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APPLICATION TO HIGH-PRESSURE PHYSICS PROBLEMS**

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**A NEW APPROACH TO MULTIPHASE EQUILIBRIA:
APPLICATION TO HIGH-PRESSURE PHYSICS PROBLEMS**

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Abstract

A multiphase, multicomponent equation-of-state (EOS) model based on first principles of statistical mechanics is described. The model has been used to study fluid-fluid phase separations in binary (H_2 -He, Ar-Ne, Xe-He, and N_2 - H_2O) and ternary or more complex systems involving species with C, H, N, and O atoms. Results of these calculations and a brief description on a new theory which can simultaneously describe both solid and fluid EOS properties are given.

Key words: multiphase, multicomponent; fluid-fluid phase separation, equations of state of solid and fluid.

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1. Model of multiphase chemical equilibrium

The objective of this paper is to describe and apply a statistical mechanical model of multicomponent and multiphase systems. Necessary ingredients of such a theory are: (a) an efficient method of solving for the concentrations of the molecular species, (b) realistic intermolecular potentials, (c) accurate solid and fluid equations of state (EOS), and (d) a reliable mixture model. During the past fifteen years there have been significant advances made in these subjects. As a result, we were able to develop the chemical equilibrium (CHEQ) computer code [1] which mostly makes use of (a)-(d) above.

The CHEQ code evaluates thermodynamic properties of a mixture of given chemical species with known atomic composition at fixed pressure (P) and temperature (T). The mixture can be in several solid and fluid phases. Equilibrium compositions $\{n_i\}$ of chemical species are calculated by minimizing the Gibbs free energy $G(P, T, \{n_i\})$ which is, in turn, expressed in terms of the chemical potentials of the constituents. The only link between the CHEQ code and EOS theories occurs through the chemical potentials. The remaining portion of the CHEQ code is concerned with numerically minimizing the free energy by using the extent-of-reaction variable method. This method has been discussed by Prigogine and Defay [2].

The model described above requires EOS expressions for each phase. In the case of fluid phase, we use the Ross theory [3] in which the Helmholtz free energy A

$$A = A_{HS} + F(\eta)NkT + (\rho N/2) \int d\mathbf{r} \phi(r) g_{HS}(r) + A_{qm} \quad (1)$$

is minimized with respect to the hard-sphere packing fraction η .

Expressions for the hard-sphere quantities A_{HS} , $g_{HS}(r)$, and $F(\eta)$ are given in [3]. The last term, A_{qm} , is the first-order Wigner-Kirkwood quantum correction:

$$A_{qm} = \frac{Nh^2}{96\pi^2 mkT} \int dr \, r^2 \phi(r) g_{HS}(r) \quad , \quad (2)$$

where m denotes the mass of constituent molecules.

In the discussion to follow, we will use the exponential-six (exp-6) potential,

$$\phi(r) = \frac{\epsilon}{\alpha-6} \{ 6 \exp [\alpha(1 - r/r^*)] - \alpha(r^*/r)^6 \} \quad , \quad (3)$$

to represent intermolecular potentials. Exp-6 parameters (ϵ , r^* , α) for chemical species of interest here are given in [1]. Thermodynamic properties computed from Eqs. (1)-(3) have been shown to agree with computer simulations [3] and experimental data [4,5].

The above one-component EOS theory has been extended to mixtures by using an improved van der Waals one-fluid model [6]. In this model the mixture potentials are replaced by an effective exp-6 potential with its parameters expressed in terms of the parameters of constituent species by

$$(r^*)^3 = \sum_{i,j} x_i x_j (r_{ij}^*)^3 \quad , \quad (4)$$

$$\epsilon = \sum_{i,j} x_i x_j \epsilon_{ij} (r_{ij}^*)^3 / (r^*)^3 \quad , \quad (5)$$

$$\alpha = \sum_{i,j} x_i x_j \alpha_{ij} \epsilon_{ij} (r_{ij}^*)^3 / \epsilon (r^*)^3 \quad , \quad (6)$$

where x_i denotes the mole fraction of species i . The quantum correction, Eq. (2), for mixtures can be accommodated, within the effective one-component framework, by introducing an effective mass m :

$$1/m = \sum_{i,j} x_i x_j (1/m_i) \epsilon_{ij} r_{ij}^* / \epsilon r^* \quad (7)$$

The accuracy of the effective one-component model has been tested against Monte Carlo (MC) results for a two-component mixture of H_2 and He [7].

2. A new EOS theory of fluid and solid

Typical calculation of a 10-component system by the CHEQ code takes approximately 10^3 to 10^4 seconds of CRAY computer time per (P,T)-point for most potentials. In the case of an exp-6 potential the computing time can be shortened by a factor of about 50 to 100. Nevertheless, computing time becomes formidable for complex calculation.

With this in mind, we have developed a new perturbation theory [8]. The new approach divides $\phi(r)$ into a reference potential $\phi_0(r)$ and a perturbation potential $\phi_1(r)$, i.e., $\phi(r) = \phi_0(r) + \phi_1(r)$ with

$$\begin{aligned} \phi_0(r) &= \phi(r) - F(r), & \text{if } r \leq \lambda, \\ &= 0, & \text{if } r > \lambda, \end{aligned} \quad (8)$$

$$\begin{aligned} \phi_1(r) &= F(r), & \text{if } r \leq \lambda, \\ &= \phi(r), & \text{if } r > \lambda, \end{aligned} \quad (9)$$

by introducing a break point $\lambda = \min(a_{fcc}, r^*)$, where a_{fcc} is the nearest-neighbor distance ($2^{1/6}/\rho^{1/3}$) of an fcc structure. Both

$\phi_0(r)$ and $\phi_1(r)$ contain a function $F(r)$ which is chosen to make the perturbation series converge fast.

The free energy A_0 of the reference system is replaced by that of hard spheres using the hard-sphere diameter of the Weeks-Chandler-Anderson (WCA) theory [9]. Note that the present perturbation scheme reduces to the WCA theory if density is less than $\rho(r^*)^3 = \sqrt{2}$. At higher densities the range, λ , of $\phi_0(r)$ shrinks with density, which is a desirable feature. Table I gives comparison of exp-6 thermodynamic properties at $kT/\epsilon=20$. An advantage of the new theory is that the hard-sphere diameter can be expressed analytically.

It is worthwhile to test the EOS theory described above for solids as well. We have obtained encouraging results for Lennard-Jones, exp-6, and inverse nth-power fcc systems [10]. Table I shows comparison of PV/NkT for an exp-6 potential. A complete study will be published in due course.

3. Fluid-fluid phase separation in binary and ternary systems

Experimental solubility data offer a reliable basis for fixing unlike-pair interactions in condensed matter. For a simple binary mixture, this can be done by directly evaluating G and solving for a pair of roots, x' and x'' (x =mole fraction of species 1), at which the excess Gibbs free energy of mixing has a common tangent. This procedure has been applied [7], in conjunction with Streett's experimental data of the H_2 -He system [11]. The resulting exp-6 parameters reproduce Streett's data at $T \geq 61.5$ K. At lower T , higher-order quantum corrections [than Eq. (2)] become important. (More recently, Schouten et al. [12] extended the experimental critical solubility line to 5 GPa.)

An alternative and more general way to compute the solubility line is to use the CHEQ code. In Fig. 1 the resulting theoretical solubility lines of the Ar-Ne system are compared with the experimental data of Streett [13] at subcritical temperatures of argon. Similar comparison on the Xe-He system is given in Fig. 2, using de Swaan Arons and Diepen's data [14]. The calculations are based on like-pair exp-6 parameters derived from the corresponding-states scaling relations [4] and the unlike-pair ϵ_{ij} values from an empirical rule [15]. Since the main purpose of the calculations was to test the CHEQ code, no attempt was made to "fine-tune" the exp-6 parameters. Therefore, it is encouraging to see reasonable agreement between theory and experiment. Near the critical region, however, the theoretical results tend to become "stiffer". This unphysical behavior is connected with our use of the free energy expression, Eq. (1), which becomes nonconvex with respect to variation of n_i 's. Its use in the CHEQ code can cause a computational problem near the critical region, because an algorithm used to minimize G in the CHEQ code takes advantage of the convexity of G .

We next consider the supercritical fluid phase separation in mixtures of polar and nonpolar molecules. Molecules such as H_2O and NH_3 have a strong electrostatic attraction. At high temperature it is possible to include the electrostatic interaction by using

$$\phi(r, T) = (1 + \lambda/T) \phi(r), \quad (10)$$

where $\phi(r)$ is given by Eq. (3) and the factor λ/T represents a spherically averaged electrostatic dipole interaction [1]. For water molecules, for example, λ is equal to 996.8 K [1].

The experimental critical solubility lines of the $\text{CO}_2\text{-H}_2\text{O}$ system [16] shows that H_2O and CO_2 molecules are soluble at $T \geq 550$ K and $P \geq 100$ MPa. In contrast, the experimental $\text{N}_2\text{-H}_2\text{O}$ data [17] shows limited solubility in the same (P,T) range. These molecules are major detonation products of condensed explosives. Since the region of interest for explosives lies above 10 GPa and 1000 K where experimental data of mixtures are not available, we applied our model to study the $\text{N}_2\text{-H}_2\text{O-CO}_2$ system. Figure 3 shows the theoretical solubility lines at 0.35eV (4062 K). Sensitivity of the solubility lines to the unlike-pair repulsive parameters and influence of CO_2 are indicated in Fig. 3. The most important conclusion from this study is that detonation properties will likely be affected by the fluid-fluid phase separation in Fig. 3.

4. High-pressure fluid-phase separation in more complex mixtures

We are now in a position to try our model to more complex systems. We first consider PBX-9404, an explosive with composition of $\text{C}_{1.4}\text{H}_{2.75}\text{N}_{2.57}\text{O}_{2.69}\text{Cl}_{0.03}\text{P}_{0.01}$. Detonation of PBX-9404 produces N_2 , CO_2 , H_2O , and solid C with minor amounts of H_2 , NH_3 , CO , O_2 , CH_4 , and NO (neglecting species with P and Cl). Two sets of calculations are carried out. The first set assumes detonation products to be in two phases, i.e., a gas-phase mixture of the aforementioned nine molecules and a solid phase of carbon (graphite or diamond). The second set is a three-phase calculation, in which a gas phase of N_2 and CO_2 is added to the first set. The additional phase is introduced to accommodate the fluid-phase separation in the $\text{N}_2\text{-H}_2\text{O}$ system. See Sec. 3.

In Fig. 4 the experimental shock pressure data of PBX-9404 [19,20] are compared with the two theoretical calculations. We note that the three-phase calculation gives a better agreement with the experimental data. It should be pointed out that the second gas phase does not occur at all pressures and temperatures. It occurs only if its inclusion lowers the Gibbs free energy. In a separate paper [21], we discuss in detail why and how a fluid phase separation affects the detonation properties of PBX-9404.

We next consider two hypothetical systems, composed of the same chemical species as in the PBX-9404 case. One of them has C/H, N/H, and O/H ratios equal to the solar abundance ratios [22] and the second with 100 times larger values. Calculations are done at $P=10$ GPa and $T=2200$ K which approximately represents the condition at an interior point of Uranus or Neptune. Fluid-fluid phase separation is allowed for the nine species. Results summarized in Table II show that the fluid phase separation does not occur in the first case. This probably is not true for the outer planets, since other species (e.g., helium, neglected in the present calculations) or concentration fluctuations (present in the planetary interiors) will favor fluid-phase separation. The second calculation which is probably more realistic predicts that H_2O and NH_3 molecules undergo a fluid-phase separation. This can explain why one expects to find the "ice" and the hydrogen-rich layers, as assumed in the current models of the outer planets [23]. The predicted phase separation could also explain the observed depletion of N/H and O/H compared with the solar values in atmospheres of Uranus and Neptune [24]. Our model predicts that CH_4 molecules prefer to coexist with H_2O and NH_3 rather than with H_2 . This prediction may conflict with the observed (2 to 20 times) enhancements of C/H [25] in the planetary atmospheres. For Jupiter and Saturn, the difficulty could be resolved if the metallic hydrogen existing

deep inside the planets is only slightly soluble with carbon. The calculation shows no diamond formation. Further study is needed to substantiate an interesting proposal by Ross [26] about possibility of diamond in Uranus and Neptune.

6. Concluding remarks

The area of multicomponent and multiphase physics and chemistry has many applications but theoretical progress in this field has been slow. In this paper we have described a nonempirical approach to multiphase, chemical equilibria. The model has been applied to several mixture systems. We have discussed possible improvements of the CHEQ code, related to a unified solid and fluid EOS theory. The CHEQ model also needs to be improved to properly describe the behavior near the critical region of fluid-phase separation. In this regard, it is important to have experimental solubility data of the N_2-H_2O system at pressures above 10 GPa.

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Table I. Comparison of PV/NkT of exact Monte Carlo calculations with the new perturbation theory for the exp-6 system at $kT/\epsilon = 20$.

	$\rho(r^*)^3/\sqrt{2}$	$PV/(NkT)$	
		Exact ^a	Theory ^b
<u>Fluid</u>	0.9	3.27	3.27
	1.0	3.81	3.80
	1.5	8.07	8.04
	2.05	16.58	16.65
<u>Solid</u>	2.308	20.28	20.19
	2.7	30.66	30.84

^a References 3, 8, and 11.

^b References 8 and 11.

Table II. Chemical compositions in multiphase equilibria at 2200° K and 10 GPa (corresponding to an interior position^a of Uranus and Neptune).

Solar Composition ^b		100 x Solar (C, N, O) ^c		
Solid	Fluid A = Fluid B (mole %)	Solid	Fluid A (mole %)	Fluid B (mole %)
H ₂	99.7467		93.5986	4.9361
H ₂ O	0.1496		0.1391	74.5971
NH ₃	0.0119		0.0052	9.0124
CH ₄	0.0888		6.2570	11.4543
CO	0.0000		0.0001	0.0001
CO ₂	0.0000		0.0000	0.0001
N ₂	0.0030		0.0000	0.0000
NO	0.0000		0.0000	0.0000
O ₂	0.0000		0.0000	0.0000
Diamond	0	0	---	---

^a W. Hubbard, private communication.

^b Input compositions: (H₂, H₂O, CH₄, NH₃) = (1, 0.0015, 0.00089, 0.00018) moles.

^c Input compositions: (H₂, H₂O, CH₄, NH₃) = (1, 0.15, 0.089, 0.018) moles.

FIGURE CAPTIONS

- Fig. 1 Liquid-gas solubility lines of Ar-Ne mixture. Comparison between the present result and the experimental data [13].
- Fig. 2 Gas-gas solubility lines of Xe-He mixture. Comparison between the present work (= dash-dot lines) and the experimental data (=solid lines) [14].
- Fig. 3 Theoretical solubility lines of N_2 - H_2O system with and without 22.6 mole% CO_2 at 0.35 eV (4062 K). Effect of changing an exp-6 potential parameter, r^* , is also examined.
- Fig. 4 Shock pressure vs compression of PBX-9404 (V_0 =initial volume = $0.543 \text{ cm}^3/\text{g}$). Comparison between the theoretical and the experimental results. Experimental data are from Kineke and West [20] and the Lawrence Livermore National Laboratory (LLNL) data by Lee and Green et al. [19]. The CHEQ-2 phase result uses a model of a fluid-phase mixture plus a solid carbon phase (graphite or diamond). The CHEQ 3-phase result is based on two fluid phases (i.e., N_2 -rich and N_2 -poor mixtures) and a solid carbon phase.

Fig. 2

Fig. 3

Fig. 4