A theoretical model for evaluation
of configurational entropy of mixing with respect to
shape and size of particles

Jan Duda [a], Janina Milewska-Duda [b]

[a] *Institute of Automatics,*
[b] *Faculty of Energochemistry of Coal and Physicochemistry of Sorbents,*
University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland

A general method of evaluation of configurational entropy of a liquid mixture is presented. It is based on a generalized lattice model with no restrictions due to particle shape being introduced. A general formula for the entropy is derived. Achieved results open a way for a rigorous analysis of particle shape effect on mixing process. As an example, a new formula for the entropy of mixing of hard spheres in continuous space is derived which may respect a physical bound for packing ratio. A systematic approach to improve the model accuracy is proposed. The resultant alternative models are discussed in details. A comparison with literature data and the Mansoori–Carnahan–Starling formula is presented. Very good agreement is shown.

1. Introduction

Evaluation of the configurational entropy and of other thermodynamic properties of heterogeneous mixtures play a crucial role in theoretical analysis of sorption phenomena in elastic materials. A great progress has been made in the last 50 years in the theory of simple liquids and their mixtures (Temperley [1], Hansen [2], Rowlinson [3]). Using statistical mechanics methods a mathematical description of the mixture thermodynamics was found to be in excellent agreement with data obtained by Monte Carlo and molecular dynamics simulation (Mansoori [4]). Nevertheless, because of the complexity of the mixtures being considered as vapour–polymer sorption systems, highly simplified approaches are usually applied in this case based on a lattice model (Flory [5], Prigogine [6]). In Flory's model [5] each particle is considered as an occupant of a single lattice cell, or of a sequence of consecutively adjacent cells (polymer chain). All the cells are assumed to be identical and larger compact particles are omitted. Such an approach enables to formulate a semi-empirical characterisation of the sorption processes which was found as quite satisfying for homogeneous polymers. In papers related to the sorption process in crystallized or filled polymers (Kraus [7], Goldstain [8],

Nikitas [9], Milewska [10], Doi [11]) Flory's model is applied only for the elastic phase. The question is how far such an approach is legitimate for heterogeneous sorbents consisting of particles of which the size is in the same range of magnitude but which essentially differ one from another in shape. Coal is an example of such a sorbent (Given [12], Marzec [13]). The problem is critical if sorption data are used for analysis of the sorbent structure (Milewska [14]). On the other hand the applicability of Flory's approach to modelling of sorption of vaporous or gaseous mixtures is questionable because of a cell size choice problem.

During the last years a polymer fluid behaviour has been extensively studied by Monte Carlo simulation and by using statistical mechanics methods (Dickman [15,16], Deutch [17], Yethiraj [18]). Noticeable improvements of lattice models and equations of state in continuous space are made. In our earlier papers [19,20] a model for enthalpy contribution to free energy changes due to sorption was developed and a simplified approach to description of entropy contribution was proposed.

The aim of this paper is to give a theoretical background for modelling of entropy of mixing in any liquid or polymeric system. A general method is proposed for evaluation of the number of configurations of molecular objects in a mixture, with no restrictions due to the object's shape being introduced. Our approach follows a line of Flory's idea [5], but some generalisations are made. As an example, based on this method a new formula for configurational entropy of mixing of hard spheres in continuous space is derived. The results and related state equation are compared with known formulae [2–4]. Very good agreement is shown.

2. Primary definitions and modeling methodology

One considers the number M of molecular objects (particles in liquid state) arranged at random (perfectly mixed) in a space having volume equal to the total volume of all the objects. The set of particles consists of subsets (referred to as components), each of them containing identical particles (with respect to size and other geometrical properties briefly referred to as shape).

A change in configurational entropy due to the mixing is

$$\Delta S = S^M - S^o = k_B \cdot (\ln \Omega - \ln \Omega^o), \tag{1}$$

where S^M, S^o denote the configurational entropy of the mixture and of its components in their standard state (separated homogeneous liquid subsystems), respectively, k_B, the Boltzmann constant; Ω, the number of configurations of objects in the mixture; Ω^o, the number of configurations of objects in the standard state.

The space of the mixture as well as each homogeneous liquid subsystem may be considered as discrete spatial lattices composed of identical cells, each of them containing one and only one element of a certain object. Thus, each object will be treated as a coherent agglomerate of one-cell elements. The cell is assumed to be small enough to make possible a good representation of size and shape of every object.

One takes that the object is composed of a hard part (hard core) being a rigid body with the shape unalterable in any configuration and of a soft part, its shape being readjusted to environmental conditions, so the full packing of system objects is always reached. The hard part of elastic chain molecules consists of consecutively adjacent segments, each of them being a rigid body.

One assumes that the number of objects, as well as the shape of their hard part, is the same in the mixture and in the standard state (no chemical reactions occur in the mixing process).

Let x_k^* denote the number of elements of the kth object; x_k, the number of its hard part elements; s_k, the number of surface elements of the kth object, i.e. such ones that belong to its hard part and which may be in contact with other objects or segments. The symbols x_k and s_k will be also used to denote the sets of elements belonging to kth object and to its surface layer, respectively. If the elements are properly small, the soft part represents the free volume of the particle [3]. If the cell size is in the segment size range one includes the soft part into surface elements ($x_k^* = x_k$ – Flory [5]), thus admitting their partial deformations.

Let n denote the total number of lattice cells: $n = \sum_{k=1}^{M} x_k^*$. One assumes $x_k \ll n$, (e.g. $n/x_k \approx 10^{25}$).

Let us consider a completely random assignment of individual elements to the lattice cells, irrespective of their occupancy. Such an assignment yields a random admissible arrangement (referred to as configuration) of the system objects if: (a) all the objects are spontaneously created and properly shaped, i.e. each element is placed in a region corresponding to its own object ($\mathcal{G}$-event); (b) each element is assigned to a vacant cell, i.e. in any cell a conflict of elements does not occur ($\mathcal{F}$-event).

Let $\mathcal{P}(\mathcal{G})$ denote the probability of $\mathcal{G}$; $\mathcal{P}(\mathcal{F}|\mathcal{G})$ – the probability that no collision of properly created objects occurs in the lattice. The total number of configurations of the system objects is

$$\Omega = n^n \mathcal{P}(\mathcal{G})\mathcal{P}(\mathcal{F}|\mathcal{G}) = \prod_{k=1}^{M} \prod_{e_k=1}^{x_k^*} n_{\mathcal{G}_{e_k}} P_{e_k}^{\{1...k-1\}}, \tag{2}$$

where $_{\mathcal{G}_{e_k}}$ is the probability that e_kth element is assigned to a cell fitting with a shape of the kth object, given that elements 1_k, 2_k, ..., $e_k - 1$ of this object satisfy the same condition (other objects do not affect $_{\mathcal{G}_{e_k}}$); $P_{e_k}^{\{1...k-1\}}$ denotes the probability that the e_kth element is assigned to a vacant cell, provided that elements 1_k, 2_k, ..., $e_k - 1$ satisfy the kth object shape condition, they are placed in vacant cells, and objects indexed as $1, 2 ... k - 1$ are arranged in the lattice with no conflict.

Equation (2) shows that a formula for Ω may be derived by a "filling" process in which successive objects should be inserted into the lattice by joining one-cell elements in a way admissible with respect to objects previously arranged only. Let D denote a set of objects arranged at random in an admissible way in the lattice prior to the object k. The symbol 0 will be used for the empty D set; the index of an object

(e.g. k), for one-object set $\{k\}$; Dk, for $D \lor k$, $D\backslash k$, for $D\backslash\{k\}$. $P_{e_k}^D$ corresponds to $P_{e_k}^{\{1...k-1\}}$ used in (2).

It should be noticed that a location order of elements, as viewed in eq. (2), may be altered in any way. It does not affect the value for Ω provided that exact values for $\mathscr{g}_{e_k}$ and $P_{e_k}^D$ are used.

One assumes that elements of the soft part of each object always take an admissible position in the lattice (i.e. intermolecular potential is constant and the particle packing is affected by repulsive forces only [3,4,6]). Let $e_k = x_k + 1, \ldots, x_k^*$ denote the soft part elements for which we have

$$P_{e_k}^D = 1 \quad \text{and} \quad \mathscr{g}_{e_k} = 1/n.$$

One can take that they have been added to the lattice after the arrangement of hard parts of all objects has been completed. So, the notion "object" will refer to its hard part only.

Let Ω_D denote the number of configurations of D-set objects in the lattice filled by these objects only; Ω_{Dk} is the same as above for the set D and object k added in an admissible way. One can write

$$\Omega_{Dk} = \Omega_D C_k^D, \tag{3}$$

where C_k^D denotes the expected number of configurations of the object k having a fixed (chosen at random) configuration of D objects. Let n_f^D denote the number of vacant cells left by D,

$$n_f^D \stackrel{\text{def}}{=} n - \sum_{o \in D} x_o. \tag{4}$$

The first element of the kth object may be placed in a vacant cell chosen at will. Thus we have

$$\mathscr{g}_{1_k} = 1, \quad P_{1_k}^D = n_f^D/n. \tag{5}$$

As an order in which the remaining elements ($e_k = 2_k, \ldots, x_k$) are being inserted is of no importance, we may do it in such a way as to keep a convenient geometry of the object during its formation. A development of eq. (2) is easier, if the inserted elements form a simply connected and suitably shaped body.

Let κ denote such a body (being the kth particle in statu nascendi) consisting of elements $1_\kappa, 2_\kappa, \ldots, e_\kappa - 1$, while we are placing the e_κth one. Let κe denote the object obtained by joining the e_κth element to κ with the demanded shape being kept. A cell chosen for the e_κth element is eligible with regard to the required shape of κe, if it is in contact with predetermined surface elements of κ, or with some subset of its surface elements. The former case occurs when a new segment starts with the e_κth element. Let $\Theta_{\kappa e}$ denote the expected number of cells eligible for joining the next element to κ. Similarly to Flory [5] one can assume that it depends only on the shape and flexibility of κ. Thus, we have

$$\mathscr{g}_{e_\kappa} = \Theta_{\kappa e}/n \leqslant \mathscr{g}_{e_k} \quad \text{for} \quad e_\kappa = 2_\kappa, \dots, x_k \, .$$

Let $C_{\kappa e}^D$ denote the expected number of configurations of κe having a fixed configuration of D objects. One can write

$$C_{\kappa e}^D = C_\kappa^D \Theta_{\kappa e} P_{e_\kappa}^D \quad \text{for} \quad e_\kappa = 2_\kappa \dots x_k \, , \tag{6}$$

where C_κ^D is defined for κ as C_k^D below eq. (3); $P_{e_\kappa}^D$ is the probability that the e_κth element of κe is placed in a vacant cell, provided that the objects of D and κ ($D\kappa$ set) are arranged in an admissible way.

Following eqs. (2)–(6) the expression for C_k^D may be written as

$$C_k^D = \gamma_k \left(n_f^D \cdot \prod_{e_\kappa=2}^{x_k} \Theta_{\kappa e} P_{e_\kappa}^D \right) = C_k^O n_f^D \mathbb{P}_{k|f}^D \, , \tag{7}$$

where

$$\mathbb{P}_{k|f}^D \overset{\text{def}}{=} \frac{C_k^D}{n_f^D C_k^0} = \prod_{e_k=2}^{x_k} P_{e_k}^D = \prod_{e_\kappa=2}^{x_k} P_{e_\kappa}^D \, , \tag{8}$$

$$C_k^0 \overset{\text{def}}{=} \gamma_k \cdot \prod_{e_\kappa=2}^{x_k} \Theta_{\kappa e} \tag{9}$$

and γ_k is the number of permutations of elements $2 \dots x_k$; C_k^0, the number of positions of the kth object in the empty lattice if the site of the first element is fixed; $\mathbb{P}_{k|f}^D$, the probability that any of C_k^0 positions is admissible, if considered as having a fixed configuration of D, under the condition that the first element of k is placed in a fixed vacant cell.

Let $\delta_k S^D$ denote the component of the expression for configurational entropy, contributed by inserting of the kth particle into the lattice. According to eqs. (1)–(3), (7) it may be expressed as

$$\delta_k S^D = k_B (\ln n_f^D - \ln \mathbb{P}_{k|f}^D) + c \, , \tag{10}$$

where $c = -k_B \ln C_k^0$ absorbs all factors referred to as internal entropy (Prigogine [6]). If the lack of chemical interactions is assumed, c may be omitted as a constant being of no importance (its value is the same in the mixture and in the standard state).

3. The probability of element non-conflict insertion

The following fundamental formula will be derived:

$$P_{e_\kappa}^D = \frac{n_f^D}{n_f^D + \sum_{i \in D} \sum_{e_i \in s_i} \alpha_{\kappa e_i}^D} \, , \tag{11}$$

where $\alpha_{\kappa e_i}^D$ is the probability that in a cell chosen as eligible for the e_κth element of

κe, the occurrence of an element e_i of the object $i \in D$ is admissible due to the presence of κ as well as of objects belonging to $D \backslash i$.

Let ξ denote the cell chosen at random for the e_κth element from among $\Theta_{\kappa e}$ cells adjacent to κ; $\kappa \xi$, a body composed of κ and the cell ξ. An arrangement of this object will be treated as admissible (disregarding the occupancy of ξ cell), if κ is arranged in an admissible way. Thus, following eq. (6) the expected number of $\kappa \xi$ configurations is

$$C_{\kappa\xi}^D = C_\kappa^D \Theta_{\kappa e} . \tag{12}$$

According to eqs. (6), (12) the probability $P_{e_\kappa}^D$ may be expressed as

$$P_{e_\kappa}^D = C_{\kappa e}^D / C_{\kappa\xi}^D = \Omega_{D\kappa e} / \Omega_{D\kappa\xi} . \tag{13}$$

Let $C_{\kappa i}^D$ denote the expected number of such configurations of $\kappa \xi$ (having fixed configuration of D objects) in which ξ cell is occupied by an element of $i \in D$. For $e_\kappa > 1$ it may be only a surface element of i ($e_i \in s_i$). The following equality is valid:

$$C_{\kappa\xi}^D = C_{\kappa e}^D + \sum_{i \in D} C_{\kappa i}^D . \tag{14}$$

The first component on the right hand side of (14) represents the configurations corresponding to the cell ξ being free, the remaining ones, those with ξ being occupied.

Using eqs. (6), (14), expression (13) for $P_{e_\kappa}^D$ may be written as

$$P_{e_\kappa}^D = \frac{n_f^D}{n_f^D + \displaystyle\sum_{i \in D} \sum_{e_i \in s_i} \frac{C_{\kappa i}^D n_f^D}{C_\kappa^D \Theta_{\kappa e} P_{e_\kappa}^D}} , \tag{15}$$

which yields the form of (11) if one takes the definition

$$\alpha_{\kappa e_i}^D \overset{\text{def}}{=} \frac{C_{\kappa i}^D n_f^D}{C_\kappa^D \Theta_{\kappa e} P_{e_\kappa}^D} . \tag{16}$$

Expression (16) will be transformed to a more useful form. For this aim, one can take that the object $i \in D$ considered as an obstacle for the e_κth element has been removed from the lattice, next inserted again into the lattice filled with κ and $D \backslash i$ objects (i.e. $D\kappa \backslash i$ set). According to eq. (4) we have

$$n_f^{D\kappa \backslash i} = n_f^D + x_i - x_\kappa . \tag{17}$$

Taking into account two possible location orders for the objects κ and i, and using eq. (3) properly developed, one can write

$$\Omega_{D\kappa} = \Omega_{D \backslash i} C_i^{D \backslash i} C_\kappa^D = \Omega_{D \backslash i} C_\kappa^{D \backslash i} C_i^{D\kappa \backslash i} . \tag{18}$$

Let $C_{i\kappa}^{D\kappa \backslash i}$ denote the expected number of such configurations of i (having a fixed

configuration of $D\kappa\backslash i$) in which any surface element of i is placed in the cell ξ, with the position of $\kappa\xi$ being fixed. The following equality is valid:

$$\Omega_{D\backslash i} C_i^{D_1} C_{\kappa i}^D = \Omega_{D\backslash i} C_\kappa^{D\backslash i} \Theta_{\kappa e} C_{i\kappa}^{D\kappa\backslash i}, \tag{19}$$

since both sides of eq. (19) count the same configurations.

Using eqs. (18), (19) one can bring the expression (16) into the form of

$$\alpha_{\kappa e_i}^D = \frac{C_{i\kappa}^{D\kappa\backslash i} n_f^D}{C_i^{D\kappa\backslash i} P_{e_\kappa}^D}. \tag{20}$$

The expression for $C_{i\kappa}^{D\kappa\backslash i}$ may be derived in a similar way as eq. (7) but relations (5) cannot be applied in this case due to the demanded contact of i with κ. Let us take that a surface element chosen from among s_i ones as occupant of the cell ξ is placed as the first. Then $\mathscr{g}_{1_i} = 1/n$ and the probability of $P_{1_i}^{D\kappa\backslash i}$ that the cell ξ is vacant for 1_i may be expressed by eq. (11) related to the set $D\kappa\backslash i$

$$P_{1_i}^{D\kappa\backslash i} = \frac{n_f^{D\kappa\backslash i}}{n_f^{D\kappa\backslash i} + \sum_{o \in D\backslash i} \sum_{e_o \in s_i} \alpha_{\kappa e_o}^{D\backslash i}} \cong P_{e_\kappa}^D \frac{(n_f^D + x_i - x_\kappa)}{n_f^D}. \tag{21}$$

Using quantities $\mathscr{g}_{1_i}$ and $P_{1_i}^{D\kappa\backslash i}$ as given above, one obtains

$$C_{\kappa i}^{D\kappa\backslash i} \cong P_{e_\kappa}^D C_i^0 \mathbb{P}_{i|\xi}^{D\kappa\backslash i} \frac{(n_f^D + x_i - x_\kappa)}{n_f^D}, \tag{22}$$

where $\mathbb{P}_{i|\xi}^{D\kappa\backslash i}$ is the probability defined for i as $\mathbb{P}_{k|f}^D$ for k, but under the condition that the first element of i is placed without conflict in the cell ξ. Substitution of eq. (22) into (20) gives

$$\alpha_{\kappa e_i}^D = \frac{\mathbb{P}_{i|\xi}^{D\kappa\backslash i}}{\mathbb{P}_{i|f}^{D\kappa\backslash i}} = \alpha_{\kappa e_i}^0 \frac{\mathbb{P}_{i|\xi\kappa}^{D\kappa\backslash i}}{\mathbb{P}_{i|f}^{D\kappa\backslash i}}, \tag{23}$$

where $\mathbb{P}_{i|f}^{D\kappa\backslash i}$ is defined as $\mathbb{P}_{k|f}^D$ (eq. (8)); $\alpha_{\kappa e_i}^0$ is the probability that the object i occupying the cell ξ is not in conflict with κ; $\mathbb{P}_{i|\xi\kappa}^{D\kappa\backslash i}$ the probability that the object i, whose first element is placed admissibly in ξ cell, is not in conflict with objects of $D\backslash i$, with the lack of conflict with κ being assumed.

The interpretation of $\mathbb{P}_{i|\xi}^{D\kappa\backslash i}$ and $\mathbb{P}_{i|f}^{D\kappa\backslash i}$ leads to the relation

$$0 \leqslant \alpha_{\kappa e_i}^D \leqslant 1. \tag{24}$$

The quantity $\alpha_{\kappa e_i}^0$ (being the first order approximation to $\alpha_{\kappa e_i}^D$) depends only on the shape of i and κ. It is defined as

$$\alpha_{\kappa e_i}^0 \overset{\text{def}}{=} \frac{C_{i\kappa}^\kappa}{C_i^0}, \tag{25}$$

where superscript κ shows that only κ is regarded as an obstacle.

Following eqs. (8), (11) one can write the expressions for $\mathbb{P}_{i|\xi}^{D\kappa\backslash i}$ and $\mathbb{P}_{i|f}^{D\kappa\backslash i}$. Their substitution into eq. (23) results in

$$\alpha_{\kappa e_i}^{D} = \alpha_{\kappa e_i}^{0} \cdot \prod_{e=2}^{x_i} \frac{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \alpha_{\iota e_o}^{D\kappa\backslash i}}{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \alpha_{\kappa\iota e_o}^{D\backslash i}}, \tag{26}$$

where ι denotes an object defined for i as κ; $\kappa\iota$, the agglomerate composed of κ and of the object ι occupying the cell ξ, while an object $o \in D\backslash i$ acts as an obstacle for placing the e_ith element in a ξ_o cell defined as ξ; $\alpha_{\kappa\iota e_o}^{D\backslash i}$, $\alpha_{\iota e_o}^{D\kappa\backslash i}$, quantities defined as $\alpha_{\kappa e_i}^{D}$ with a role of κ being taken by the agglomerate $\kappa\iota$ or single ι, respectively, and the role of D being taken by the set $D\backslash i$ or $D\kappa\backslash i$ (in the first case κ cannot act as an obstacle, according to definition of $\mathbb{P}_{i|\xi\kappa}^{D\kappa\backslash i}$).

Equation (26) may be expanded step by step, by using itself for successive $\alpha_{(\cdot)}^{(\cdot)}$ with proper reinterpretation of symbols $\kappa\iota$ and D. In every step an object regarded as an obstacle is removed from the lattice, next inserted again in two ways: (a) starting with a vacant cell chosen at will (the numerator in eq. (26)); (b) starting with a cell assumed to be vacant and adjacent to the obstacle considered in the previous step (the nominator in eq. (26)). In order to calculate the exact value for $\alpha_{\kappa e_i}^{D}$ the procedure ought to be continued until an empty lattice is reached. However, this is impossible to perform because of the enormous number of the steps needed, thus an approximation to $\alpha_{\kappa_i}^{D}$ must be made.

Equation (26) may be shortly written in the form of

$$\alpha_{\kappa e_i}^{D} = \alpha_{\kappa e_i}^{0} \exp(B_{\kappa i}^{D}), \tag{27}$$

where, according to eq. (23) and eq. (26), the quantity $B_{\kappa i}^{D}$ is

$$B_{\kappa i}^{D} \stackrel{\text{def}}{=} \ln\left(\frac{\mathbb{P}_{i|\xi\kappa}^{D\kappa\backslash i}}{\mathbb{P}_{i|f}^{D\kappa\backslash i}}\right) = \sum_{e=2}^{x_i} \ln\left(\frac{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \alpha_{\iota e_o}^{D\kappa\backslash i}}{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \cdot \alpha_{\kappa\iota e_o}^{D\backslash i}}\right). \tag{28}$$

The relation $B_{\kappa i}^{D} \geqslant 0$ is fulfilled since κ, when adjacent to i, eliminates such obstacles for i which might occupy the region corresponding to κ in any other arrangement of i. Thus, from eqs. (24), (27) we can deduce that $\exp(B_{\kappa i}^{D}) \in \langle 1, 1/\alpha_{\kappa i}^{0} \rangle$.

In certain cases it is more convenient to form the obstacle starting with an element which is not placed in the cell ξ. The cell for this element must be chosen in such a way as to ensure a non-conflict arrangement of the obstacle with respect to the object κ and to meet the tangency condition in the cell ξ. In this case the equality (21) for $P_{1_i}^{D\kappa\backslash i}$ is no longer valid, hence eq. (11) transforms into the formula

$$P_{e_\kappa}^{D} = 1 - \frac{1}{n_f^D} \sum_{i \in D} \sum_{e_i \in s_i} \alpha_{\kappa e}^{D} \tag{29}$$

and eq. (28) must be completed to the form of

$$B_{\kappa i}^D = -\ln P_{1_i}^{D\kappa\backslash i} + \sum_{e_i=2}^{x_i} \ln \left(\frac{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \alpha_{\iota e_o}^{D\kappa\backslash i}}{n_f^D + x_i - x_\kappa + \sum_{o \in D\kappa\backslash i} \sum_{e_o \in s_o} \cdot\alpha_{\kappa\iota e_o}^{D\kappa\backslash i}} \right). \tag{30}$$

4. Differential lattice model – continuous mixture space

4.1. GENERAL FORMULAE

In order to show the applicability of the presented approach let us consider the lattice consisting of infinitesimal cells. It enables us to represent exactly any particle of the mixture and to get some insight into the nature of the model. Let us take that the free volume n_f^D and volume of each particle $x_{(\cdot)}$, $x_{(\cdot)}^*$ are expressed in relation to a certain basic volume (e.g. volume of the first particle); and the surface of the particle hard part $s_{(\cdot)}$, in a corresponding surface unit. Let $ds_{(\cdot)}$ denote an infinitesimal part of $(\cdot)$th particle surface; $dx_{(\cdot)}$, the volume of an infinitesimal element of $(\cdot)$th particle (cell volume).

Surfacial terms in eqs. (11), (26), (29) and (30) are infinitesimally small in relation to volumetric terms n_f^D. Thus, using eqs. (8), (11) we can write the formula for $\mathbb{P}_{k|f}^D$ in the form of

$$\mathbb{P}_{k|f}^D = \exp\left\{ -\frac{1}{n_f^D} \int_{x_k} \sum_{i \in D} \int_{s_i} \frac{\alpha_{\kappa e_i}^D}{ds_i} \, ds_i \, dx_k \right\}. \tag{31}$$

The symbol ds_i formally placed in the nominator will be reduced as $\alpha_{\kappa e_i}^D$ is of range ds_i. Using of eq. (29) results in the same formula.

Similarly, we can get the expression for the quantity $B_{\kappa i}$ (def in eq. (28)) and hence for $\alpha_{\kappa e_i}^D$ (eq. (27)). Equation (28), while expanded up to the second neighbourhood terms, reduces to the form

$$B_{\kappa i}^D = \int_{x_i} \left[\sum_{o \in D\backslash i} \int_{s_o} \frac{\alpha_{\iota e_o}^0 \exp(B_{\iota o}^{D\backslash i}) - \alpha_{\kappa\iota e_o}^0 \exp(B_{\kappa\iota o}^{D\backslash i})}{n_f^D + x_i - x_\kappa} \frac{ds_o}{ds_o} \right] dx_i, \tag{32}$$

where

$$B_{\iota o}^{D\backslash i} = \int_{x_o} \left[\sum_{l \in D\backslash i\backslash o} \int_{s_l} \frac{\alpha_{oe_l}^{D\backslash i\backslash o} - \alpha_{\iota oe_l}^{D\backslash i\backslash o}}{n_f^D + x_i + x_o - x_\kappa} \frac{ds_l}{ds_l} \right] dx_o \tag{33}$$

and

$$B_{\kappa\iota o}^{D\backslash i} = \int_{x_o} \left[\sum_{l \in D\backslash i\backslash o} \int_{s_l} \frac{\alpha_{oe_l}^{D\backslash i\backslash o} - \alpha_{\kappa\iota oe_l}^{D\backslash i\backslash o}}{n_f^D + x_i + x_o - x_\kappa} \frac{ds_l}{ds_l} \right] dx_o. \tag{34}$$

Higher order neighbourhood terms may be written similarly by proper develop-
ment of expressions for $\alpha_{oe_l}^{D\backslash i\backslash o}$, $\alpha_{\iota oe_l}^{D\backslash i\backslash o}$ and $\alpha_{\kappa\iota oe_l}^{D\backslash i\backslash o}$ (like in eqs. (27), (32)) with the suc-
ceeding particle being regarded as an obstacle and being removed from the lattice.
As it is seen, to evaluate a value for $\alpha_{\kappa e_i}^{D}$, the geometric factors: $\alpha_{\kappa e_i}^{0}$, $\alpha_{\iota e_o}^{0}$, $\alpha_{oe_l}^{0}$,
$\alpha_{\kappa\iota e_o}^{0}$, $\alpha_{\iota oe_l}^{0}$, $\alpha_{\kappa\iota oe_l}^{0}$ ... must be found for each pair of surfacial elements of the two
objects which are considered as being in conflict.

Following the eq. (25) the value for $\alpha_{\kappa e_i}^{0}$ may be calculated using the formula

$$\alpha_{\kappa e_i}^{0} = \frac{\mathcal{V}_{i\xi}^{\kappa}}{\mathcal{V}_{i\xi}}, \tag{35}$$

where $\mathcal{V}_{i\xi}^{\kappa}$ is the volume of a region in which a certain selected point of the object i
can be located, while its surface element e_i is placed in the cell ξ, providing that no
element of i is in conflict with any element of κ; $\mathcal{V}_{i\xi}$, the volume of a region in which
the same point of the object i can be located when the considered surface element
is placed in the cell ξ, disregarding possible conflicts of this and other elements of i
with elements of κ. In the same way, the values for $\alpha_{\kappa\iota e_o}^{0}$, $\alpha_{\iota oe_l}^{0}$, $\alpha_{\kappa\iota oe_l}^{0}$ may be calcu-
lated if the volume in the numerator of eq. (35) is found in such a manner as to
exclude conflicts of the obstacle o or l with suitable agglomerate $\kappa\iota$, ιo or $\kappa\iota o$,
respectively.

Let index o denote a particle being considered as an obstacle; $\bar{\alpha}_{\kappa o}^{0}$, $\bar{B}_{\kappa o}^{D}$, $\bar{B}_{\kappa o}^{0}$,
values for $\alpha_{\kappa e_o}^{0}$, $B_{\kappa e_o}^{D}$, $B_{\kappa e_o}^{0}$, respectively, averaged over the surfacial elements s_o; a_i,
specific surface area of the oth particle. Equation (31) may be rewritten in the fol-
lowing form:

$$\ln \mathbb{P}_{k|f}^{D} = - \sum_{o \in D} \frac{x_o}{n_f^D} \int_{x_k} \frac{a_o \bar{\alpha}_{\kappa o}^{0}}{ds_o} dx_k - \sum_{p=1}^{\infty} \frac{1}{p!} \sum_{i \in D} \frac{x_o}{n_f^D} \int_{x_k} \frac{a_o \bar{\alpha}_{\kappa o}^{0}}{ds_o} \left(\bar{B}_{\kappa o}^{D}\right)^p dx_k, \tag{36}$$

where $\left(\bar{B}_{\kappa o}^{D}\right)^p$ denotes the pth order product of terms $\bar{B}_{\kappa o}^{D}$ (in the general case, the
multiplication of functions $\bar{B}_{\kappa o}^{D}$ is not commutative). Let O^p denote a sequence of p
indices (each of them representing any particle $o \in D$). The double index o_i will be
used to differentiate between obstacles, thus $O^p = \{o_1, o_2, \ldots, o_p\}$. Let us define the
scalar product $\odot$

$$\left(\sum_{o \in D} x_o\right)^p \odot \mathbf{G}_k^p[O^p] \stackrel{\text{def}}{=} \sum_{o_1} \cdots \sum_{o_p} (x_{o_1} \cdots x_{o_p}) \cdot G_k^p[o_1, \ldots, o_p], \tag{37}$$

where $\mathbf{G}_k^p[O^p]$ denotes a vector of pth order factors $G_k^p[o_1, \ldots, o_p]$ depending only
on geometrical parameters of particles $\kappa, o_1, \ldots, o_p$:

$$G_k^p[o_1, \ldots, o_p] \stackrel{\text{def}}{=} \int_{x_k} \int_{x_{o_1}} \cdots \int_{x_{o_{p-1}}} g_{\kappa}^p[o_1, \ldots, o_p] \, dx_{o_{p-1}} \cdots dx_{o_1} \, dx_k. \tag{38}$$

The function $g^p[\kappa, O]$ gathers all geometrical terms associated with $(x_{o_1} \cdots x_{o_p})$ in
consecutive series nested in $\bar{B}_{\kappa o_1}^{D}$, $\bar{B}_{o_1 o_2}^{D}$, $\bar{B}_{\kappa o_1 o_2}^{D}$, ..., (see eqs. (32)–(34)). The lack of x_o
in the set D and the volume $x_o - x_\kappa$ may be neglected as being of little importance.

A particle considered as the pth order obstacle contributes into the factors $\mathbf{G}_k^i[D]$, starting with that of pth order up to infinity. For $p = 1, 2, 3$, we have

$$g_\kappa^1[o_1] \stackrel{\text{def}}{=} \frac{a_{o_1} \cdot \bar{\alpha}_{\kappa o_1}^0}{ds_{o_1}}, \tag{39}$$

$$g_\kappa^2[o_1, o_2] \stackrel{\text{def}}{=} \frac{a_{o_1} \cdot \bar{\alpha}_{\kappa o_1}^0}{ds_{o_1}} \frac{a_{o_2} \cdot (\bar{\alpha}_{o_1 o_2}^0 - \bar{\alpha}_{\kappa o_1 o_2}^0)}{ds_{o_2}}, \tag{40}$$

$$g_\kappa^3[o_1, o_2, o_3] \stackrel{\text{def}}{=} \frac{a_{o_1} \cdot \bar{\alpha}_{\kappa o_1}^0}{ds_{o_1}} \left[\frac{a_{o_2} \cdot \bar{\alpha}_{o_1 o_2}^0}{ds_{o_2}} \frac{a_{o_3} \cdot (\bar{\alpha}_{o_2 o_3}^0 - \bar{\alpha}_{o_1 o_2 o_3}^0)}{ds_{o_3}} \right.$$
$$- \frac{a_{o_2} \cdot \bar{\alpha}_{\kappa o_1 o_2}^0}{ds_{o_2}} \frac{a_{o_3} \cdot (\bar{\alpha}_{o_2 o_3}^0 - \bar{\alpha}_{\kappa o_1 o_2 o_3}^0)}{ds_{o_3}} \right]$$
$$+ \frac{1}{2} \frac{a_{o_1} \cdot \bar{\alpha}_{\kappa o_1}^0}{ds_{o_1}} \left[\frac{a_{o_2} \cdot (\bar{\alpha}_{o_1 o_2}^0 - \bar{\alpha}_{\kappa o_1 o_2}^0)}{ds_{o_2}} \frac{a_{o_3} \cdot (\bar{\alpha}_{o_1 o_3}^0 - \bar{\alpha}_{\kappa o_1 o_3}^0)}{ds_{o_3}} \right]. \tag{41}$$

The first term in the square brackets in eq. (41) represents $\bar{B}_{o_1 o_2}^0$, the second one is $\bar{B}_{\kappa o_1 o_2}^0$ and the third one is the second order element $0.5\bar{B}_{\kappa o_1}^0 \cdot \bar{B}_{\kappa o_1}^0$ in the series shown in eq. (36).

Let $(O^p|i^l)_c$ denote the cth combination of l identical indices (representing the same particle) in the sequence O^p ($l \leqslant p$). The following equality is valid:

$$\left(\sum_{o \in D \setminus i} x_o + x_i \right)^p \odot \mathbf{G}_k^p[O^p] = \sum_{l=0}^{p} \sum_{c=1}^{\binom{p}{l}} \left(\sum_{o \in D \setminus i} x_o \right)^{p-1} \cdot (x_i)^l \odot \mathbf{G}_k^p[(O^p|i^l)_c]. \tag{42}$$

By using symbols (37) formula (36) may be expanded up to infinity and, next, formula (10) may be expressed as

$$\delta_k S^D = k_B \left\{ \ln n_f^D - \sum_{p=1}^{\infty} \frac{1}{(n_f^D)^p} \left(\sum_{o \in D} x_o \right)^p \odot \mathbf{G}_k^p[O^p] \right\}. \tag{43}$$

By summation of all terms $\delta_k S^D$ corresponding to consecutive particles being placed in the lattice we arrive at a rigorous formula for configurational entropy S^M of mixture. The order in which particles are added (i.e. summation order) should not affect the value of S^M. Let us consider a mixture of J components, each of them having identical particles. The summation over the set of the mixture particles may be split into summation over the sets of identical particles belonging to the consecutive components $i = 1, \ldots, J$. Let us take that the kth particle (being inserted into the lattice) belongs to the jth component. The coefficients $\mathbf{G}_k^p[O^p]$ may be

attributed to components and to individual particles as well ($\mathbf{G}_k^p[O^p] = \mathbf{G}_j^p[O^p]$).
Let M_i denote the total number of ith component particles in the mixture; m_j, the
number of particles of the jth component arranged in the lattice prior to the kth par-
ticle. Thus, the free space n_f^D available for the kth particle is

$$n_f^D = n - \sum_{i=1}^{j-1} M_i x_i - m_j x_j = \sum_{i=1}^{J} M_i x_i^* - \sum_{i=1}^{j-1} M_i x_i - m_j x_j \tag{44}$$

and

$$\sum_{o \in D} x_o = \sum_{i=1}^{j-1} M_i x_i + m_j x_j . \tag{45}$$

While expressing the numbers n, M_i and m_j in moles we can treat m_j as a continu-
ous variable (with a negligible error), and perform the summation of the terms
(43) over the set of jth component particles by integration with $dm_j = 1/$(Avogadro
number).

Let v_j denote the volume fraction of the hard parts of jth component particles
in the mixture

$$v_j \stackrel{\text{def}}{=} \frac{M_j x_j}{n} . \tag{46}$$

By integration of formula (43) (with respect to (42)) and summation of the resul-
tant terms corresponding to consecutive components we arrive at the general for-
mula for S^M:

$$
\begin{aligned}
S^M = k_B \sum_{j=1}^{J} \Bigg\{ & M_j(1 - \ln M_j - A^0) - \frac{n}{x_j} \sum_{q=2}^{\infty} \left[\left(1 - \sum_{i=1}^{j} v_i\right)^{1-q} \left(\sum_{o=1}^{j} v_o\right)^{q} \odot \mathbf{A}_j^q[O^q] \right] \\
& + \frac{n}{x_j} \sum_{q=2}^{\infty} \left[\left(1 - \sum_{i=1}^{j-1} v_i\right)^{1-q} \left(\sum_{o=1}^{j-1} v_o\right)^{q} \odot \mathbf{A}_j^q[O^q] \right] \\
& - \frac{n}{x_j} A^0 \left[\left(1 - \sum_{i=1}^{j} v_i\right) \ln n \left(1 - \sum_{i=1}^{j} v_i\right) - \left(1 - \sum_{i=1}^{j-1} v_i\right) \ln n \left(1 - \sum_{i=1}^{j-1} v_i\right) \right] \\
& - \frac{n}{x_j} \left[\sum_{o=1}^{j} v_o A_j^1[o] \ln n \left(1 - \sum_{i=1}^{j} v_i\right) - \sum_{o=1}^{j-1} v_o A_j^1[o] \ln n \left(1 - \sum_{i=1}^{j-1} v_i\right) \right] \Bigg\},
\end{aligned}
\tag{47}
$$

where the term $M_j(1 - \ln M_j) \cong - \ln(M_j!)$ is added in order to respect indistin-
guishability of particles within components; A^0 denotes a constant; $\mathbf{A}_j^q[O^q]$, vector
of geometrical factors $A_j^q[O^q]$, which are defined as below (see eqs. (37), (42)):

(a) the constant A^0:

$$A^0 \overset{\text{def}}{=} 1 + \sum_{p=1}^{\infty} (-1)^p p G_j^p[j^p]; \tag{48}$$

(b) the factors $A_j^1[O^1] = A_j^1[o]$:

$$A_j^1[O^1] \overset{\text{def}}{=} \sum_{p=1}^{\infty} (-1)^p \sum_{c=1}^{p} G_j^p[(O^p|j^{p-1})_c]; \tag{49}$$

(d) the remaining $A_j^q[O^q]$ $(q = 2, 3, \ldots, \infty)$:

$$A_j^q[O^q] \overset{\text{def}}{=} \sum_{p=q}^{\infty} \sum_{l=q}^{p} \frac{(-1)^{p-l}}{l-1} \sum_{c=1}^{\binom{p}{l}} \sum_{d=1}^{\binom{l}{q}} G_j^p[((O^l|j^{l-q})_c^p|j^{p-l})_d]. \tag{50}$$

As the value for S^M is not affected by the order of components in eq. (47), the following equalities are valid:

$$A^0 = 0 \quad (A^0 \text{ does not depend on } j), \tag{51}$$

$$x_i A_j^q[O^q] = x_j A_i^q[O^q] \quad \text{for each set } \{i, j, o_1, \ldots, o_q\}, q > 0. \tag{52}$$

Let η^M denote the fraction of the hard part of all particles in the mixture, i.e. the average packing ratio of particles

$$\eta^M \overset{\text{def}}{=} \frac{1}{n} \sum_{j=1}^{J} M_j x_j. \tag{53}$$

Due to eqs. (51), (52), the formula (47) reduces to the form of

$$S^M = k_B \sum_{j=1}^{J} M_j$$

$$\times \left\{ 1 - \ln M_j - A_j^1[j](\ln n + \ln(1 - \eta^M)) - \sum_{q=2}^{\infty} \frac{\left(\sum_{o=1}^{J} v_o\right)^{q-1} \odot \mathbf{A}_j^q[j, O^{q-1}]}{(1 - \eta^M)^{q-1}} \right\}. \tag{54}$$

The configurational entropy of the mixture components in their standard state (pure liquid state) may be expressed using eq. (47), but for each individual j the value for v_j ought to be computed as related to the component volume $n_j = M_j x_j^{*o}$ (x_j^{*o} – particle volume in its standard state), and $v_o = 0$ for $o = 1, j - 1$ must be taken. Let η_j^o denote the hard part fraction (packing ratio) in the volume of jth component particle in its standard state,

$$\eta_j^o \overset{\text{def}}{=} \frac{x_j^o}{x_j^{*o}} .$$

(55)

If no volume changes occur in the mixing process and η_j^o is the same for the all components we have $\eta_j^o = \eta^M$. Let A^q denote the value of $A_j^q[j^q]$ (for identical particles). Using the quantity η_j^o and eq. (47) we arrive at the formula

$$S^o = k_B \sum_{j=1}^{J} M_j$$

$$\times \left\{ 1 - \ln M_j - \left(A^1 + \frac{A^0}{\eta_j^o} \right) \ln(M_j x_j^{*o}(1 - \eta_j^o)) - \sum_{q=2}^{\infty} \left[\frac{\eta_j^o}{1 - \eta_j^o} \right]^{q-1} A^q \right\}, \quad (56)$$

which reduces (due to eq. (51)) to the form

$$S^o = k_B \sum_{j=1}^{J} M_j$$

$$\times \left\{ 1 - \ln M_j - A^1 \left(\ln(M_j x_j^{*o}) + \ln(1 - \eta_j^o) \right) - \sum_{q=2}^{\infty} \left[\frac{\eta_j^o}{1 - \eta_j^o} \right]^{q-1} A^q \right\}. \quad (57)$$

4.3. APPLICATION TO MIXTURES OF SPHERICAL PARTICLES

Let us recall eq. (35). While assuming the hard parts of the particles κ and obstacle o to be simple solid figures, an accurate expression for $\alpha_{\kappa e_o}^0$ may be derived. In particular, for many small molecule substances we can take that the hard part of each particle is a sphere, thus arriving at the well-known mixture of hard spheres [1–4]. In this special case $\alpha_{\kappa e_o}^0 = \bar{\alpha}_{\kappa o}^0$ for any surfacial element e_o, hence it will be shortly referred to as $\alpha_{\kappa o}^0$.

The way in which the kth particle is built has no effect on the final expression for the entropy. Thus, let us take that κ is enlarged by joining infinitesimal elements on a spherical surface, as it is shown in fig. 1. The number of elements neighboring ξ cell within the layer is mostly two. Other cases (one or no neighbour) are of no importance. Let R_o denote the radius of the oth particle $(x_o = (4\pi/3)R_o^3;$ $a_o = 3/R_o)$; r_k, the actual value for the radius of κ. A solid in which the center O_o of the oth sphere may be placed when the oth sphere has one and only one element in conflict with ξ cell is rather complicated, as schematically shown in the fig. 1. However, the expression for $\mathcal{V}_{o\xi}^\kappa$ is quite simple and it has the following form:

$$\mathcal{V}_{o\xi}^\kappa = \frac{(R_o + r_k)^2}{r_k^2} \, ds_o \, dr_k .$$
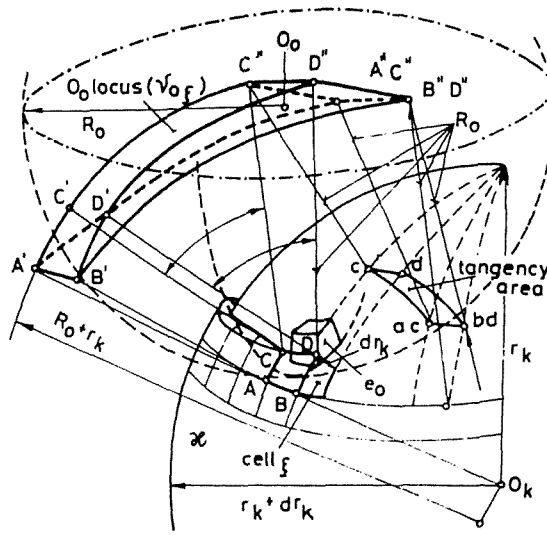
(58)

Fig. 1. The locus of the oth sphere center with an element e_o being in conflict with the cell ξ placed on a spherical surface of κ.

In order to prove the above formula we notice that the effects of rotation of the oth sphere around upper and right edges (CDB) of the cell ξ are compensated by identical effects for the left and lower edges (BAC) (see fig. 1).

It may be easy shown that the volume $\mathcal{V}_{o\xi}$ is

$$\mathcal{V}_{o\xi} = 4\pi R_o^2 \, dr_k \, . \tag{59}$$

Thus, the expression for $\alpha_{\kappa o}^0$ has the form

$$\alpha_{\kappa o}^0 = \frac{(R_o + r_k)^2}{4\pi R_o^2 r_k^2} \, ds_o \, . \tag{60}$$

Notice that eq. (58) (and hence eq. (60)) is also valid for any pair of objects having curvature locally smooth around the considered points ($R_o > 0$ and $r_k > 0$). Thus, generally, R_o and r_k in eq. (60) might be treated as local radii of curvature.

Using eq. (60) we can derive the accurate formula for the first geometrical factor $G_k^1[o]$ (see eqs. (38), (39)). It has the form

$$G_k^1[o] = 3 \int_0^{R_k} \frac{(R_o + r_k)^2}{R_o^3} \, dr_k = \left(1 + \frac{R_k}{R_o}\right)^3 - 1 \, . \tag{61}$$

In order to get some insight into the nature of our model let us apply the above to express the first order approximation $\mathbb{P}_{k|f}^1$ to the probability $\mathbb{P}_{k|f}^D$. According to eq. (36), after simple transformations it may be written (with negligible error) as

$$\mathbb{P}_{k|f}^1 \cong \prod_{o \in D} \left[1 - \frac{4\pi}{3} \frac{(R_o + R_k)^3 - R_o^3}{n_f^D}\right] \, . \tag{62}$$

The expression in the square brackets is approximately equal to the probability, that a free cell chosen at random for the center of the kth sphere is not placed within the inadmissible region surrounding the oth particle, as shown in fig. 2. Such events, concerning a position of the kth sphere center related to individual particles o, are mutually independent ones. Thus, the probability of non-conflict location of the kth sphere is equal to the product of probabilities of the above events, which is expressed by eq. (62). Higher order terms in eq. (43) correct this value due to the presence of inaccessible regions (fig. 2), i.e. due to the impossibility of complete overlapping of inaccessible regions in the lattice.

In order to derive the formula for $G_k^2[o^2]$ (see eqs. (38), (40)), let us take that the object κ is a sphere with the radius r_k, and the first order obstacle (i.e. the particle o_1) is rebuilt by joining consecutive circular layers, starting with any surfacial element placed in the cell ξ. It is noteworthy, that such a forming way might also be used for the kth sphere to derive the formula (61). The shape of the object κ and corresponding positions of the oth sphere center are shown in fig. 3, and the resultant inadmissible region is illustrated in fig. 4. If applied for the obstacle o_1, this forming way gives object o_1 tangent to κ, thus it allows us to use the relatively simple eqs. (28) (instead of eq. (30)) and next, to apply the formula (40). The former may be written as

$$G_k^2[o_1, o_2] = \frac{3}{R_{o_1}} \frac{3}{R_{o_2}} \int_0^{R_k} \int_{x_{o_1}} \left[1 + \frac{r_k}{R_{o_1}}\right]^2 \frac{(\alpha^0_{o_1 o_2} - \alpha^0_{\kappa o_1 o_2})}{ds_{o_2}} \, dx_{o_1} \, dr_k . \qquad (63)$$

It is shown in fig. 5 that $(\alpha^0_{o_1 o_2} - \alpha^0_{\kappa o_1 o_2})$ is non-zero only for circumferential elements of each layer of o_1, within a range of the angle denoted as ϕ. For the whole
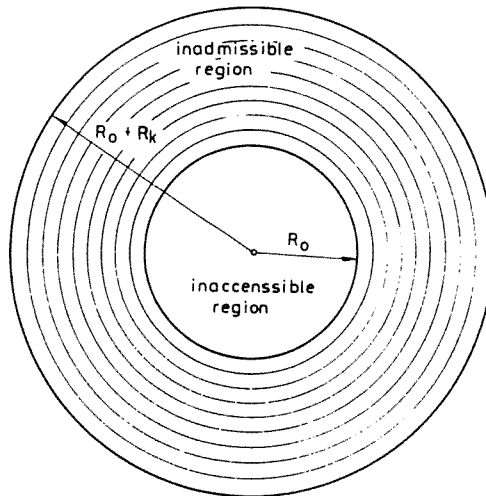

Fig. 2. Conflictable locations of the center of the kth particle being formed as a ball κ in a neighbourhood of an obstacle o.
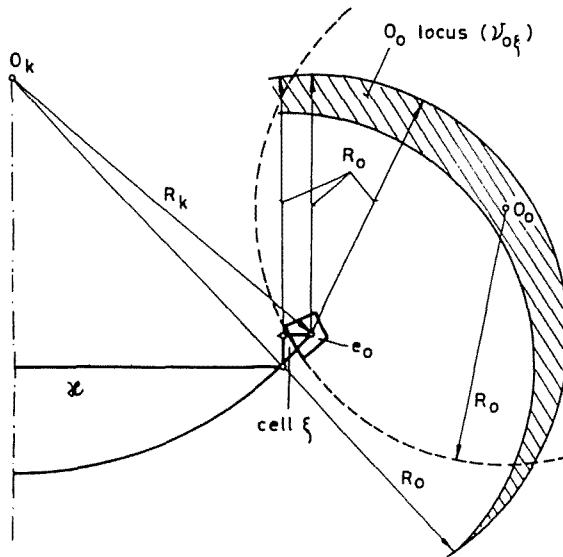
Fig. 3. The locus of the oth sphere center with an element e_o being in conflict with the cell ξ, if the kth particle is built in the form of the spherical segment κ.

particle o_1 (with κ being fixed) it results in a region of which a section is shown in fig. 6 as the striped area. By integration over this region and using eqs. (35) and (59) one can prove that
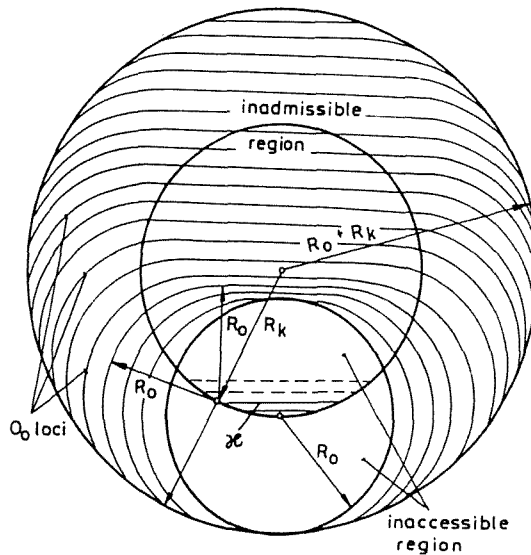

Fig. 4. Conflictable locations of the center of an obstacle o if the particle k is built in the form of a spherical segment κ.
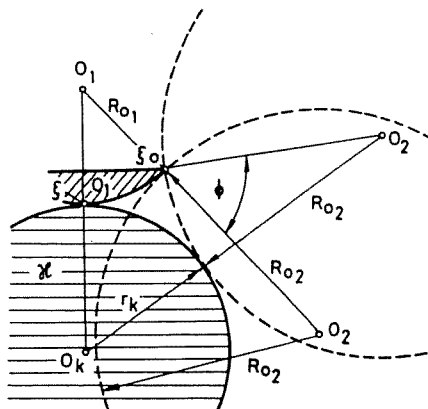
Fig. 5. Boundary positions of an obstacle o_2 (conflicting with a circumferential element of the particle o_1) related to the single o_1 and to the agglomerate κo_1. The particle o_1 is rebuilt as the spherical section o_1, κ is the sphere.

$$a_{o_2} \int_{x_{o_1}} \frac{(\alpha^0_{o_1 o_2} - \alpha^0_{\kappa o_1 o_2})}{ds_{o_2}} \, dx_{o_1} = \frac{3}{R_{o_2}} \frac{R_{o_1} r_k}{R_{o_1} + r} \, . \tag{64}$$

After substitution of eq. (64) into eq. (63) we arrive at the formula

$$G^2_k[o_1, o_2] = \frac{9}{2} \frac{R^2_k}{R_{o_1} R_{o_2}} + 3 \frac{R^3_k}{R^2_{o_1} R_{o_2}} \, . \tag{65}$$

The same result may be reached in a more general (but also more complicated) way, by forming of the o_1th particle as a growing sphere o_1 like the kth particle (see
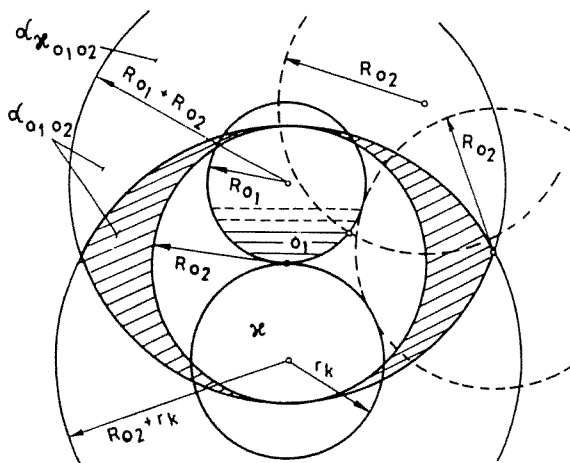

Fig. 6. Region representing the result of integration of the function $(\alpha^0_{o_1 o_2} - \alpha^0_{\kappa o_1 o_2})$ over the volume of an obstacle o_1 being formed as the spherical section o_1 tangent to κ.

fig. 7). To meet the tangency condition, the center of o_1 must be placed on a spherical surface having radius $(R_{o_1} + r_k)$, thus eq. (30) should be applied to express $B_{\kappa o_1}^D$ and to derive the formula for G_k^2. Consequently, each element of o_2 ought to be analysed as a possible occupant of the cell chosen as the center of o_1. The regions corresponding to $\alpha_{o_1 o_2}^0$ and $\alpha_{\kappa o_1 o_2}^0$ are shown in fig. 7. The area enveloped by the thickened line has to be subtracted as contributed by $\alpha_{\kappa o_1 o_2}^0$.

In the same unified way, effects of further neighbourhood may be analysed with a proper spatial configuration of spheres representing consecutive obstacles. Let $*$ denote a spatial system (agglomerate) of spheres being formed due to previous steps of the procedure, except for the foregoing one; o_{p-1}, the object being rebuilt as the obstacle in the former step; o_p, the currently analysed obstacle. The value for $\alpha_{*o_{p-1}o_p}^0$ is

$$\alpha_{*o_{p-1}o_p}^0 = \begin{cases} \dfrac{(R_{o_p}+r_{o_{p-1}})^2}{4\pi R_{o_p}^2 r_{o_{p-1}}^2}\, ds_o \,, & \text{if a position of the } o_p\text{th sphere center} \\ & \text{does not imply any conflict with } *, \\ 0 & \text{if a conflict of } o_p \text{ with } * \text{ occurs}. \end{cases} \tag{66}$$

In order to get the coefficient $G_k^3[o_1, o_2, o_3]$ a suitable three sphere system should be analysed (see eq. (41)). The problem is very involved and till the present day we did not find any analytical formula for $\alpha_{\kappa o_1 o_2 o_3}^0$, to say nothing of higher order terms.

Let us try to deduce an approximating formula for ΔS using eqs. (48)–(56) and having the accurate formulae for G_k^1 (eq. (61)) and G_k^2 (eq. (65)). By substitution of G_j^1 and G_j^2 into eqs. (48)–(50) one can get the following equalities:
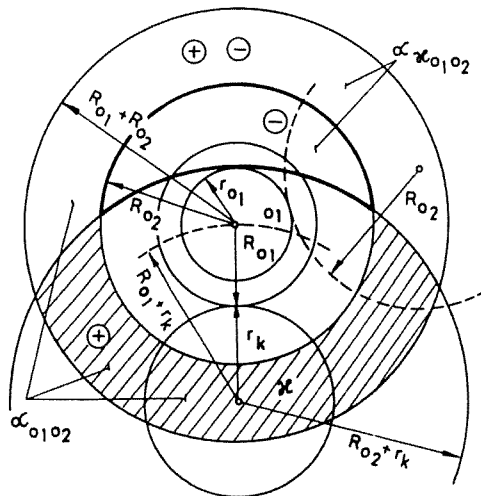

Fig. 7. Region representing the result of integration of the function $(\alpha_{o_1 o_2}^0 - \alpha_{\kappa o_1 o_2}^0)$ over the volume of an obstacle o_1 being formed as the sphere o_1 in a neighbourhood of κ.

$$A^0 = 9 + \sum_{p=3}^{\infty} (-1)^p \cdot p \cdot G_j^p[j^p] = 0, \tag{67}$$

$$A_j^1[o] = -\left(\frac{R_j}{R_o}\right)^3 + 9\frac{R_j}{R_o} + \sum_{p=3}^{\infty} (-1)^p \sum_{c=1}^{p} G_j^p[O^p][j^{p-1}], \tag{68}$$

$$A_j^2[O^2] = 3\frac{R_j^3}{R_{o_1}^2 R_{o_2}} + \frac{9}{2}\frac{R_j^2}{R_{o_1} R_{o_2}}$$
$$+ \sum_{p=3}^{\infty} \sum_{l=2}^{p} \frac{(-1)^{p-l}}{l-1} \sum_{c=1}^{\binom{p}{l}} \sum_{d=1}^{\binom{l}{2}} G_j^p[((O^l|j^{l-2})_c^p|j^{p-l})_d]. \tag{69}$$

While bearing in mind that $x_j = \frac{4\pi}{3}R_j^3$, it is evident that eq. (52) can be fulfilled for any set $\{i, j, o_1, \ldots, o_q\}$, and $q>0$ (i.e.: $x_i \cdot A_j^q[O^q] = x_j \cdot A_i^q[O^q]$) if and only if $A_j^q[O^q]$ are of the form

$$A_j^q[O^q] = R_j^3 \mathbb{F}_q(R_{o_1}, R_{o_2}, \ldots, R_{o_q}), \tag{70}$$

where a function $\mathbb{F}_q()$ does not depend explicitly on R_j.

In order to get some insight into a structure of $\mathbb{F}_q()$, let us consider the function $\exp(\bar{B}_{\kappa o}^0)$ which represents the effect of the second order obstacles on $\mathbb{P}_{k|f}^D$ (see eqs. (36), (40), (41)). Using eqs. (60) and (64) one can show, like in eq. (63), that the contribution Δ_{ko}^p of $\bar{B}_{\kappa o}^0$ to the function $G_k^p[O^p]$ $(p>1)$ has the following form

$$\Delta_{ko}^p = \frac{R_o^{p-1}}{(R_O)^{p-1}} \frac{3^p}{(p-1)!} \left\{ \frac{1}{3}\frac{R_k^3}{R_o^3} - \frac{3}{2}(p-3)\frac{R_k^2}{R_o^2} + \frac{3}{2}(p-3)(p-2)\frac{R_k}{R_o} \right.$$
$$- \frac{(p-3)(p-2)(p-1)}{6} \ln\left(1 + \frac{R_k}{R_o}\right)$$
$$\left. - \sum_{t=4}^{p-1} \frac{(-1)^t}{t-3} \binom{p-1}{t} \frac{R_o^{t-3} - (R_o + R_k)^{t-3}}{(R_o + R_k)^{t-3}} \right\}, \tag{71}$$

where $(R_O)^{p-1}$ denotes the product $(R_{o_2} \cdot \ldots \cdot R_{o_p})$; o, a particle acting as the first order obstacle $(o \notin O)$. The factor $(3/R_O)^{p-1}$ represents the product $(a_O)^{p-1}$ (see eqs. (40), (41)). In particular, for $p = 2$ the above formula reduces to eq. (65), and for $p = 3$ it may be used as an approximation to $G_k^3[O^3]$

$$G_k^3[o_1, o_2, o_3] \approx \frac{9}{2}\frac{R_k^3}{R_{o_1} R_{o_2} R_{o_3}}. \tag{72}$$

The coefficient $A_j^q[O^q]$ (see eq. (50)) consists of terms $G_j^p[O^p]$ with a subset of $p - q$ indices being substituted with j (the kth particle belongs to the jth component). Notice that for $p>3$ in eq. (71) we must take $R_o = R_k = R_j$ and $q = 3$, as eq.

(70) has to be satisfied. It means that Δ_{jo}^p contributes only into $A_j^3[O^3]$ and only with terms proportional to $R^3/(R_O)^3$. In the same way one can also show that for $q = 2$ formula (71) yields terms proportional to $R^2/(R_O)^2$ only. Terms corresponding to other substitutions ($R_{o_i} = R_j$, $o_i \neq o$) shall be canceled in proper series defining $A_j^q[O^q]$.

Let us recall the function $G_k^p[O^p]$ defined in eq. (38). Let $\bar{\beta}[o_i, \ldots, o_{p-2}, o_{p-1}, o_p]$ denote the function integrated over x_{p-1} in the formula for $\bar{B}_{o_i\ldots o_{p-2}o_{p-1}o_p}^0$ (like in eqs. (32)–(34)):

$$\bar{\beta}[o_i, \ldots, o_{p-2}, o_{p-1}, o_p] \overset{\text{def}}{=} \frac{a_{o_p}(\bar{\alpha}_{o_{p-1}o_p}^0 - \bar{\alpha}_{o_i\ldots o_{p-2}o_{p-1}o_p}^0)}{ds_{o_p}} . \tag{73}$$

Let $\delta_\kappa^1[O^p]$ denote the first order contribution of obstacles $\{o_1, \ldots, o_p\}$ to the factor $g_\kappa^p[O^p]$. It may be found recursively: for $p = 2$

$$\delta_\kappa^1[o_1, o_2] \overset{\text{def}}{=} \bar{\beta}[\kappa, o_1, o_2]; \qquad b_\kappa^2 \overset{\text{def}}{=} \frac{a_{o_1}\bar{\alpha}_{\kappa o_1}^0}{ds_{o_1}} , \tag{74}$$

and for consecutive $p > 2$

$$\delta_\kappa^1[o_1, O^{p-2}, o_p] \overset{\text{def}}{=} \delta_\kappa^1[o_1, O^{p-2}] \cdot \bar{\beta}[o_{p-2}o_{p-1}o_p]$$

$$+ \sum_{o_i=\kappa}^{o_{p-3}} b_{o_i}^p(\bar{\beta}[o_{p-2}, o_{p-1}, o_p] - \bar{\beta}[o_i, \ldots, o_p]) , \tag{75}$$

where

$$b_{o_i}^p \overset{\text{def}}{=} -b_{o_i}^{p-1} \frac{a_{o_p}\bar{\alpha}_{o_i\ldots o_{p-1}o_p}^0}{ds_{o_p}} \quad \text{for } o_i = \kappa, o_1, \ldots, o_{p-2} \tag{76}$$

and

$$b_{o_{p-1}}^p \overset{\text{def}}{=} \sum_{o_i=\kappa}^{o_{p-2}} b_{o_i}^{p-1} \frac{a_{o_p}\bar{\alpha}_{o_{p-1}o_p}^0}{ds_{o_p}} . \tag{77}$$

Based on the above formulae and bearing in mind the expansion for functions $\exp(\bar{B}_{(.)o_i}^0)$ in series one can deduce that the function $g_\kappa^p[O^p]$ is a sum of products, each of them consisting of subproducts of factors $(a_{o_i} \cdot \bar{\alpha}_{o_i\ldots o_{l-1}o_l}^0)$ or $\bar{\beta}[o_i, \ldots, o_l]$. Each product starts with the factor $(a_{o_p} \cdot \bar{\alpha}_{\kappa o_1}^0)$ which appears only once. The remaining subproducts may be of order from 1 to p, with only last element in the sequence $[o_i, \ldots, o_l]$ being altered. Each two neighboring factors involve at least one common index in the latter part of sequences, i.e. $[\ldots o_{l-1}, o_l] [\ldots o_l, o_{l+1}]$ or $[\ldots o_l, o_{l+1}] [\ldots o_l, o_{l+2}]$. Moreover, any substitution of any index in the sequence $[o_i \ldots, o_l, \ldots]$ implies the same substitution in each other sequence containing this index.

In order to reach the function $G_k^p[o_1 \ldots o_p]$ the integration of $g_\kappa^p[o_1 \ldots o_p]$ over

$x_{o_{p-1}}, \ldots, x_k$ has to be done (see eq. (38)). By analogy to eq. (71), the result may be written generally in the form of

$$G_k^p[o_1 \ldots o_p] = \Gamma(R_k, R_{o_1} \ldots R_{o_p}) + \sum_i \Gamma_{fi}(R_k, R_{o_1} \ldots R_{o_p}) f_i(R_k, R_{o_1} \ldots R_{o_p}) , \quad (78)$$

where $\Gamma(.)$, $\Gamma_{fi}(.)$ denote polynomial functions of relative radii; $f_i(.)$, a nonpolynomial function corresponding to the ith product in $g_k^p[o_1 \ldots o_p]$. The polynomials $\Gamma(.)$ and $\Gamma_{fi}(.)$ may be of order $3p$, as each factor in (75)–(77) contributes to the nominator with R_o^3.

While considering the factors $A_j^q[O^q]$ defined in eqs. (49), (50) we are interested in functions $G_j^p[j^{p-q}, O^q]$ obtained by substitution of $p - q$ elements in O^p with j. Before such a substitution, monomials $\mathcal{M}(O^q)$ obtained in $\Gamma(.)$ or in $\Gamma_{fi}(.)$ may be written as

$$\mathcal{M}(O^q) = (R_j)^{l_j} \cdot \prod_{i=1}^{p-q} \frac{(R_i)^{l_i}}{R_i^3} \cdot \prod_{o=1}^{q} \frac{(R_o)^{l_o}}{R_o^3} , \quad (79)$$

where i points to the elements of O selected to be replaced by j. In any case, at least one monomial of form (79) contributes to $A_j^q[O^q]$ as the factor R_j^3 must be extracted (see eq. (70)).

Let us recall eq. (68). It shows that for $q = 1$ the sum of the 3rd and higher order terms does not yield second order monomials (R_j^2/R_O^2), albeit according to eq. (79) it might be possible. Similarly, in eq. (69) the first order terms do not appear. These facts and the form of eq. (71) suggest that for $p > 2$,

$$l_j > 0; \quad l_i \geqslant 2; \quad l_o \geqslant 2 . \quad (80)$$

Let us take that the above inequalities (concerning l_i and l_o) are valid. It allows us to rewrite the function (79) in the form

$$\mathcal{M}^1(O^q) = (R_j)^{l_j} \cdot \prod_{i=1}^{p-q} \frac{(R_i)^{l_i}}{R_i} \cdot \prod_{o=1}^{q} \frac{(R_o)^{l_o}}{R_o} , \quad (81)$$

where new $l_i \in [0, p - q]$ and new $l_o \in [0, q]$.

In order to provide some basis for analysis of the consequences of the above assumption let us propose also an alternative model consisting of monomials $\mathcal{M}^2(O^q)$

$$\mathcal{M}^2(O^q) = (R_j)^{l_j} \cdot \prod_{i=1}^{p-q} \frac{(R_i)^{l_i}}{R_i^2} \cdot \prod_{o=1}^{q} \frac{(R_o)^{l_o}}{R_o^2} . \quad (82)$$

By virtue of eq. (70), a monomial $\mathcal{M}^m(O^q)$ (being of form either (81), if $m = 1$, or (82), if $m = 2$) contributes to $A_j^q[O^q]$ *if and only if*:

(1)   it is a component of $\Gamma_{fi}(.)$ in eq. (78) and the corresponding function $f_i(.)$ is not affected by R_j and all R_i; or else it is contained in $\Gamma(.)$

(2)   the following equality is satisfied:

$$\sum_{i=1}^{p-q} l_i = m(p - q) - l_j + 3 .$$ (83)

All remaining components of the function (78) are reduced by identical terms or yield a constant value due to substitution of R_j.

Based on eqs. (67)–(70) with respect to (80) we can conclude that the coefficients $A_j^1[o]$ and $A_j^2[O^2]$ are expressed by the following formulae:

$$A_j^1[o] = -\left(\frac{R_j}{R_o}\right)^3, \quad (A^1 = -1);$$

$$A_j^2[O^2] = 3\frac{R_j^3}{R_{o_1}^2 R_{o_2}}, \quad (A^2 = 3).$$ (84)

At the present stage, the higher order coefficients $A_j^q[O^q]$ $(q > 2)$ may be only supposed as some functions taken arbitrarily.

Let G^p denote shortly the value for $G_j^p[j^p]$ which does not depend on j (the factor $G_j^p[\,]$ for identical particles). According to eqs. (51) and (67) we have

$$\sum_{p=3}^{\infty}(-1)^q pG^p = -9 .$$ (85)

While respecting the formulae (84), eqs. (68) and (69) may be rewritten in the form

$$\sum_{p=3}^{\infty}(-1)^p \sum_{c=1}^{p} G_j^p[(O^p|j^{p-1})_c] = -9\frac{R_j}{R_o} ,$$ (86)

$$\sum_{p=3}^{\infty}\sum_{l=2}^{p}\frac{(-1)^{p-l}}{l-1}\sum_{c=1}^{\binom{p}{l}}\sum_{d=1}^{\binom{l}{2}} G_j^p[((O^l|j^{l-2})_d^p|j^{p-l})_d] = -\frac{9}{2}\frac{R_j^2}{R_{o_1} R_{o_2}} .$$ (87)

One can prove that the following equality is valid:

$$\sum_{l=2}^{p}\frac{(-1)^{p-l}}{l-1}\binom{p}{l}\binom{l}{2} = (-1)^p\frac{p}{2} .$$ (88)

Notice that the replacing of functions $G_j^p[\,]$ in formulae (86) and (87) by monomials $G^p R_j/R_o$ and $G^p \cdot R_j^2/(R_{o_1} R_{o_2})$, respectively, brings the series (86) and (87) to the form of (85). It allows us to the conclusion that for $p > 2$ a term obtained by substitution of $p - 2$ arguments with j in the function $G_j^p[O^p]$, if averaged over all possible combinations c and d of the subset j^{p-2} within the sequence O^p $(j \in O)$, is equal to $G^p \cdot R_j^2/(R_{o_1} R_{o_2})$. Similarly, a substitution of $p - 1$ arguments of $G_j[O^p]$ with j results at average in the monomial $G^p \cdot R_j/R_o$.

Let us assume that the above conclusion is valid for any $q > 2$ as well, i.e. that for any $p > 2$, $q \in [3, p]$ and $1 \in [q, p]$ one can take

$$G_j^p[((O^l|j^{l-q})_c^p|j^{p-l})_d] \stackrel{\text{avg}}{=} G^p R_j^3 F_q[O^q],\tag{89}$$

where the symbol $\stackrel{\text{avg}}{=}$ denotes equality related to the left hand side function averaged over all combinations c and d; $F_q[O^q]$ is a function such that $F_q[j^q] = 1/R_j^3$.

As far as the above hypothesis is true the formula (50) may be written in the following form:

$$A_j^q[O^q] = \sum_{p=q}^{\infty} \sum_{l=q}^{p} \frac{(-1)^{p-l}}{l-1} \binom{p}{l}\binom{l}{q} G^p R_j^3 F_q[O^q] = A^q R_j^3 F_q[O^q].\tag{90}$$

Basing on eq. (88) one can prove by mathematical induction that

$$\sum_{p=q}^{\infty} \sum_{l=q}^{p} \frac{(-1)^{p-l}}{l-1}\binom{p}{l}\binom{l}{q} = \sum_{p=q}^{\infty} (-1)^{p-q}\frac{p}{q(q-1)}.\tag{91}$$

Thus, the formula for the coefficients A^q has the form

$$A^q = \sum_{p=q}^{\infty} (-1)^{p-q}\frac{p}{q(q-1)} G^p.\tag{92}$$

Let us take that all terms essentially contributing to $A_j^q[O^q]$ originate from the polynomial $\Gamma(\dots)$ only (see eq. (78)), and they are of the form of either (81) or (82).

In general, the first may not be true, as the function (78) may contain components in which $f_i(\dots)$ is not affected by R_j, whereas monomials having the form (81) or (82) are present in $\Gamma_{fi}(\dots)$. Equations (74)–(77) show that it may occur if only higher order obstacles are substituted with j, as factors $\bar{\beta}(o_i, \dots, o_l]$ yield generally nonpolynomial terms (see formula (71)). Moreover, the inequalities (80) may not be valid for terms involving more than 2 obstacles. Nevertheless, the above assumptions are legitimate if:
(a)   components being of form $\Gamma_{fi}(R_j^3, R_O) \cdot f_i(R_O)$ are reduced by identical terms in a formula expressing accurately $G_j^p[j^{p-q}, O^q]$;
(b)   series of the components as above converge (with $p \to \infty$) to a polynomial form
(c)   all the components being omitted are of little importance (as yielding a relatively small or zero value).

The form of eqs. (85)–(87) and of eq. (71) suggests that at least (a) or (b) could be true. If not, we may only hope that (c) is met. According to the above assumption we take that the function $R_j^3 \cdot F_q()$ is a polynomial $R_j^3 \cdot \Gamma^{mq}[O^q]$ of relative radii consisting of monomials having the form either (81) ($m = 1$) or (82) ($m = 2$).

Let us consider possible structures of the function $\Gamma^{mq}[O^q]$. First we notice that the two accurate coefficients $G_k^1[o]$ (eq. (61)) and $G_k^2[O^2]$ (eq. (65)) and that approxi-

mated one $G_k^3[O^3]$ (eq. (72)) do not satisfy the equalities (48)–(50) truncated up to the third order terms ($p = 1, 2, 3$). However, if we take G_k^3 modified as below:

$$G_k^3[o_1, o_2, o_3] = 3 \frac{R_k^3}{R_{o_1} R_{o_2} R_{o_3}} , \tag{93}$$

we arrive at the third order model for ΔS which is not affected by particle location order.

Let v_j^* denote the volume fraction of the jth component in the mixture

$$v_j^* \overset{\text{def}}{=} \frac{M_j x_j^*}{n} = \frac{M_j x_j^{*o}}{n} \frac{\eta_j^o}{\eta^M} , \tag{94}$$

which may replace the fraction v_j in eqs. (54)–(57)

$$v_j = \eta^M v_j^* . \tag{95}$$

Thus, following eqs. (1), (54), (57), (84) and (93) the approximating formula for ΔS (denoted as ΔS_a) may be written in the form of

$$\Delta S_a = k_B \sum_{j=1}^{J} M_j \left\{ -\ln v_j^* + \ln \left(\frac{1 - \eta^M}{1 - \eta_j^o} \frac{\eta_j^o}{\eta^M} \right) + 3 \frac{\eta_j^o}{1 - \eta_j^o} + \frac{3}{2} \left(\frac{\eta_j^o}{1 - \eta_j^o} \right)^2 \right.$$
$$\left. - 3 \sum_{o=1}^{J} v_o^* \frac{\eta^M}{1 - \eta^M} \frac{R_j^2}{R_o^2} - \frac{3}{2} \sum_{o=1}^{J} \sum_{i=1}^{J} v_o^* v_i^* \left(\frac{\eta^M}{1 - \eta^M} \right)^2 \frac{R_j^2}{R_o R_i} \right\} . \tag{96}$$

Let us complete the above model by taking in eq. (92) the function $F_q(\ ) = \Gamma^q[O^q]$ to express the factors $A_j^q[O^q]$ for $q = 3, 5, \ldots, \infty$, where the polynomial $R_j^3 \cdot \Gamma^q[O^q]$ consists of monomials being of form (81). As there is no basis to distinguish between the effects of particular arguments of $\Gamma^q[O^q]$, the following function is proposed:

$$\Gamma^q[O^q] = \frac{1}{(R_O)^q q^{q-3}} \left(\sum_{i=1}^{q} R_{o_i} \right)^{q-3} \tag{97}$$

with the factor q^{3-q} being used to get $\Gamma^q[j^q] = 1/R_j^3$. Similarly, the alternative function $\Gamma^{2q}[O^q]$ has the form

$$\Gamma^{2q}[O^q] = \frac{1}{(R_O)^{2q} q^{2q-3}} \left(\sum_{i=1}^{q} R_{o_i} \right)^{2q-3} . \tag{98}$$

Based on eq. (92) the following recursive formula is valid:

$$A^{q+1} = \frac{G^q - (q-1)A^q}{q+1} . \tag{99}$$

Hence, having $G^2 = 7.5$ and $A^2 = 3$ we can calculate the exact A^3:

$$A^3 = 1.5. \tag{100}$$

In order to perform further analysis let us take arbitrarily that

$$G^p = \mathcal{C}\frac{\varphi^p}{p} \quad \text{for } p > 2, \tag{101}$$

where φ is a converging factor ($\varphi < 1$) and $\mathcal{C}$ denotes a constant. The factor φ may be positive or negative. By substitution of eq. (101) the series (85) is brought to the form

$$\sum_{p=3}^{\infty}(-1)^p p G^p = \mathcal{C}\sum_{p=3}^{\infty}(-\varphi)^p = -\mathcal{C}\varphi^3\frac{1}{1+\varphi} = -9. \tag{102}$$

Thus

$$\mathcal{C} = 9\frac{1+\varphi}{\varphi^3}. \tag{103}$$

By using functions (101), (103) in eq. (92) we arrive at the formula

$$A^q = 9\frac{\varphi^{q-3}}{q(q-1)} \quad \text{for } q > 3. \tag{104}$$

The factors $A_j^q[j, O^{q-1}]$ occurring in the infinite series in eq. (54) have the following form:

$$A_j^q[j, O^{q-1}] = A^q R_j^{3-m} \Gamma^{mq}[j, O^{q-1}], \tag{105}$$

where $\Gamma^{mq}[\cdot]$ denotes either $\Gamma^q[\cdot]$ ($m = 1$) or $\Gamma^{2q}[\cdot]$ ($m = 2$), and

$$\Gamma^{mq}[j, O^{q-1}] = \frac{1}{(R_O)^{mq-m}q^{mq-3}}\left(\sum_{i=1}^{q-1} R_{o_i} + R_j\right)^{mq-3}. \tag{106}$$

Notice that $A_j^3[j, O^2]$ is always positive and for $m = 1$ it is the same as the last term factor in eq. (96).

By substitution of eq. (104) into (57) we arrive at the expression for the configurational entropy S^o of the standard state

$$S_1^o = k_B\sum_{j=1}^{J} M_j\left\{ \ln(x_j^{*o}) + \ln(1 - \eta_j^o) + 1 - 3\frac{\eta_j^o}{1 - \eta_j^o} \right.$$
$$\left. - \frac{9}{\varphi^2}\sum_{q=3}^{\infty}\frac{1}{q(q-1)}\left(\frac{\eta_j^o}{1 - \eta_j^o}\right)^{q-1}\varphi^{q-1} \right\}, \tag{107}$$

which converges (provided that $\varphi \cdot \eta_j^o/(1 - \eta_j^o) < 1$) to the form of

$$S_1^o = k_B \sum_{j=1}^{J} M_j \left\{ \ln x_j^{*o} + \ln(1 - \eta_j^o) + 1 - 3\frac{\eta_j^o}{1 - \eta_j^o} \right.$$

$$\left. - \frac{9}{\varphi^2} \left[1 - \frac{\eta_j^o}{2(1 - \eta_j^o)}\varphi + \left(\frac{1 - \eta_j^o}{\varphi \cdot \eta_j^o} - 1 \right) \ln\left(1 - \frac{\eta_j^o}{1 - \eta_j^o}\varphi \right) \right] \right\}. \quad (108)$$

Using eqs. (54, 105) and (108) we arrive at the formulae for the configurational entropy of mixing ΔS_{1m} (for either, $m = 1$ or $m = 2$)

$$\Delta S_{1m} = k_B \sum_{j=1}^{J} M_j \left\{ -\ln v_j^* + \ln\left(\frac{1 - \eta^M}{1 - \eta_j^o} \frac{\eta_j^o}{\eta^M} \right) + 3\frac{\eta_j^o}{1 - \eta_j^o} - 3\frac{\eta^M}{1 - \eta^M} \sum_{o=1}^{J} v_o^* \frac{R_j^2}{R_o^2} \right.$$

$$+ \frac{9}{\varphi^2} \left[1 - \frac{\eta_j^o}{2(1 - \eta_j^o)}\varphi + \left(\frac{1 - \eta_j^o}{\varphi \cdot \eta_j^o} - 1 \right) \ln\left(1 - \frac{\eta_j^o}{1 - \eta_j^o} \cdot \varphi \right) \right]$$

$$\left. - R_j^{3-m} \sum_{q=3}^{\infty} \frac{9\varphi^{q-3}}{q(q-1)} \left(\frac{\eta^M}{1 - \eta^M} \right)^{q-1} \sum_{o_1=1}^{J} \cdots \sum_{o_q=1}^{J} (v_{o_2}^* \ldots v_{o_q}^*) \Gamma^{mq}[j, O^{q-1}] \right\}. \quad (109)$$

The model (109) may be inconvenient in practical use because of the infinite series contained in. Let us propose an approximating formula for ΔS being of analytical form. One of the possible ways to reach such a model is to take the following $F_q[O^q]$ in eq. (90):

$$F_q[O^q] = \frac{1}{(R_O)^q} \left(\sum_{i=1}^{J} v_i^* R_i \right)^{q-3}, \quad (110)$$

where the average radius of all particles replaces the radius averaged over the set O^q, as present in $\Gamma^q[O^q]$ (see eq. (97)).

Let us define a variable ω

$$\omega \stackrel{\text{def}}{=} \left(\sum_{i=1}^{J} v_i^* R_i \right) \left(\sum_{o=1}^{J} \frac{\eta^M}{1 - \eta^M} \frac{v_o^*}{R_o} \right). \quad (111)$$

Using the function (110) and the variable ω we obtain

$$\left(\sum_{o=1}^{J} \frac{v_o}{1 - \eta^M} \right)^{q-1} \odot A_j^q[j, O^{q-1}] = R_j^2 \rho \frac{(\varphi\omega)^{q-1}}{q(q-1)}, \quad (112)$$

where the constant factor ρ is defined as

$$\rho \stackrel{\text{def}}{=} \frac{9}{\varphi^2} \left(\sum_{i=1}^{J} v_i^* R_i \right)^{-2}. \quad (113)$$

The resultant model (denoted as ΔS_{1a}) has the following form

$$\Delta S_{1a} = k_B \sum_{j=1}^{J} M_j \left\{ - \ln v_j^* + \ln\left(\frac{1 - \eta^M}{1 - \eta_j^o} \frac{\eta_j^o}{\eta^M} \right) + 3\frac{\eta_j^o}{1 - \eta_j^o} \right.$$

$$- 3 \sum_{o=1}^{J} v_o^* \frac{\eta^M}{1 - \eta^M} \frac{R_j^2}{R_o^2} - R_j^2 \rho \left(1 - \frac{\varphi\omega}{2} + \left(\frac{1}{\varphi \cdot \omega} - 1 \right) \ln(1 - \varphi \cdot \omega) \right)$$

$$\left. + \frac{9}{\varphi^2} \left[1 - \frac{\eta_j^o}{2(1 - \eta_j^o)} \varphi + \left(\frac{1 - \eta_j^o}{\varphi \cdot \eta_j^o} - 1 \right) \ln\left(1 - \frac{\eta_j^o}{1 - \eta_j^o} \varphi \right) \right] \right\}. \quad (114)$$

The models (109) and (114) are based on eq. (101) being taken quite arbitrarily. In order to get some insight into the effects on ΔS of modeling errors inherent in this assumption let us take an alternative formula for G^p. For example, let

$$G^p = \mathcal{C}\varphi^p, \quad (115)$$

which converges more slowly than (101). The corresponding model involving the function (106) has the following form:

$$\Delta S_{2m} = k_B \sum_{j=1}^{J} M_j \left\{ - \ln v_j^* + \ln\left(\frac{1 - \eta^M}{1 - \eta_j^o} \frac{\eta_j^o}{\eta^M} \right) + 3\frac{\eta_j^o}{1 - \eta_j^o} - 3\frac{\eta^M}{1 - \eta^M} \sum_{o=1}^{J} v_o^* \frac{R_j^2}{R_o^2} \right.$$

$$- \frac{9}{\varphi^2(3 + 2\varphi)} \left[\left(1 + \frac{\eta_j^o}{1 - \eta_j^o} \right) \varphi + \frac{\eta_j^o}{2(1 - \eta_j^o)} \varphi^2 \right.$$

$$\left. + \left(\frac{1 - \eta_j^o}{\eta_j^o} + 1 \right) \ln\left(1 - \frac{\eta_j^o}{1 - \eta_j^o} \varphi \right) \right] - \frac{9 \cdot R_j^{3-m}}{\varphi^3(3 + 2\varphi)} \sum_{q=3}^{\infty} \frac{q(1 + \varphi) - \varphi}{q(q - 1)} \varphi^q$$

$$\left. \times \left(\frac{\eta^M}{1 - \eta^M} \right)^{q-1} \sum_{o_1=1}^{J} \cdots \sum_{o_q=1}^{J} (v_{o_1}^* \ldots v_{o_q}^*) \Gamma^{mq}[O^{q-1}, j] \right\}, \quad (116)$$

and the model with the approximating formula (110) being taken is

$$\Delta S_{2a} = k_B \sum_{j=1}^{J} M_j \left\{ - \ln v_j^* + \ln\left(\frac{1 - \eta^M}{1 - \eta_j^o} \frac{\eta_j^o}{\eta^M} \right) + 3\frac{\eta_j^o}{1 - \eta_j^o} - 3 \sum_{o=1}^{J} v_o^* \frac{\eta_o^o}{1 - \eta^M} \frac{R_j^2}{R_o^2} \right.$$

$$- \frac{9}{\varphi^2(3 + 2\varphi)} \left[\frac{\varphi}{1 - \eta_j^o} + \frac{\eta_j^o}{2(1 - \eta_j^o)} \varphi^2 + \frac{1}{\eta_j^o} \ln\left(1 - \frac{\eta_j^o}{1 - \eta_j^o} \cdot \varphi \right) \right]$$

$$\left. + R_j^2 \frac{\rho}{3 + 2\varphi} \left((1 + \omega)\varphi + \frac{\varphi^2\omega}{2} + \left(\frac{1}{\omega} + 1 \right) \ln(1 - \varphi \cdot \omega) \right) \right\}. \quad (117)$$

All the models (96), (109), (114), (116), (117) contain the well-known formula for the configurational entropy of mixing (Flory [5]),

$$\Delta S_F = -k_B \sum_{j=1}^{J} M_j \ln v_j^* .$$ (118)

Thus, the remaining terms in the proposed formulae express the entropy excess over the value predicted by this simplest model.

4.3. EVALUATION OF THE MODEL PARAMETERS

Let us apply our model to a homogeneous liquid containing the number M of spherical molecules. A free space attributed to each molecule (i.e. the soft part of the molecule) consists of a volume being a consequence of limited packing ratio of spheres (hard parts of molecules), and of an additional volume which makes possible thermal vibrations of molecules. Let η_0 denote the maximal fraction of the hard part of particle. One can prove that

$$\eta_0 = \frac{\pi}{6}\sqrt{2} \cong 0.74 .$$ (119)

It seems to be the most appropriate to take the parameter φ as

$$\varphi = (1 - \eta_0)/\eta_0 \cong 0.35047 ,$$ (120)

thus involving the physical constraint for η^o ($\eta^o < \eta_0$) in the model equations (107)–(117).

In order to compare our model with other known formulae [2,3] let us derive the state equation [2,3] in the form of

$$Z^o \stackrel{\text{def}}{=} \frac{PV}{Mk_B T} = 1 + \eta^o \frac{\partial}{\partial \eta^o}\left(\frac{F^{ex}}{Mk_B T}\right)_T = 1 + \sum_{k=1}^{\infty} \mathcal{B}_k(\eta^o)^k ,$$ (121)

where Z^o denotes the compressibility; $\mathcal{B}_k$, coefficients of virial series; F^{ex}, the excess Helmholtz free energy over that of an ideal gas under the same pressure P; V, volume; T, temperature. For the considered system the following relation is valid:

$$\frac{F^{ex}}{Mk_B T} = -\frac{S^o}{Mk_B} + \ln(x^{*o}) + 1 .$$ (122)

Hence, by virtue of eq. (57) we arrive at the formula

$$\frac{F^{ex}}{Mk_B T} = A^1 \ln(1 - \eta^o) + \sum_{q=2}^{\infty} A^q \left(\frac{\eta^o}{1 - \eta^o}\right)^{q-1} .$$ (123)

According to eq. (121) the state equation has the form

$$Z^o = 1 - A^1 \frac{\eta^o}{1 - \eta^o} + \sum_{q=2}^{\infty} A^q (q-1)\frac{(\eta^o)^{q-1}}{(1 - \eta^o)^q} .$$ (124)

Using the sequence $\{A^q, q = 1, \ldots, \infty\}$ taken for the model (107), i.e.: $A^1 = -1$, $A^2 = 3$, and $A^q = 9\varphi^{q-3}/(q(q-1))$ for $q > 2$, we get the formula

$$Z_1^o = 1 + \frac{(\eta^o\varphi^2 - 9)}{\varphi^2(1 - \eta^o)} + \frac{\eta^o(6\varphi - 9)}{2\varphi(1 - \eta^o)^2} - \frac{9}{\eta^o\varphi^3}\ln\left(1 - \frac{\varphi\eta^o}{1 - \eta^o}\right). \tag{125}$$

Equation (124), if truncated to $q = 3$ (see eq. (96)) gives

$$Z_a^o = \frac{1 + \eta^o + (\eta^o)^2}{(1 - \eta^o)^3}, \tag{126}$$

i.e. the well-known formula derived in completely another way by solving the Percus–Yevick compressibility equation [2,4]. The best analytical formula is due to Carnahan and Starling [2],

$$Z_{CS}^o = \frac{1 + \eta^o + (\eta^o)^2 - (\eta^o)^3}{(1 - \eta^o)^3}. \tag{127}$$

The model (125) with $\varphi = 0.35047$ (see eq. (120)) respects the geometrical bound for η^o ($\eta^o < 0.74$), while the Carnahan–Starling formula (127) as well as eq. (126) miss a physical meaning for a very high packing ratio. However, it is known [2] that the model (126) overestimates Z^o, therefore it is evident from eq. (124) that any improvement of it by using the model (125) needs a negative value for φ. Unfortunately, such an improved model does no longer respect the bound for η^o.

Equation (124) may be transformed into the virial series (see eq. (121)) by substitution: $(1 - \eta^o)^{-q} = (\sum_{i=0}^{\infty}(\eta^o)^i)^q$. One can prove that the virial coefficients $\mathcal{B}_k$ are expressed as

$$\mathcal{B}_k = -A^1 + k\sum_{j=2}^{k+1}\binom{k-1}{j-2}A^j. \tag{128}$$

The well-known Carnahan–Starling expression [2] is

$$\mathcal{B}_k = k^2 + 3k. \tag{129}$$

In table 1 the first six resultant virial coefficients are compared to accurate ones [2]. The coefficients A^q and G^p are also shown. Their values corresponding to the exact virial coefficients and to those of the Carnahan–Starling formula have been computed using eqs. (128), (99). For the model (125) with $\varphi < 0$ the value for φ was found so as to fit $\mathcal{B}_3$ exactly ($\varphi = -43/150$).

Using eq. (128) and a sequence $\mathcal{B}_1, \mathcal{B}_2, \ldots, \mathcal{B}_K$ of known virial coefficients one can compute exact values for $A^1, A^2, \ldots, A^{K+1}$, and next apply the formula (101) for $q > K$ with $\varphi = 0.35047$, to complete the sequence up to infinity. In such a way a model may be arrived at which meets both an accuracy demand and a geometrical bound for η^o.

Like eq. (125) a similar formula for Z_2^o may be derived based on the model invol-

Table 1
Comparison of coefficients of considered models.

	Exact	Carnahan–Starling	Formula (126)	Eq. (125) $\varphi = 0.35047$	Eq. (125) $\varphi = -0.28222$
B_1	4.0	4.0	4.0	4.0	4.0
B_2	10.0	10.0	10.0	10.0	10.0
B_3	18.365	18.0	19.0	19.789	18.365
B_4	28.24	28.0	31.0	34.374	28.603
B_5	39.50	40.0	46.0	55.056	40.333
B_6	56.50	54.0	64.0	83.495	53.240
G^1	7.0	7.0	7.0	7.0	7.0
G^2	7.5	7.5	7.5	7.5	7.5
G^3	2.153	1.667	3.0	4.052	2.1533
G^4	−0.91	1.5	0.0	1.065	−0.4558
G^5	0.92	−5.2	0.0	0.299	0.1029
G^6	4.217	12.667	0.0	0.087	−0.0242
A^1	−1.0	−1.0	−1.0	−1.0	−1.0
A^2	3.0	3.0	3.0	3.0	3.0
A^3	1.5	1.5	1.5	1.5	1.5
A^4	−0.2117	−0.333	0.0	0.2630	−0.2117
A^5	−0.0550	0.5	0.0	0.0553	0.0358
A^6	0.1900	−1.2	0.0	0.0129	−0.0067
A^7	0.4667	2.667	0.0	0.0032	0.0014

ving the sequence (115) (see eq. (116)). However, in this case the value $\varphi = 0.35047$ (being the most suitable from the physical point of view) results in stronger increasing of consecutive A^q ($q > 3$). Thus, such a model seems to have no advantage in relation to eq. (125).

Let us evaluate a range of η^o corresponding to the liquid state. Equation (122) may be written in the following form:

$$-\frac{F^{ex}}{Mk_BT} = \ln \nu_1 , \tag{130}$$

where ν_1 denotes the ratio of an ideal gas molal volume to that of the liquid, both having the same entropy. It can be deduced from the Trouton's rule (Barrow [21]) that near the boiling point ν_1 ranges from 0.01 to 0.03. The values for ν_1 computed using eq. (130), with different formulae taken to express the left hand side, are collected, in table 2. As it is seen, the parameter η^o has a value ranging from 0.42 to 0.46 (differences between values predicted by the models under consideration are of little importance). On the other hand, the value $\eta^o \cong 0.5$ was found by simulation [2,3] as a solidification bound. Therefore, from the sorption viewpoint an accuracy of a model within the range $\eta^o \in (0.42, 0.5)$ is crucial.

The values of Z and $-F^{ex}/(Mk_BT)$ predicted by the models being analysed,

Table 2
Parameter ν_1 v.s. packing ratio η^o according to different models.

η^o	Model F_a^{ex}	F_{1+}^{ex} $\varphi = 0.3505$	F_{1-}^{ex} $\varphi = -0.282$	F_{2+}^{ex} $\varphi = 0.3505$	F_{2-}^{ex} $\varphi = -0.282$	F_{CS}^{ex}
0.41	0.036	0.032	0.038	0.031	0.039	0.038
0.42	0.030	0.027	0.032	0.025	0.033	0.033
0.43	0.025	0.022	0.027	0.021	0.028	0.028
0.44	0.021	0.018	0.023	0.017	0.024	0.023
0.45	0.017	0.015	0.019	0.013	0.020	0.019
0.46	0.014	0.012	0.016	0.011	0.016	0.016
0.47	0.011	0.009	0.013	0.008	0.013	0.013
0.48	0.009	0.007	0.010	0.006	0.011	0.011
0.49	0.007	0.005	0.008	0.005	0.009	0.009

Subscripts: a – approximated 4-term model as used in eqs. (96), (125); 1 – the model involving the sequence A^q as taken in eqs. (107), (126); 2 – the model involving the sequence A^q as in eq. (116). CS – Carnahan–Starling formula.

are plotted against η^o in fig. 8. The curves F_{1-}^{ex} and F_{CS}^{ex} are practically undistinguishable.

4.4. DISCUSSION AND NUMERICAL RESULTS

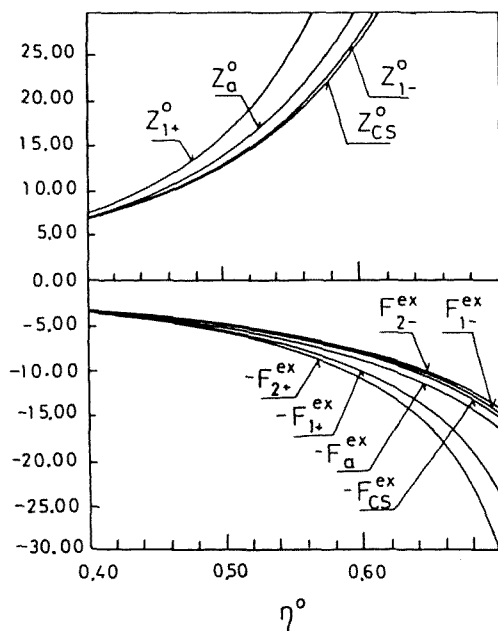The achieved results may be summarised as follows:

Fig. 8. The values of Z and $-F^{ex}/(Mk_BT)$ for a homogeneous liquid. Subscripts explained in the footnote to table 2.

(a) Based on general formulae derived in sections 2 and 3, applied for infinitesimal cells (continuous space), we arrived at the universal formula (54) for the configurational entropy of mixture S^M.

(b) The formula (54) involves an infinite number of coefficients $A_j^q[\,]$ ($q = 2, \ldots, \infty$) which are expressed in the form of universal infinite series (48)–(50), and which meet the universal relations (51), (52), as the value for S^M has to be independent of indices attributed arbitrarily to particles and components (particle location order).

(c) In order to compute the coefficients $A_j^q[\,]$ suitable formulae for geometrical factors $G_j^p[\,]$ ($p = 1, \ldots, \infty$) should be found.

(d) The factors $G_j^p[\,]$ depend only on geometrical parameters of particles present in the mixture (see eqs. (35), (38)–(41) and (66), (73)–(77)), thus further analysis needs the geometrical properties of the mixed particles to be specified.

(e) The considerations made in section 4.2 relate to sphere-like particles, i.e. to particles having a spherical hard core.

(f) Till the present day we derived accurate formulae for $G_j^1[o]$ (eq. (61)) and $G_j^2[O^2]$ (eq. (65)) for spherical particles. An approximation to $G_j^3[O^3]$ is also found (eq. (72)). Higher order coefficients may be computed using the general formula (66): however, it is a much more complicated geometrical task.

(g) The universal formulae (48)–(50), if applied to spherical particles with $G_j^1[o]$ and $G_j^2[O^2]$ being known, yield the form of (67)–(69), which enable us to deduce a general structure of a function $\mathbb{F}_q[R_O]$ (eq. (70)) expressing effects of particles radii R_O on the coefficients $A_j^q[\,]$. A general formula for $G_j^p[\,]$ may be written in the form of (78) consisting of polynomial and nonpolynomial functions of relative radii.

(h) Further considerations are based on certain suppositions concerning the function $\mathbb{F}_q[R_O]$.

(i) An astounding similarity of eqs. (85)–(87) and the universal equality (91) suggest that the formulae (84) for $A_j^1[o]$ and $A_j^2[O^2]$ may be taken, and a general formula for A_j^q ($q > 2$) is of form (92). This suggests also that $A_j^q[O^q]$ may be expressed in the form of a qth order polynomial function of relative radii.

(j) The formulae (84) and (92) were taken as the basis for our model. Further considerations were focused on two questions, i.e.: how to get an adequate representation of the sequence of constant factors $\{G^p, p = 3, \ldots, \infty\}$, and what monomials $\mathcal{M}[O^p]$ should be taken to express the effects of size of particles on $A_j^q[O^q]$ for $q > 2$.

(k) First we proposed an approximating formula (96), i.e. the third order model (denoted as ΔS_a), involving only the known factors $G_j^1[o]$, $G_j^2[O^2]$ and relatively well established $G_j^3[O^3]$.

(l) Next, two alternative formulae, i.e. $\Gamma^{1p}[O^p]$ – eq. (97) – and $\Gamma^{2p}[O^p]$ – eq. (98), were taken as the function $F_q(\,)$, and two sequences (101), (115) as alternative representations of the factors G^p. Using the sequence (101) we arrived at the formula (109) which expresses two models, i.e. ΔS_{11} – involving $\Gamma^{1p}[O^p]$ (97), and

ΔS_{12} – with $\Gamma^{2p}[O^p]$ (98). Application of the sequence (115) results in the formula (116) which represents the models ΔS_{21} and ΔS_{22} with functions (97) and (98) being taken into account, respectively.

(m) The formulae (109) and (116) contain infinite series, and so they are not convenient in use. Thus, we proposed an approximating function (110) to express $F_q(\ )$ in eq. (89). It has no theoretical grounds, but it enables us to reach the analytical formulae (114) (model ΔS_{1a}) and (117) (model ΔS_{2a}) based on the sequence (101) and (115), respectively.

(n) Using well-known thermodynamic relations the state equation for a simple liquid was derived in section 4.3. It was shown that the approximating formula (96), i.e. the model ΔS_a, if applied to a simple liquid, leads to the well-known expression (126). The model (125) was found as being in very good agreement with the Carnahan–Starling formula [3] providing that suitable negative value for the parameter φ (i.e. φ −0.282222) is taken (subscript −). But the model with $\varphi = 0.35047$ (subscript +) is also interesting as it respects the physical bound for packing ratio ($\eta^o < 0.74$).

The model being elaborated is aimed at the analysis of the effects of volume fractions of components and of the size of their particles on the configurational entropy of mixing. Thus, we should answer the question, do the arbitrary assumptions mentioned in points (k), (l) and (m) affect significantly a function $\Delta S(v_j^*, R_J)$.

To this aim, having the formula proposed by Mansoori [4] (ΔS_{CS}) as the reference model, we examined numerically all the proposed formulae applied to a two component mixture with positive (+) and negative (−) values for φ being taken, i.e.: ΔS_a – eq. (98); $\Delta S_{11\mp}$, $\Delta S_{12\mp}$ – eq. (109); $\Delta S_{21\mp}$, $\Delta S_{22\mp}$ – eq. (116); $\Delta S_{1a\mp}$ – eq. (114); $\Delta S_{2a\mp}$ – eq. (117). No volume changes in the mixing process as well as the same packing fraction $\eta_j^o = \eta^M$ for each component j have been assumed. The parameter φ has been taken to be the same as for homogeneous liquid, i.e. $\varphi = 0.35047\,(+)$ or $\varphi = -0.282222\,(-)$.

In fig. 9, the entropy predicted by all the above models is plotted against v_2. It is expressed as the excess over the value ΔS_F given by the formula (118) and related to ΔS_F (relative entropy excess). One observes large discrepancies between $\Delta S_{12\mp}$, $\Delta S_{22\mp}$ and the remaining curves. This means that the function Γ^{2q} (eq. (98)) is not an adequate representation of the particle size effect (which meets our earlier suggestion – see point (i)) and so, these four models should be rejected. Hence, they are not longer analysed in further figures. The second observation is that the parameter $\varphi = 0.35047\,(+)$ yields much larger deviations from the reference curve ΔS_{CS} than $\varphi = -0.28222\,(-)$. This is explainable if one bears in mind the parameters shown in table 1. Relatively small differences between the curves ΔS_{11-} and ΔS_{21-} suggest that a choice of the sequence representing the coefficients G^p is of little importance. This is also shown in fig. 8 and table 2 for homogeneous liquids. It may be seen that the curves ΔS_{11-} and ΔS_{CS} are practically undistinguishable. The same conclusions may be drawn on the basis of figs. 10–13. In particular, in fig.
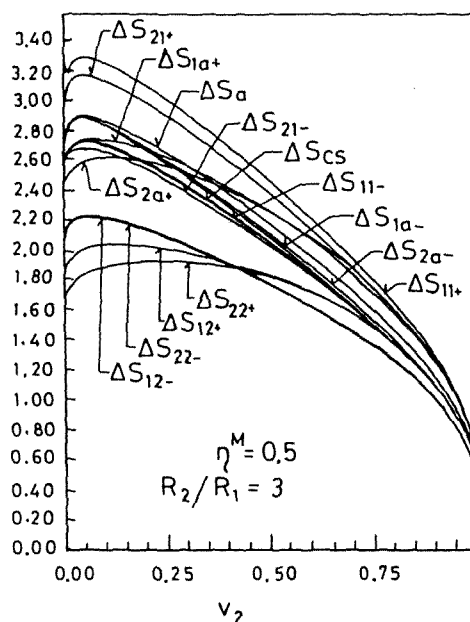
Fig. 9. Relative entropy excess vs. volume fraction of larger particles, with large packing ratio η^M and large R_2/R_1. First subscript indicates the formula taken for A^q: a – truncated 4-term formula (98); 1 – sequence (101), model (109); 2 – sequence (115), model (116); CS – Carnahan–Starling. Second subscript shows the function Γ^{mp} applied to express the particle size effect: a – approximating formula (111), (models (114), (117)); 1 – pth order monomials ($m = 1$, eq. (97)); 2 – $2p$th order monomials ($m = 2$, eq. (98)). Third subscript: $+$ $\varphi = 0.35047$; $-$ $\varphi = -0.282222$.

12 we compare the models under consideration using the data applied in ref. [4], i.e.: $R_2/R_1 = 3$, $v_2 = 0.9643$ ($M_1 = M_2$). Discrepancies between the formula (109) (ΔS_{11-}) and the generalized Carnahan–Starling model ΔS_{CS} [4] are in the same range of magnitude as deviations from molecular dynamics simulation data [4].

The above observations allows us to the conclusion that a qth order polynomial $\Gamma^{1p}[O^p]$ (eq. (97)) is adequate enough to represent effects of the relative size of particles on the entropy of mixing, and the formula (109) is practically equivalent to that proposed in ref. [4].

As far as the models ΔS_{1a-} and ΔS_{2a-} are considered for rather small R_2/R_1 ($R_2 \in \langle R_1, 3R_1 \rangle$) they yield similar results. This allows us to propose the analytical formulae (114) or (117) as a convenient and adequate enough improvement of the third order formula (98) (model ΔS_a).

5. Final remarks

A formal discretisation of mixture space (generalised lattice model) makes possible a statistical analysis of configurations of mixed particles, with no restrictions
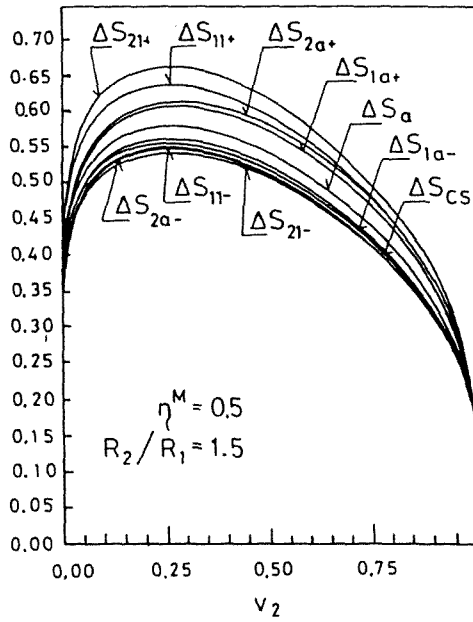
Fig. 10. Relative entropy excess vs. volume fraction of larger particles, with large packing ratio η^M and moderate R_2/R_1. Subscripts explained in the caption of fig. 9.
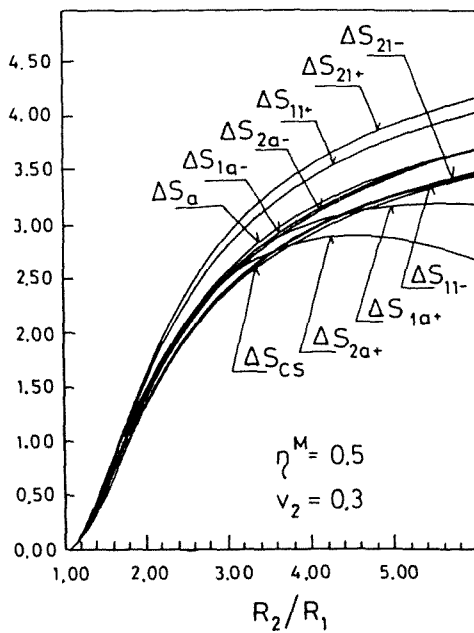

Fig. 11. Relative entropy excess vs. relative radius R_2/R_1. Volume fraction v_2 corresponds to maximal discrepancies in fig. 10. Subscripts explained in the caption of fig. 9.
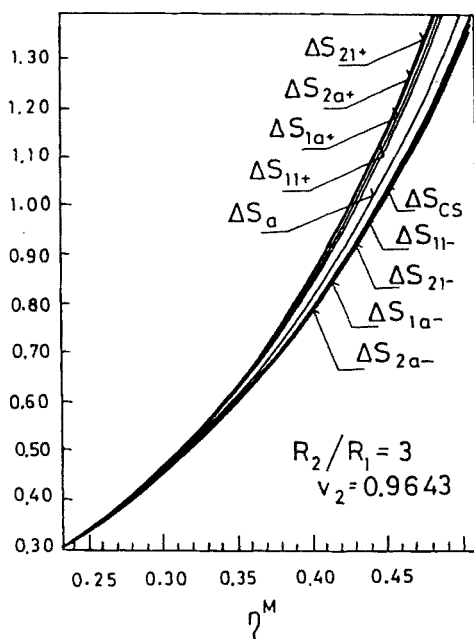
Fig. 12. Entropy excess vs. packing ratio η^M. Large relative radius R_2/R_1 and large v_2 (according to Mansoori [4]). Subscripts explained in the caption of fig. 9.
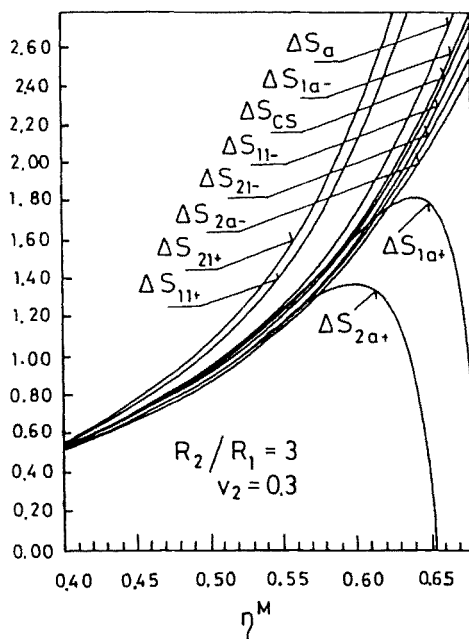

Fig. 13. Entropy excess vs. packing ratio η^M for large relative radius R_2/R_1 and v_2 corresponding to maximal discrepancies in fig. 10. Subscripts explained in the caption of fig. 9.

due to their shape. The general formulae for the number of configurations derived in sections 2 and 3 may be applied in two ways. By taking a cell size comparable to the smallest particle in the mixture one can reach a formula being a generalisation of Flory's model [12]. It provides a basis for a rough evaluation of particle shape effects on the mixing process. The second way (exploited in this paper) is based on the differential lattice idea. It enables us to derive the universal rigorous formula (54) for the configurational entropy of mixture S^M involving the infinite number of geometrical factors $G_j^p[\,]$, each of them depending only on the shape and size of particles.

The method proposed in section 4 may be used to derive the required formulae for $G_j^p[\,]$ with any shape of particles being assumed. As the above task is very complicated all the factors cannot be found. Thus, a final form of the model may only be supposed. However, accurate formulae for the first two factors $G_j^1[\,]$ and $G_j^2[\,]$ may be relatively easily derived and, based on certain formal properties of the model (54), one can evaluate the effects of higher order factors on the value for ΔS.

The results obtained for the mixture of spherical particles (section 4.4) indicate that some arbitrary assumptions concerning possible formulae for $G_j^p[\,]$ $(p > 2)$ enable us to reach acceptable models for the configurational entropy. Each of them fit exactly the first two coefficients of the virial state equation. The simplest one, i.e. the four-term model is equivalent to that derived earlier [2,3] by solving the Percus–Yevick compressibility equation. The relations derived in the paper provide a method for the systematic improvement of the model accuracy by including higher order terms. In this way, a general model was found which is in very good agreement with the formula proposed by Mansoori [4].

Table 1 and fig. 8 show that the predicted entropy is not significantly affected by the estimation errors of higher order coefficients G^3, G^4, …. It allows us to expect that the method presented in section 2.3 is also applicable to more complex molecules.

Acknowledgement

List of principal symbols

$A_j^q[O^q]$ coefficients in formulae (47), (54) defined in eqs. (48)–(50);
A^q coefficient $A_j^q[j^q]$ for identical particles;
a_o specific surface area of the oth particle;
$B_{\kappa i}^D$ factor representing the effect of particles belonging to $D \backslash \kappa$ (1st and further neighbors of κ) on probability $\alpha_{\kappa e_i}^D$ (eq. (28));

$C_k^D, C_\kappa^D, C_{\kappa e}^D, C_i^{D\kappa\backslash i}$ the expected number of configurations of a single object k, κ, κe, i, respectively, having a fixed (taken at random) configuration of objects belonging to the set D, $D\kappa\backslash r$;

$C_{i\kappa}^{D\kappa\backslash i}$ the expected number of configurations of object i (having a fixed configuration of $D\kappa\backslash i$) in which i is adjacent to κ;

D set of objects arranged in lattice prior to that being placed;

$D\kappa\backslash i$ same as D, while object i is removed and κ added to lattice;

e_k, e_i index of an element of the kth, ith object, respectively;

e_κ index of an element of previously formed part κ of object k;

$F_q(\ )$ a general function representing effects of the shape and size of particles on coefficients $A_j^q[O^q]$ (defined in eq. (89));

F^{ex} Helmholtz free energy excess (see eq. (121));

$G_j^p[O^p]$ geometrical factors depending only on the shape and size of particles present in the mixture (defined in eq. (38));

G^p constant factor $G_j^p[j^p]$ (for identical particles);

g_{e_k} probability that a cell chosen for an element e_k is eligible with respect to the shape of the kth object, provided that previously arranged elements of k satisfy the same condition;

g_{e_κ} same as g_{e_k} for the previously formed part κ of the kth object;

k_{B} Boltzmann constant;

M the number of particles in the mixture;

M_j the number of the jth component particles;

n the total number of lattice cells (volume of the mixture);

n_f^D the number of vacant cells left by objects belonging to D;

O^q a sequence consisting of q indices, each of them representing geometrical parameters of a particle as the argument of functions $A_j^q[O^q]$ or $G_j^q[O^q]$;

$(O^q|j^l)_c$ cth combination of l identical indices j within the sequence O^q ($j \in O^q$);

$P_{e_\kappa}^D$ probability that a cell chosen for the e_κth element of κe is vacant, providing that the objects of D and κ are arranged in an admissible way (def. (eq. (11));

p, q superscripts used to indicate an order of products and of factors;

$\mathbb{P}_{i|f}^{D\kappa\backslash i}, \mathbb{P}_{i|\xi}^{D\kappa\backslash i}$ probability of non-conflict arrangement of the ith object with fixed configuration of $D\kappa\backslash i$ objects) provided that its first element is placed in any vacant cell, in ξ cell, respectively;

$\mathbb{P}_{i|\xi\kappa}^{D\kappa\backslash i}$ same as $\mathbb{P}_{i|\xi}^{D\kappa\backslash i}$ but with the lack of conflict with κ assumed;

R_k radius of a sphere representing the hard part of the kth object;

$(R_O)^q$ qth order product of $R_{o_1}, \ldots, R_{o_q}$;

r_k current value for a radius of the kth particle being located;

δR thickness of a soft spherical layer in a particle;

Δr radius of a spherical region occupied by the vibrating center of a molecule in liquid state;

S^M, S^o configurational entropy of a mixture and of its components in their standard states, respectively;

ΔS configurational entropy of mixing (eq. (1));

ΔS_F approximation to ΔS disregarding differences in the size of particles (def. eq. (118));

$\delta_k S^D$ component of the expression for configurational entropy contributed by inserting of the kth particle into the lattice (eq. (43));

s_k the number of elements in a surface layer of the kth object;

s_k the set of surface elements of the kth object;

v_j^*, v_j volume fraction of the jth component and of the hard part of its particles, respectively, in the mixture;

x_k the number of hard part elements (volume) of the kth object;

x_k the set of elements of the hard part of the kth object;

x_k^* the number of elements (volume) of the kth object;

Z^o compressibility (eq. (121));

$\alpha_{\kappa e_i}^D$ probability that an element e_i of the ith object, occupying the cell ξ (chosen for the e_κth element of κe), is not in conflict with κ and with objects belonging to the set $D \setminus i$ (def. (eq. (11));

$\alpha_{\kappa e_i}^0$ probability that an element e_i of the ith object occupying the cell ξ is not in conflict with κ (def. eqs. (11), (16));

$\Gamma^{mq}[O^q]$ mqth order function used to compute the value for $A_j^q[\,]$;

κ a simply connected and properly shaped body, being a formed part of the kth particle, while its e_κth element is being placed;

$\kappa e, \kappa \xi$ κ and the next eth element of k, κ and ξ cell;

ι, o, λ same as κ for the ith, oth, lth object, respectively;

η_j^o, η^M packing fraction of the jth component particles in a standard state and in the mixture, respectively;

ξ an eligible cell chosen for joining the e_κth element to κ;

$\Theta_{\kappa e}$ the number of cells eligible for joining the e_κth element to κ;

φ constant factor taken in eqs. (101) and (115) to express the sequence $\{G^p, p = 3, \ldots, \infty\}$;

Ω the number of configurations of objects in the mixture;

Ω_D the number of configurations of D-set objects in the lattice.

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