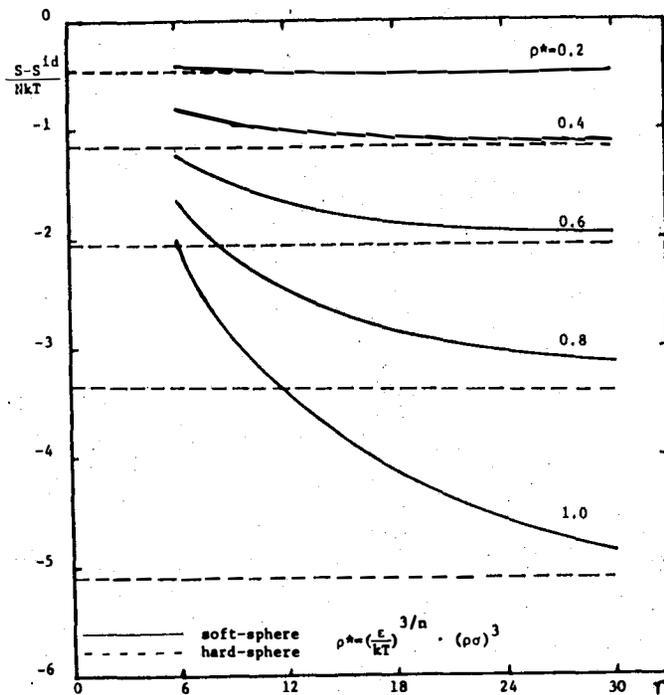


Figure III: Entropy versus soft-sphere exponent for pure systems according to the variational theory.

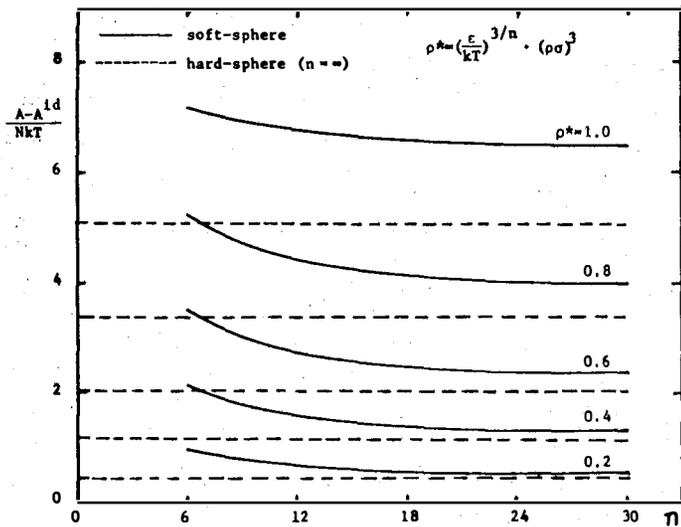


Figure II: Helmholtz free energy versus soft-sphere exponent for pure systems according to the variational theory.

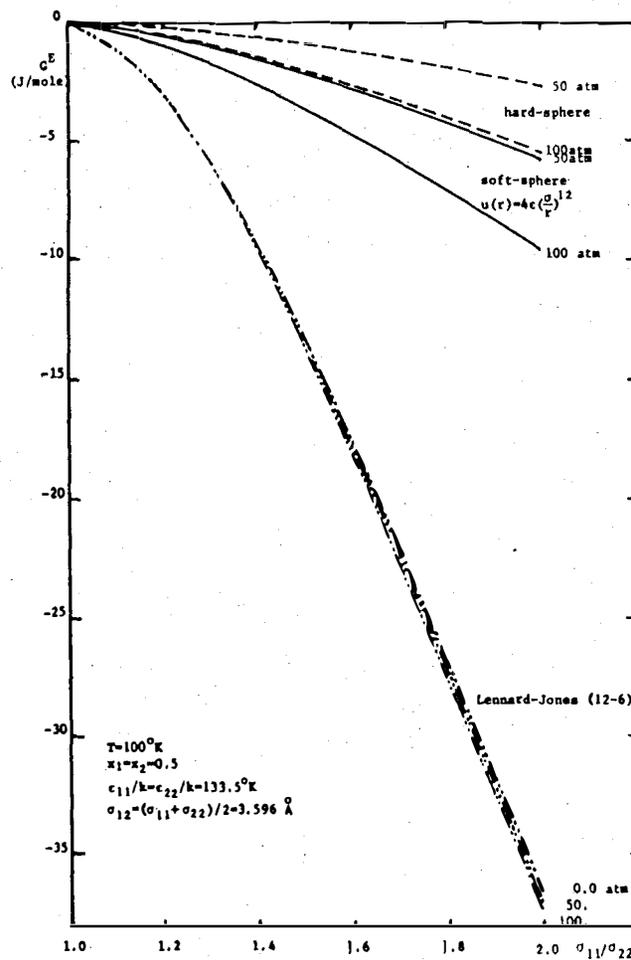


Figure IV: Excess Gills function of binary mixtures calculated by the variational theory.

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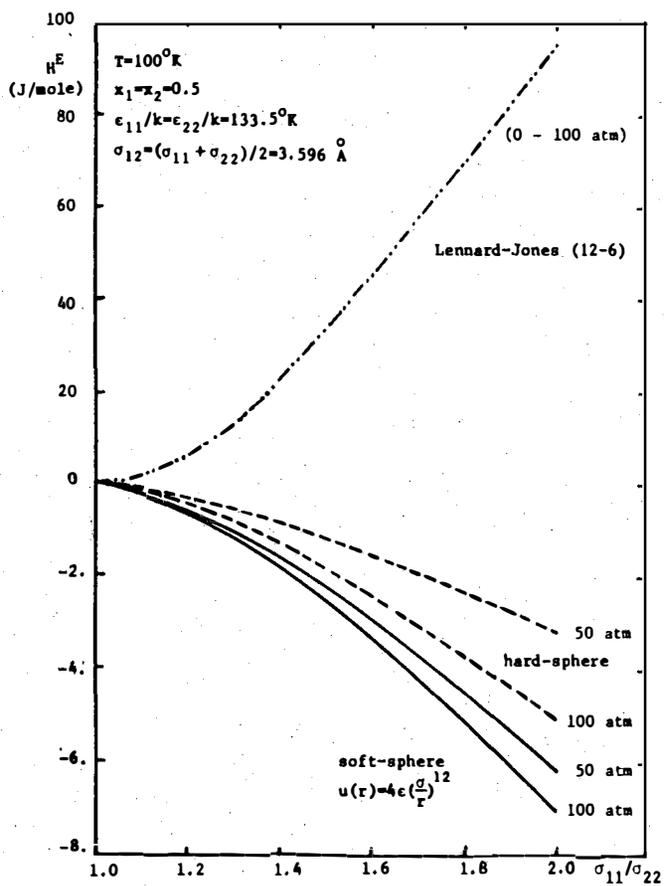


Figure V: Excess enthalpy of binary mixtures calculated by the variational theory.

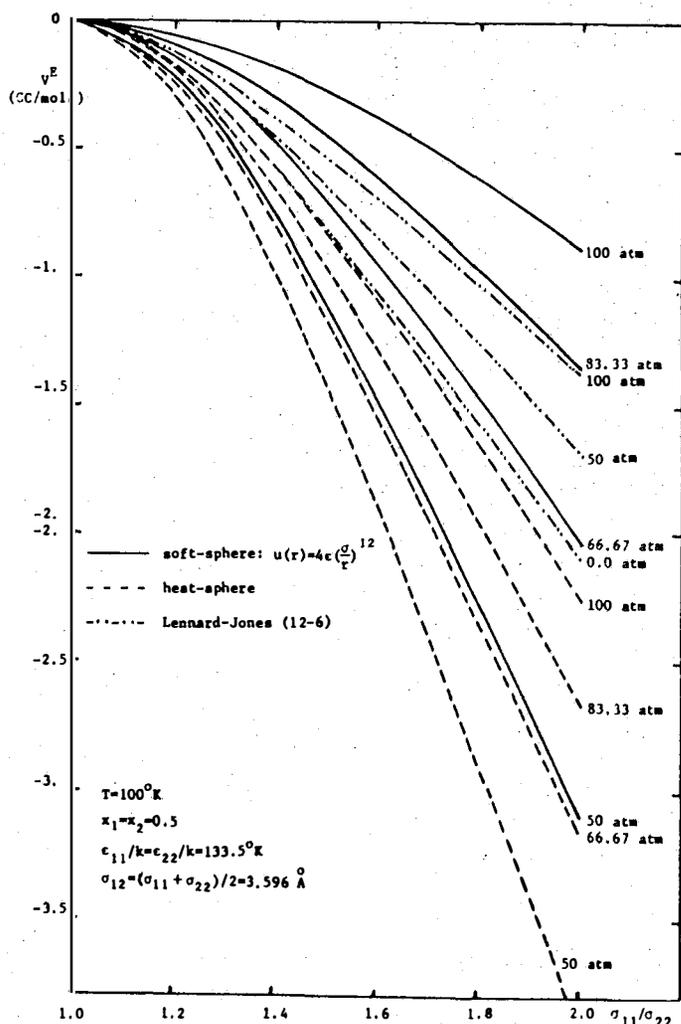


Figure VI: Excess volume of binary mixture according to variational theory

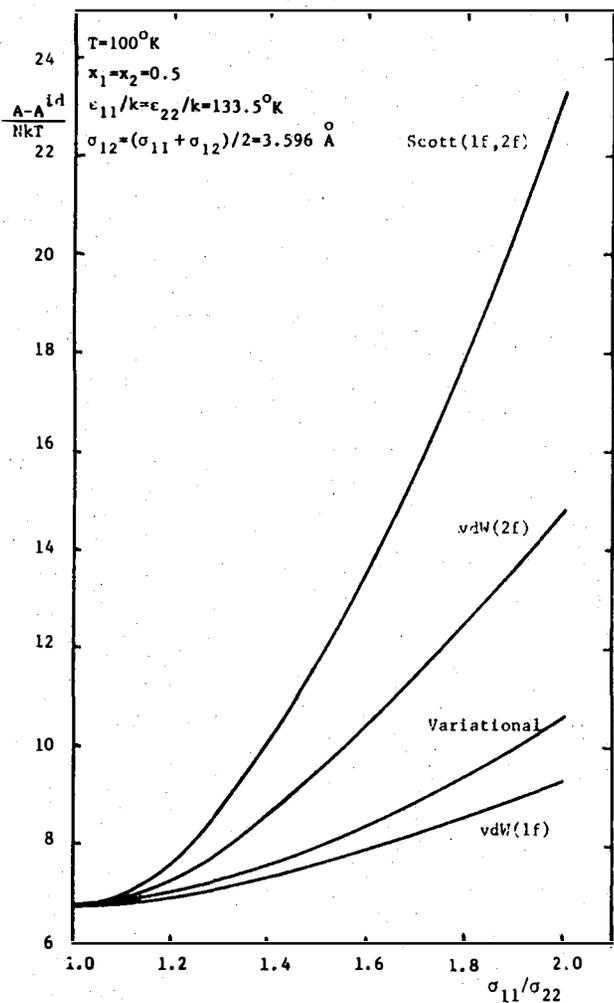


Figure VII: Helmholtz function of binary mixture of soft-spheres according to different theories.

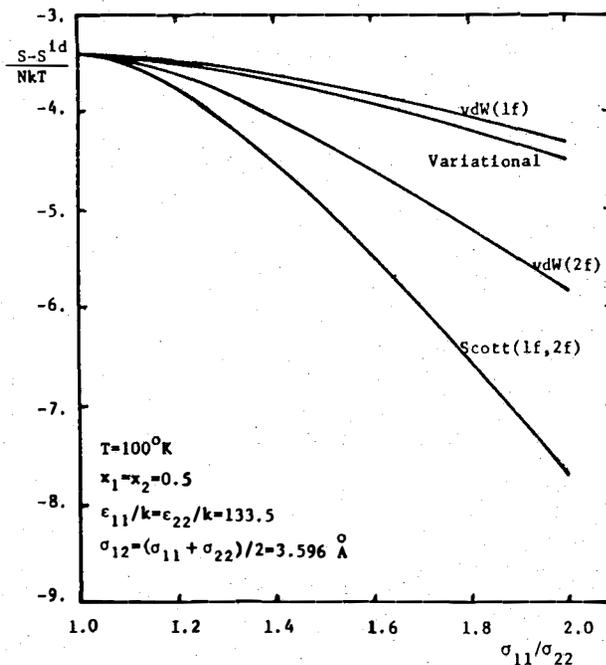


Figure VIII: Entropy of binary mixture of soft-spheres according to different theories.