PERTURBATION THEORY OF NON-POLAR CONVEX MOLECULE FLUIDS

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The second-order perturbation expansion is proposed for describing the equilibrium behaviour of non-polar fluids whose intermolecular interactions are expressed by the Kihara non-central pair potential. The definition of the predominant action range of the attractive and repulsive forces as well as the expression for the first-order perturbation term correspond to the WCA formulation for particles with central interactions; to determine the second-order perturbation term the extended macroscopic compressibility approximation is used. The system of soft convex bodies parallel to molecule cores is taken as the reference system; its equilibrium behaviour is described by thermodynamic functions of representative hard convex bodies with temperature and density dependent thickness. For calculating these functions, a very accurate equation of state was used; the average correlation function was approximated on the basis of the correlation function of corresponding hard spheres. The perturbation method was used for determining thermodynamic functions of nitrogen and for studying its phase behaviour; the calculated coexistence curve is compared with experiment.

During last years, perturbation methods proved to describe well the equilibrium behaviour of simple fluids, *i.e.* the molecule systems with intermolecular interactions of central character. A number of recent works have dealt with the extension of perturbation theories to molecular fluids. The procedures proposed depend to a considerable extent on the kind of non-central pair potential used to describe the intermolecular forces. The multicentral potentials (interaction site model, ISM) and the Kihara-type potentials[1] have met with a more extensive use.

The perturbation expansions with ISM employ hard bodies (so-called RISM) formed by two and more mutually overlapping spheres as the reference system. The description of P-V-T behaviour and the course of distribution functions follow from the extension of the Percus–Yevick approximation to the RISM systems proposed by Chandler[2]. The resulting description of P-V-T behaviour is, however, rather rough and therefore the approximative expression on the basis of equation of state of hard convex bodies[3] is sometimes used. Another possibility is offered by the methods[4,5], in which the effective potential of the central type is obtained by a suitable averaging of a non-central potential and the known methods for simple fluids are then used for calculating the thermodynamic functions for this new potential. A disadvantage of the mentioned procedures, which are considerably general, is the fact that the accuracy of description decreases rapidly with increasing non-sphericity of repulsive forces.

The perturbation procedures for the systems of molecules interacting *via* the Kihara non-central potential have been studied in our laboratory[6]. An advantage of the Kihara potential is a good description of anisotropic character of the repulsive forces of more complex molecules; the description of attractive forces is not so good. A considerable advantage from the standpoint of applications consists in the fact that the simplicity of the potential remains unchanged even for very complex polyatomic molecules. To describe the reference (or representative) systems of hard convex bodies it is possible, in perturbation methods, to employ some of very accurate equations of state[7-9]. Very accurate relations are known as well for determining the values of the average correlation function of convex particles at contact; however, the course of dependence of the given function on the distance is not known from the theory, so that it is necessary to use approximate expressions based on the knowledge of the hard sphere distribution function and on the simulation results in convex body systems. The perturbation expansion of the first order (of the Barker–Henderson type[11]) was shown[10] to lead to a good description of behaviour of the rod-core molecules. Recently, this procedure has been extended to the second order for a general type of convex molecules[12].

In this work, a variant of the second-order perturbation method is derived which is an extension of the Weeks–Chandler and Andersen theory[13] (WCA); the second-order perturbation term is expressed by means of the macroscopic compressibility approximation[14] whose extension to the convex molecule system was formulated in another our work[12].

THEORETICAL

We assume that the intermolecular interactions of the studied system are described by the Kihara pair potential

$$u(l) = \begin{cases} \infty & \text{for} \quad l < 0 \\ \varepsilon[(\nu/l)^{12} - 2(\nu/l)^{6}] & \qquad l < 0\,, \end{cases} \tag{1}$$

where ε and ν is the depth of the potential minimum and the distance corresponding to it; l denotes the distance between surfaces of convex cores of interacting molecules. The cores – the hard convex bodies – are characterized by their volume V_i, surface area S_i and the mean curvature integral, divided by 4π, R_i. Similarly to the WCA procedure for simple fluids[13], we assume that the range of predominant action of repulsive forces is delimited by the distance ν. Then we have for the reference and perturbation potential

$$u^0(l) = \begin{cases} \infty \\ \varepsilon[(\nu/l)^6 - 1]^2\,, \\ 0 \end{cases} \quad u^\mathrm{p}(l) = \begin{cases} 0 & \text{for} \quad l < 0 \\ -\varepsilon & \qquad 0 < l < \nu\,, \\ u(l) & \qquad l < \nu \end{cases} \tag{2}$$

where u^0 and u^p denote the reference potential (of soft convex bodies) and the perturbation, respectively.

The second-order perturbation expansion in the macroscopic compressibility approximation of the convex molecule system can be written in the following form[12]

$$\frac{F - F^*}{NkT} = \frac{F^0 - F^*}{NkT} + \frac{1}{2}\beta\varrho\int_0^\infty \langle g^0(l, \varrho, T)\rangle\, u^{\mathrm{p}}(l)\, S_{\mathrm{i+l+i}}\,\mathrm{d}l\, +$$

$$- \frac{1}{4}\beta^2\varrho kT(\partial\varrho/\partial P)^0 \int_0^\infty [u^{\mathrm{p}}(l)]^2\, \langle g^0(l, \varrho, T)\rangle\, S_{\mathrm{i+l+i}}\,\mathrm{d}l\,. \qquad (3)$$

Here F, F^0 and F^* denote the free energy of the studied, reference and ideal gas system, respectively, ϱ stands for the particle density, $\varrho = N/V$, $\beta = 1/kT$, $\langle g^0\rangle$ the average correlation function (see definition in ref[6]) and $S_{\mathrm{i+l+i}}$ is the average surface given by the motion of centre of gravity of one convex molecule around the second one keeping a constant surface-to-surface distance l. It follows for $S_{\mathrm{i+l+i}}$

$$S_{\mathrm{i+l+i}} = 2S_{\mathrm{i}} + 8\pi R_{\mathrm{i}}^2 + 16\pi R_{\mathrm{i}}l + 4\pi l^2\,. \qquad (4)$$

The free energy of the reference system, F^0, can be expressed in terms of F^{h}, the free energy of the system of representative hard convex bodies, *i.e.* the parallel bodies to the convex cores of molecules with thickness ξ given explicitly by relation (5) which follows from the blip-function expansion of F^0

$$\Delta = -\int_0^v Y^{\mathrm{h}}(l, \xi)\left(\exp\left[-\beta u^0\right] - \exp\left[-\beta u^{\mathrm{h}}\right]\right) S_{\mathrm{i+l+i}}\,\mathrm{d}l = 0\,, \qquad (5)$$

where $Y = \exp\left[\beta u\right]\langle g\rangle$ and u^{h} denotes the pair potential of the representative hard convex bodies,

$$u^{\mathrm{h}}(l) = \infty \quad \text{for} \quad l < 2\xi\,, \quad u^{\mathrm{h}}(l) = 0 \quad \text{for} \quad l > 2\xi\,. \qquad (6)$$

For the first estimation of thickness ξ or the parameter $c = 2\xi/v$ it is possible to set $Y^{\mathrm{h}} = 1$ in Eq. (5); then

$$(2S_{\mathrm{i}} + 8\pi R_{\mathrm{i}}^2)(c - I_1)/v^2 + 8\pi R_{\mathrm{i}}(c^2 - I_2)/v + \tfrac{4}{3}\pi(c^3 - I_3) = 0\,, \qquad (7)$$

where

$$I_{\mathrm{j}} = \int_0^1 (1 - \exp\left[-\beta u^0(z)\right])\,\mathrm{d}(z^{\mathrm{j}})\,. \qquad (8)$$

The thickness ξ following from Eq. (5) is temperature and density dependent as well as the volume, surface area and the $(1/4\pi)$-multiple of mean curvature integral of the representative hard convex bodies for which we have

$$\begin{aligned} R_{ci} &= R_i + \xi\,, \\ S_{ci} &= S_i + 8\pi R_i \xi + 4\pi\xi^2\,, \\ V_{ci} &= V_i + S_i\xi + 4\pi R_i \xi^2 + \tfrac{4}{3}\pi\xi^3\,. \end{aligned} \tag{9}$$

On the basis of these geometric functionals of the representative bodies it is possible to determine the packing fraction y, $y = \varrho V_{ci}$ and the non-sphericity parameter α, $\alpha = R_{ci}S_{ci}/3V_{ci}$; the knowledge of y and α suffices fully to the description of the P–V–T behaviour of the representative system.

In this work we have used, for characterizing the P–V–T behaviour of the representative system, the equation of state of hard convex bodies in the form[9]

$$\frac{P}{\varrho kT} = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{3\alpha^2 y^2 - \alpha(6\alpha - 5)\,y^3}{(1-y)^3}\,, \tag{10}$$

which proved to be in excellent agreement with all available pseudoexperimenta data for hard convex bodies. For free energy of the representative system and, consequently in this procedure also for free energy of the reference system, it holds

TABLE I

Thermodynamic Functions $(F - F^*)/NkT$, $P/\varrho kT$ and $(U - U^*)/NkT$ for Nitrogen at a Temperature $T^* = 0.75$

y	$-\dfrac{(F - F^*)}{NkT}$	$\dfrac{P}{\varrho kT}$	$-\dfrac{(U - U^*)}{NkT}$
0·007	0·08	0·91	0·07
0·069	0·67	0·33	0·73
0·138	1·21	—0·22	1·61
0·207	1·71	—0·72	2·61
0·276	2·19	—1·05	3·72
0·345	2·60	—0·96	4·95
0·415	2·87	—0·04	6·27
0·449	2·90	0·87	6·93

$$\frac{F^{\mathrm{h}} - F^*}{NkT} = (6\alpha^2 - 5\alpha - 1)\ln(1 - y) + \frac{1}{2}(15\alpha^2 - 9\alpha)\frac{y}{1 - y} +$$
$$+ \frac{1}{2}(-3\alpha^2 + 5\alpha)\frac{1}{(1 - y)^2}\,. \tag{11}$$

In the framework of the WCA formalism, the average correlation function $\langle g^0 \rangle$ is approximated by the product of the Bolzmann factor $\exp[-\beta u^0]$ of the reference potential and the function Y^{h} of the representative system. Then it is possible to rearrange the first-order perturbation term with respect to Eqs (*2*) and (*5*) in the following way:

$$\int_0^\infty Y^{\mathrm{h}}(l)\exp[-\beta u^0]\,u^{\mathrm{p}}(l)\,S_{\mathrm{i+1+i}}\,\mathrm{d}l =$$
$$= \varepsilon v^3\left\{v^{-3}\int_{2\xi}^\infty [u^{\mathrm{p}}(l)/\varepsilon]\,S_{\mathrm{i+1+i}}\,\mathrm{d}l + \int_{2\xi}^\infty [Y^{\mathrm{h}}(l) - 1]\,[u^{\mathrm{p}}(l)/\varepsilon]\,S_{\mathrm{i+1+i}}\,\mathrm{d}l +\right.$$
$$\left. - v^{-3}\int_0^v Y^{\mathrm{h}}(l)\,\{\exp[-\beta u^0] - H(l - 2\xi)\}\,S_{\mathrm{i+1+i}}\,\mathrm{d}l\right\} =$$
$$= \varepsilon v^3\left\{(S_{\mathrm{i+i}}/v^2)(c - 72/55) + 8\pi(R_{\mathrm{i}}/v)(c^2 - 9/5) + \tfrac{4}{3}\pi(c^3 - 8/3) +\right.$$
$$+ c^3\int_1^\infty [Y^{\mathrm{h}}(x) - 1]\,[H(x - c^{-1}) - 1 + H(x - c^{-1})(c^{-12}x^{-12} - 2c^{-6}x^{-6})]\,.$$
$$\left.\cdot (S_{\mathrm{i+i}}/4\xi^2) + 8\pi x R_{\mathrm{i}}/\xi + 4\pi x^2)\,\mathrm{d}x + \Delta\right\}. \tag{12}$$

In Eq. (*12*), $H(z)$ denotes the Heaviside step function and $x = l/2\xi$. Analogously to the first-order term we have rearranged the second-order perturbation term. To determine the second integral in Eq. (*12*) it is necessary to know the course of function $Y^{\mathrm{h}}(x) - 1 = h(x)$, *i.e.* the average total correlation function of the representative system. For the system of hard convex bodies it has been approximated by the relation

$$h^{\mathrm{HCB}}(x, \varrho) = h^{\mathrm{HCB}}(1, \varrho)\,h^{\mathrm{HS}}(s, \varrho)/h^{\mathrm{HS}}(1, \varrho)\,, \tag{13}$$

where the symbols HCB and HS stand for the properties of hard convex bodies and hard spheres. For the dimensionless distance, s, of the corresponding pair of hard spheres, the relation has been used

$$x = (s - 1)\,f\,g^{\mathrm{HS}}(1, \varrho)/\langle g^{\mathrm{HCB}}(1, \varrho)\rangle + 1\,. \tag{14}$$

The factor f is given as the ratio of minimum dimensions of spheres and the given hard bodies, both of the same volume. For instance, for spherocylinders with $\gamma = 2$ we have $f = (5/2)^{1/3}$. In Fig. 1 the course of function h^{HCB} for spherocylinders with $\gamma = 2$ and $y = 0{\cdot}446$ calculated from Eq. (*13*) is compared with the data obtained by the Monte Carlo simulation[15]. Good agreement of the predicted total correlation function with pseudoexperimental data is evident from Fig. 1.

RESULTS

In Table I the values of thermodynamic functions $(F - F^*)/NkT$, $P/\varrho kT$ and $(U - U^*)/NkT$ are given as calculated from Eq. (*3*) (by using the Padé approximant from F_1 and F_2) for nitrogen at a temperature $T^* = kT/\varepsilon = 0{\cdot}75$. The N_2 core has been assumed in the shape of a spherocylinder – a parallel body to the rod 0·093 nm long and 0·025v thick. In such a way obtained data for temperatures $T^* = 0{\cdot}75 - 1{\cdot}20$ have been used to determine vapour–liquid equilibrium.

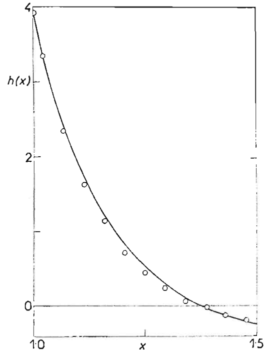

FIG. 1

Average Total Correlation Function of Hard Spherocylinders ($\gamma = 2$) for $y = 0{\cdot}446$

——— Theoretical curve, ○ Monte Carlo data[15].

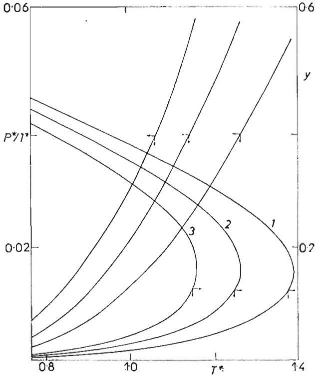

FIG. 2

Coexistence Curves and Dependences of Saturated Vapour Pressures on Temperature for the Kihara Spherical Potential

1 Point core, *2* core with diameter 0·05ν, *3* core with diameter 0·1ν.

The vapour–liquid equilibrium in one-component system is given by the conditions

$$P'/kT = P''/kT\,, \tag{15a}$$

$$\mu'/kT = \mu''/kT\,, \tag{15b}$$

where μ_i is the chemical potential per one molecule and $'$ or $''$ denotes the liquid and vapour phase, respectively. Condition (*15b*) can be expressed suitably in terms of the quantities following directly from the perturbation expansion:

$$\frac{(F - F^*)'}{NkT} + \frac{P'}{\varrho' kT} - 1 = \frac{(F - F^*)''}{NkT} + \frac{P''}{\varrho'' kT} - 1 + \frac{F^{*''} - F^{*'}}{NkT}\,, \tag{16}$$

where

$$\frac{F^{*''} - F^{*'}}{NkT} = \ln \frac{\varrho''}{\varrho'}\,. \tag{17}$$

The first calculations of vapour–liquid equilibrium have been carried out for the special case of the Kihara potential with spherical core. In Fig. 2 the effect is shown of the core size (for the Kihara spherical potential) on the coexistence curve and saturated vapour pressure (The curves in Fig. 2 are plotted for dimensionless quantities, y *vs* T^* and P^*/T^* *vs* T^* for cores with diameters 0, $0{\cdot}05v$ and $0{\cdot}1v$). The critical density, the ratio P_c^*/T_c^* (where $P_c^* = PV_{ci}/\varepsilon$) and the critical compressibility factor are shown not to change practically (within the range of the numerical operation errors) with the core size ($y_c = 0{\cdot}16$, $P_c^*/T_c^* = 0{\cdot}060$ and $z_c = 0{\cdot}37$), whereas the critical temperature gradually decreases ($1{\cdot}38 - 1{\cdot}16$).

The exact temperature dependence of saturated vapour pressures obtained in this way has been used to verify two approximative methods for calculating the saturated vapour pressures proposed for the low-pressure region. In the first case it is assumed that *a*) the compressibility factor of liquids is negligibly small and the liquid density at the given pressure does not differ from the value at $P \to 0$, *b*) the vapour phase behaves ideally.
Then

$$\frac{(F - F^*)'}{NkT} - 1 = \ln \frac{P}{\varrho' kT}\,. \tag{18}$$

In the second case the assumption *a*) is kept but the vapour phase behaviour is not considered ideal. In the simplest case it can be described by the virial expansion truncated after the second order. Providing that B_2 is the second virial coefficient related to one molecule, then

$$\frac{(F - F^*)'}{NkT} - 1 = 2\frac{B_2P}{kT} + \ln\frac{P}{\varrho' kT(1 + B_2P/kT)} . \qquad (19)$$

The exact and both approximative ways of calculating densities and saturated vapour pressures are compared in Fig. 3. (Symbol *1* stands for the exact curve, symbols *2* and *3* for the dependences corresponding to Eqs (*18*) and (*19*)). It is evident from the comparison that the first approximation is suitable only at the lowest temperatures, while the second one gives a good prediction up to a considerably high temperatures.

To be able to compare the quality of predicting the equilibrium behaviour of non-spherical particle systems with the results for simple fluids (following essentially from the WCA method) only the results of exact methods have been considered further. For comparing the results of calculations with experimental data it is necessary to know the Kihara potential parameters. These parameters have been adjusted to the low-temperature equilibrium data. Their values are given in Table II. The comparison of calculated and experimental[16,17] coexistence curves for krypton (spherical core with radius 0·01 nm) and nitrogen (the above-mentioned model with spherocylinder-shaped core) is illustrated in Figs 4 and 5.

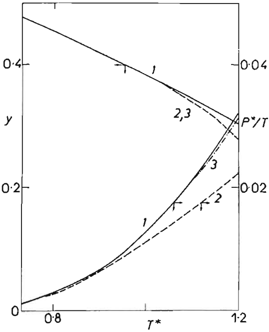

FIG. 3

Saturated Vapour Pressures in Dependence on Temperature

1 Exact calculation, *2* approximation assuming ideal behaviour of the vapour phase, *3* approximation using the 2nd virial coefficient.

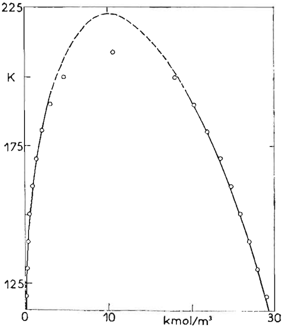

FIG. 4

Coexistence Curve of Krypton

—— Theoretical curve, ○ experimental data[17].

It follows from the comparison that the perturbation theory of convex molecules yields the prediction of equilibrium behaviour of the non-spherical molecule systems which, as to the accuracy, does not differ from the results obtained by perturbation methods for the spherical particle systems. In both cases the theoretical coexistence curves are in good agreement with experiments as far as the system temperature differs from the critical one by more than approximately 10 K. We have not succeded in describing the region close to the critical point by changing the Kihara potential parameters without getting the agreement in the low-temperature region drastically worse. This fact is probably connected with the pretransitional behaviour[18] of fluids.

DISCUSSION

The perturbation procedure described in this work can be compared with the variant of perturbation method[12], which represents an extention of the Barker–Henderson

TABLE II

Parameters of the Kihara Potential, Characteristics of Core and Standard Deviations in Coexisting Densities and in Pressure for Ar (85—140 K), Kr (120—190 K), Xe (165—270 K), CH_4 (95—180 K) and N_2 (65—120 K)

Quantity	Ar	Kr	Xe	CH_4	N_2
$(\varepsilon/k)/\mathrm{K}$	126·4	176·1	244·2	174·7	122·8
ν/nm	0·3826	0·4085	0·4445	0·4190	0·3481
l^*/nm	0·0000	0·0000	0·0000	0·0000	0·0930
ξ/nm	0·0090	0·0100	0·0110	0·0210	0·0090
Std. dev. in ϱ_1, 10^3 mol m^{-3}	0·213	0·145	0·138	0·246	0·265
Std. dev. in ϱ_v, 10^3 mol m^{-3}	0·135	0·117	0·088	0·092	0·115
Std. dev. in P, MPa	0·0233	0·0195	0·0298	0·0329	0·0252

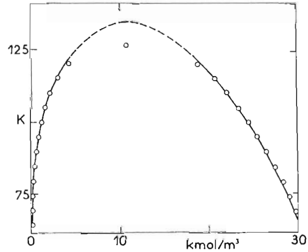

FIG. 5

Coexistence Curve of Nitrogen

——— Theoretical curve, ○ experimental data[17].

formulation for the description of molecular fluids. Both use the macroscopic compressibility approximation to determine the second-order perturbation term, which gives good results for low densities but less good for densities typical of liquids. However, in both cases, by the choice of the range of reference potential $(0, v)$, a good convergence of the perturbation expansion is ensured, *i.e.* relatively small values of the second-order term. for higher densities; in the variant studied in this work, the convergence – owing to the determination of thickness of the representative hard convex bodies from Eq. (5) – is slightly better. The contribution of perturbation terms of the second- and higher orders is significant in the region of low densities; the purpose of making use of the Padé approximant, formulated from the second- and third-order terms, is to improve the description of termodynamic behaviour in the given range. The study of the vapour–liquid equilibrium of the spherical and non-spherical molecule systems proves that the main features of the description of the given phase equilibrium, *i.e.* the good representation of the middle- and low-temperature region and insufficiency in the region close to critical point are not substantially influenced by the pair potential used (type and size of core) as well as by the variant of perturbation method used.

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