

THE SECOND ORDER PERTURBATION TERM IN THE THEORY OF MULTICOMPONENT LIQUID SYSTEMS

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The Barker and Henderson perturbation theory was used for deriving an expression for the second order perturbation term in the free energy expansion of liquid mixtures. This extended theory was then employed to calculate excess thermodynamic functions ΔV^E , ΔG^E and ΔH^E of several model binary systems. The use of the second order term leads to a better agreement between the theoretical values and experimental or Monte Carlo data.

Prediction of thermodynamic functions and a correct quantitative interpretation of thermodynamic behaviour of liquids and liquid mixtures in a wide temperature and pressure range is important not only from a theoretical point of view, but it also plays a significant role in chemical engineering applications. Because of this fact, a great deal of attention is now being paid to modern exact theories of the liquid state.

Especially good results have been obtained with perturbation methods¹⁻⁵, which are based on the knowledge of thermodynamic functions of simpler model systems (*e.g.* a system of hard spheres)⁶⁻⁹.

One of the best variants of the perturbation theory is that by Barker and Henderson, which takes into account both the "softness" (finite steepness) of the repulsive part of the potential and interactions due to the attractive forces. These authors have formulated the perturbation expansion for pure substances to second order^{1,2}, whereas for mixtures only to first order³.

It was the aim of our work to derive an expression which would define the second order perturbation term in the free energy expansion of a liquid mixture and to verify the applicability of the extended perturbation method to the description of real systems.

THEORETICAL

For an *s*-component mixture Barker and Henderson³ have derived the following first order perturbation expansion for the free energy *F*

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$$\frac{F - F_0}{NkT} = -4\pi n \sum_{k < l}^s x_k x_l d_{kl}^2 g_0^{kl}(d_{kl}) (d_{kl} - \delta_{kl}) + 2\pi\beta n \sum_{k,l}^s x_k x_l \int_{\sigma_{kl}}^{\infty} u_{kl}(r) g_0^{kl}(r) r^2 dr + O(\beta^2), \quad (1)$$

with F_0 being the free energy of the hard sphere reference mixture⁹, N the total number of particles, and n the total number density; the symbols $g_0^{kl}(r)$ denote the radial distribution functions of individual components in the mixture of additive hard spheres⁸, $u_{kl}(r)$ is the interaction potential and x_k stands for the mole fraction of component i .

The quantities δ_{kl} are given by

$$\delta_{kl} = \int_0^{\sigma_{kl}} \{1 - \exp[-\beta u_{kl}(r)]\} dr, \quad (2)$$

where σ_{kl} is a parameter in the interaction potential for which it holds $u_{kl}(r = \sigma_{kl}) = 0$.

The hard sphere diameters in the Barker and Henderson treatment are defined by

$$d_{kl} = 0.5(\delta_{kk} + \delta_{ll}). \quad (3)$$

In comparison with pure liquids, considerable difficulties arise in deriving the second order term and no procedure has been published so far which would follow the original Barker and Henderson ideas without employing any further approximation. (The expression published in¹⁰ for the second order term of a mixture cannot be derived without further simplifying assumptions.)

We have developed a method which allows one to derive and compute this term without introducing any further simplifications and in which the examined system of interacting particles is interpreted as an ensemble of subsystems formed by particles lying in microscopically thin spherical shells which surround arbitrary central particles.

Within terms of the Barker and Henderson theory we also assume the existence of correlations among particle number fluctuations only in shells surrounding the same central particle. The partition function of a s -component mixture may be then written in the form

$$Q = Q_0 \prod_{j=1}^s \{ \langle \exp[-\beta \sum_{k=1}^s \sum_i (N_k^i)_1 u_{ki}^i] \rangle_{0j} \}^{N_j/2}. \quad (4)$$

The symbol Q_0 denotes the partition function of the reference hard sphere mixture,

$(N_k^i)_1$ is the number of particles k lying in a spherical shell i of the radius r_i and microscopical thickness $|r_{i+1} - r_i|$ surrounding an arbitrary fixed central particle l , and u_{k1}^i represents the mean value of the interaction potential $u_{k1}(r)$ on the interval (r_i, r_{i+1}) . The mean denoted by the angle brackets $\langle \rangle_0$ is performed over all configurations of the reference system with one fixed particle.

From a formal point of view expression (4) is the product of partition functions of mutually non-interacting subsystems and may be rewritten as

$$Q = Q_0 Q_1 \prod_{i=1}^s \langle \exp [-\beta \sum_{k=1}^s \sum_i (A_k^i)_1 u_{k1}^i] \rangle^{N_i/2}, \quad (5)$$

where $(A_k^i)_1$ denotes the actual deviation in the number of particles k in a spherical shell i surrounding an arbitrary central particle l from its value averaged over all reference system configurations,

$$(A_k^i)_1 = (N_k^i)_1 - \langle (N_k^i)_1 \rangle_0. \quad (6)$$

The partition function Q_1 includes the first order perturbation term and is equal to

$$Q_1 = \prod_{i=1}^s \{ \exp [-\beta \sum_{k=1}^s \sum_i \langle (N_k^i)_1 \rangle_0 u_{k1}^i] \}^{N_i/2}. \quad (7)$$

If, following the Barker and Henderson ideas, we will further assume that mutual interactions among particles belonging to different shells around the same central particle are insignificant, the correlations of the type $\langle (A_k^i)_1 (A_{k'}^{i'})_1 \rangle_0$ for $i' \neq i$ or $k' \neq k$ may be neglected. This leads to

$$\langle (A_k^i)_1 (A_{k'}^{i'})_1 \rangle_0 = \begin{cases} 0 & \text{for } i' \neq i \text{ or } k' \neq k, \\ kT \left[\frac{\partial (N_k^i)_1}{\partial (\mu_k^i)_1} \right]_{T, V_i, \mu^{i, k' \neq k}} & \text{for } i' = i \text{ and } k' = k. \end{cases} \quad (8)$$

This approximation is somewhat more crude than neglecting correlations in shells belonging to different central molecules. However, because the contribution from the second order terms amounts to several percent of the absolute value due to a rapid convergence of the derived expressions, it is fully acceptable.

Considering validity of the relation

$$\left[\frac{\partial (N_k^i)_1}{\partial (\mu_k^i)_1} \right]_{T, V_i, \mu^{i, k' \neq k}} = V_i \left[\frac{\partial (n_k^i)_1}{\partial (\mu_k^i)_1} \right]_{T, V_i, \mu^{i, k' \neq k}}, \quad (9)$$

(in which V_i denotes the microscopical volume of the shell and $(\mu_k^i)_1$ resp. $(n_k^i)_1$ repre-

sents the chemical potential resp. density of reference particles k in a spherical shell i surrounding an arbitrary central particle l), we obtain the following relation for the second order perturbation term in the expression for the free energy of the mixture ($F = \sum_{i=0} F_i$)

$$\frac{F_2}{NkT} = -(4kT)^{-1} \sum_{k,l}^s x_l \int_{\sigma_{kl}}^{\infty} \left\{ \left[\frac{\partial n_k}{\partial \mu_k}(r) \right]_{T,V,\mu_{k'' \neq k}} \right\} u_{kl}^2(r) 4\pi r^2 dr, \quad (10)$$

where the expression in the outermost brackets contains quantities in the reference hard sphere mixture and subscript l denotes the type of the central particle.

The derivative of density n_k with respect to chemical potential μ_k cannot be calculated directly because it must be performed at constant chemical potentials of particles of all remaining components, $(\partial n_k / \partial \mu_k)_{T,V,\mu_{k'' \neq k}}$.

However, it can be obtained by using relations valid in multicomponent systems¹¹.

To this purpose let us define an $s \times s$ square matrix, $\mathbf{A} = \{a_{kl}\}$, whose elements are defined by

$$a_{kl} = (\partial \mu_k / \partial n_l)_{n_{l' \neq l}, T, V}, \quad k, l = 1, \dots, s. \quad (11)$$

Then we can write

$$\left[\frac{\partial n_k}{\partial \mu_l} \right]_{\mu_{l' \neq l}, T, V} = \frac{\partial}{\partial a_{kl}} (\det \mathbf{A}) / \det \mathbf{A}. \quad (12)$$

An expression resulting after substitution of relation (12) into Eq. (10) makes it then possible to calculate numerically the second order perturbation term from radial distribution functions of the reference hard sphere mixture, because in a system with

TABLE I
Parameters of the Lennard-Jones Potential for Pure Components of the Investigated Mixtures

Substance	$\sigma, \text{\AA}$	$\varepsilon/k, \text{K}$	σ/σ_{Ar}	$\varepsilon/\varepsilon_{Ar}$	Ref.
Ar	3.405	119.8	1.000	1.000	3
Kr	3.633	167.3	1.067	1.396	3
CS ₂	4.430	446.0	1.301	3.723	13, 16
CCl ₄	5.310	454.5	1.559	3.794	13, 16
C ₂ Cl ₄	5.390	480.0	1.583	4.007	13, 17

one fixed particle any density n_k is a function of the shell radius and it holds

$$[n_k(r)]_1 = n_k^0 g_0^{k1}(r), \quad (13)$$

in which n_k^0 denotes the mean number density of particles k .

The calculation of the thermodynamic functions of a mixture which would take into account relation (10) is rather complicated in comparison with pure substances. It is not possible to employ the well-known Laplace transforms of the radial distribution functions⁸, but instead it is necessary to perform inversions of these Laplace transforms in a wider range of intermolecular separations.

RESULTS AND DISCUSSION

The outlined theory was used in a usual manner to obtain values of the excess thermodynamic functions ΔV^E , ΔG^E and ΔH^E for several model binary systems. The results were compared with experimental data and with existing pseudoexperimental Monte Carlo data.

Concentration dependences of functions ΔV^E , ΔG^E and ΔH^E were calculated for the following mixtures: (I) Ar(1)–Kr(2), (II) CS₂(1)–CCl₄(2), (III) CS₂(1)–C₂Cl₄(2).

From the point of view of intermolecular interactions the system Ar–Kr represents one of simplest and most thoroughly examined cases and together with the corresponding Monte Carlo data¹² it may serve for evaluating the correctness of the proposed method.

The other two systems were selected to verify the applicability of the theory, which itself works with spherically symmetrical functions only, to the description of binary mixtures whose one or both components are formed by molecules exhibiting unnegligible deviations from spherical symmetry.

The pair intermolecular interactions of all the components were described by the spherically symmetrical Lennard–Jones 12–6 potential. The parameters ϵ and σ in this potential were taken for Ar and Kr from the literature³ or for CS₂, CCl₄, and C₂Cl₄ they were calculated from critical data according to generalized rules recommended by Bellemans and coworkers¹³. The employed parameters are collected in Table I.

Cross parameters ϵ_{12} and σ_{12} were obtained by using the Lorentz–Berthelot rule¹⁴. Besides that, we have also tried the harmonic-mean rule¹⁴ for ϵ_{12} ; however, within the framework of the other approximations employed, the use of the two rules leads to insignificant differences between the thermodynamic functions. (Although these rules cannot be so far fully justified theoretically, they seem to be appropriate for the selected substances. This problem as well as effects of the other approximations will be discussed below.)

TABLE II
Values of Excess Thermodynamic Functions of MC, Ar-Kr, CS₂-CCl₄ and CS₂-C₂Cl₄ Systems^a

Mixture	T, K	x ₁	k ^c	Order ^d	ΔV ^E , cm ³ /mol		ΔG ^E , J/mol		ΔH ^E , J/mol	
					theor.	exptl.	theor.	exptl.	theor.	exptl.
MC ^b	115.8	0.50	L	2	-0.43	-0.54 ± 0.20	35.61	34 ± 10	-37.54	-34 ± 40
Ar-Kr	115.8	0.50	L	1	-0.43	-0.52	31.47	84.0	-42.2	—
CS ₂ -CCl ₄	298.16	0.25	L	1	0.91	0.28	324.8	147.7	510.6	345.3
CS ₂ -CCl ₄	298.16	0.50	L	1	1.06	0.32	370.0	157.4	678.8	465.8
CS ₂ -CCl ₄	298.16	0.75	L	1	0.80	0.26	322.3	147.7	581.7	360.3
CS ₂ -CCl ₄	298.16	0.50	H	1	1.06	0.32	358.2	157.4	656.6	465.8
CS ₂ -CCl ₄	298.16	0.50	L	2	1.06	0.32	370.4	157.4	679.2	465.8
CS ₂ -C ₂ Cl ₄	298.16	0.25	L	1	0.91	0.36	338.6	190.8	497.2	272.0
CS ₂ -C ₂ Cl ₄	298.16	0.40	L	1	1.12	0.49	382.5	269.9	628.2	450.7
CS ₂ -C ₂ Cl ₄	298.16	0.50	L	1	1.16	0.53	387.1	293.8	667.9	539.0
CS ₂ -C ₂ Cl ₄	298.16	0.60	L	1	1.12	0.50	375.0	295.5	664.6	583.0
CS ₂ -C ₂ Cl ₄	298.16	0.75	L	1	0.91	0.43	334.8	243.2	580.0	530.2
CS ₂ -C ₂ Cl ₄	298.16	0.50	L	2	1.16	0.53	376.2	293.8	647.0	539.0
CS ₂ -C ₂ Cl ₄	298.16	0.50	H	1	1.16	0.53	390.9	293.8	672.1	539.0

^a Experimental data are from the following references: MC numerical results of stochastic computations¹², Ar-Kr (ref.¹⁵), CS₂-C₂Cl₄ (ref.¹⁶), CS₂-C₂Cl₄ (ref.¹⁷). ^b The symbol MC denotes Monte Carlo values corresponding to experimental conditions of the Ar-Kr system, ^c Mixing rule for ε₁₂ (L Lorentz-Berthelot, H harmonic mean), ^d Order of the perturbation expansion employed.

The comparison of results obtained by the perturbation method with the Monte Carlo and experimental data is given in Table II.

Table III contains a comparison between our results and available values computed by other common theories of the liquid state.

Although high machine-time demands have prevented us from performing the computations for more systems (the perturbation theory extended to second order was used only for equimolecular mixtures), the comparison between the theory and experiment yields important results and leads to the following conclusions: The use of the second order term leads in all the investigated cases to better agreement with experimental data. This improvement is not too significant, but it conforms to the basic assumption of a rapid convergence of the derived expansions.

Comparisons with experimental data on real systems are not fully adequate, since to approximations necessarily imposed on derived formulas by requirements of possible mathematical elaboration, simplifications in the intermolecular potential and in the geometry of the molecules must be added. Only a comparison with corresponding Monte Carlo data may be considered as quite rigorous; these data, however, may be often inaccurate. In our work, the main emphasis is put on comparisons with the Monte Carlo data.

The inaccurate representation of the course of the interaction potential is closely related to the unambiguity in the determination of parameters ϵ and σ . Similarly,

TABLE III

Comparison of Results of Some Theories of the Liquid State with Experiment. Values of Excess Thermodynamic Functions ΔV^E , ΔG^E and ΔH^E of Equimolecular Ar-Kr and CS₂-CCl₄ Mixtures

Function	System	T, K	Expt. ^a	MC	Pert.	vdW ^b	HT ^c	vdW-2 ^d
ΔV^E (cm ³ /mol)	Ar-Kr	115.8	-0.52	-0.54 ± 0.20	-0.43	-0.78	-0.04	-0.50
	CS ₂ -CCl ₄	298.15	+0.32	—	+1.06	—	4.42	-0.99
ΔG^E (J/mol)	Ar-Kr	115.8	84.0	34 ± 10	35.6	37.0	96.0	54.0
	CS ₂ -CCl ₄	298.15	157	—	358	—	1 095	-51
ΔH^E (J/mol)	Ar-Kr	115.8	—	-34 ± 40	-42.2	-50.0	—	—
	CS ₂ -CCl ₄	298.15	466	—	657	—	1 523	-19

^a The data are from the following references: Ar-Kr (ref.¹⁵), CS₂-CCl₄ (ref.¹⁶), MC (ref.¹²),

^b Results of the van der Waals theory³, ^c Results of the two-fluid hole theory¹⁶, ^d Results of the two-fluid corresponding states theory with van der Waals mixing rules¹⁶.

rules for calculation of ε_{12} and σ_{12} are to a large extent of empirical origin. In our work we have employed relations whose applicability to similar substances (nonpolar and approximately spherically symmetrical) has been verified in other works^{3,16}.

The outlined inaccuracies will be reflected mainly in the value of the first order perturbation term; they affect the second order term in a similar manner, however, their contribution to the resulting absolute value of the thermodynamic quantity will be substantially lower due to a rapid convergence of the derived expressions.

Our results show good agreement with the Monte Carlo data. Consequently they describe well also nonpolar liquids whose molecules exhibit neither larger deviations from spherical symmetry nor any specific interactions, so that their intermolecular potentials might be well described by the Lennard–Jones function. In this case, good agreement with experimental data is obtained not only for values of the excess functions but also for the computed volume V ($\pm 1.5\%$) and the enthalpy of vaporization ΔH^{vap} ($\pm 3.0\%$) of both pure components and the mixture (system Ar–Kr).

The use of the spherically symmetrical potential for substances such as CS_2 and C_2Cl_4 represents the largest source of inaccuracies in applying the perturbation expansion. Agreement with the experimental data is not so good here. However, it was found that although the perturbation variant is in such cases inappropriate for calculation of absolute values of the volume or the heat of vaporization, it leads to satisfactory agreement for the excess functions.

In conclusion it may be stated that the investigated method, which – in comparison with other theories of fluids – employs fewer approximations, does not introduce any experimental findings into the theory nor does it create *a priori* and unjustified assumptions on the liquid structure, can offer satisfactory prediction for all thermodynamic excess functions even in cases if one or both components display smaller deviations from spherical symmetry or if molecules of both components differ considerably in their magnitudes. A minimum of parameters (*e.g.* parameters in the Lennard–Jones potential) is required for the computation. Agreement with experiment is comparable or even better than for other common theories.

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