PHYSICAL REVIEW E **79**, 031204 (2009)

Soret effect in molecular mixtures

Konstantin I. Morozov[*,†]
Institute of Continuous Media Mechanics, Ural Branch of RAS, Perm 614013, Russia

(Received 16 January 2009; published 30 March 2009)

A theoretical approach to the description of the Soret effect in binary nonpolar liquids is proposed. The temperature gradient of the partial pressure is determined as the driving force of thermal diffusion. The hard-sphere fluid is chosen as a reference system and an explicit relation for the Soret coefficient is found. Two additive contributions owing to steric repulsions and attractive interactions form the so-called chemical contribution to S_T [C. Debuschewitz and W. Köhler, Phys. Rev. Lett. **87**, 055901 (2001)]. The parameters of interparticle interactions are defined with the help of the solvation theory. In particular, the van der Waals constant of cross interactions is expressed via the excess volume of mixture. The proposed theory is applied to the benzene-cyclohexane system. A reasonable agreement of theoretical and experimental results is revealed for the Soret coefficient and its temperature dependence.

DOI: 10.1103/PhysRevE.79.031204 PACS number(s): 66.10.cd, 82.60.Lf

I. INTRODUCTION

The phenomenon of separation of substances in a binary mixture under the influence of an inhomogeneous temperature field has been known for more than a hundred years and is called thermal diffusion or the Soret effect [1,2]. A temperature gradient induces a diffusive mass flow of component 1,

$$\mathbf{j}_T = -\rho D_T w(1-w)\nabla T, \tag{1}$$

where ρ denotes the mass density, D_T the thermal diffusion coefficient, and w the concentration of component 1 in weight fractions [3]. In the stationary state, the flow is balanced by the diffusion mass flow $\mathbf{j}_D = -\rho D\nabla w$ owing to the concentration gradient. Here D is the collective diffusion coefficient. The efficiency of separation of substances in the stationary state can be judged by the ratio $S_T = D_T/D$, which is known as the Soret coefficient.

The thermal diffusion is observed in an enormous number of molecular systems such as gas and simple liquid mixtures, electrolytes, etc. In the last 15 years the thermal diffusion in complex fluids such as polymer solutions [4–6], colloidal dispersions [7–9], and magnetic fluids [10,11] has become the focus of experimental investigations. The result of these works is an accurate determination of the Soret coefficient S_T.

The brightest manifestation of the Soret effect is related to convective mixing. A crucial influence of thermal diffusion on convection has been established in many systems, differing by their compounds and scales, such as the water-methanol mixtures [12,13], the colloidal suspensions of silica in water [14–16], the DNA solutions [17,18], the ocean's salt fingers [19], and the Earth's mantle [20]. It is worth noting that the thermal diffusion coefficient S_T used in these studies was a phenomenological parameter or measured variable. This is due to the absence of an adequate physical picture of thermal diffusion in liquids. The difficulties of theoretical description of the Soret effect are universally recognized and connected directly with the statistical mechanics problems of accounting for the interparticle interactions in the binary nonequilibrium system [5,21]. Recent investigations of the thermophoresis in micellar and protein solutions [7,8] and in ionic and surfacted colloids [22–25] revealed a strong sensitivity of the phenomenon to the electrostatic and solvation effects. Variety of interparticle interactions in complex fluids impedes the theoretical consideration so that it is very difficult and even impossible to extract the leading mechanism of the thermal diffusion and its main trend.

The aim of this work is to establish the source of the Soret effect. As the physical system, we study the *nonpolar molecular mixtures* where the interparticle effects are not so manifold as in other liquids such as electrolytes or that which molecules possess the permanent dipolar moments.

From the very beginning we underline the principal distinction between the molecular mixtures and the *colloidal or polymer solutions*. In the latter systems, there is a giant difference in size of solute particles (colloids or polymer coils) and the solvent molecules. This allows to use the hydrodynamic approach considering the liquid solvent as a continuous medium [7,8,21–25]. In contrast to the polymer solutions and colloids, molecules of components of *molecular mixtures* are comparable in size. The usage of the hydrodynamic approach to these systems becomes impossible.

The paper is organized as follows. In Sec. II the driving force of usual diffusion is considered and the difficulties of generalization of the result to the case of thermal diffusion are clarified. The main statements of the Bearman-Kirkwood approach are discussed in Sec. III. It is argued that the thermodiffusional driving force is a sum of equilibrium and nonequilibrium terms and the former is proportional to the gradient of the partial pressure. The required modification of the original Bearman-Kirkwood relation for the driving force is done. In Sec. IV three alternative general relations for the Soret coefficient are given. The ways of determination of partial pressure and compressibility factor of liquid mixture are considered within the framework of perturbation theory in Sec. V. The solvation theory is used in Sec. VI to relate the van der Waals (vdW) constant of cross interactions with the

---

[*] Present address: Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

[†] mrk@icmm.ru

volume change on mixing the components. The chemical contribution to the Soret effect is discussed in Sec. VII. It is established that the Soret coefficient proves to be a result of balance of repulsive and attractive forces in the liquid mixture. In Sec. VIII the proposed theory is applied to the benzene-cyclohexane system. A reasonable agreement of theoretical and experimental results is revealed for the Soret coefficient and its temperature dependence. The results of the paper are summarized and discussed in Sec. IX.

II. DRIVING FORCE OF DIFFUSION

When we consider a particle movement we seek the cause generating this movement. Mechanically, we try to find some *force* responsible for the movement. The identification of such a force in the Soret problem is a formidable task [21,24]. To clarify this point let us remind the reader the more simple and related problem of usual diffusion solved by Einstein in his classical paper [26]. So, let us consider the Brownian grains suspended in the liquid. Let us assume that at some point in time the one-particle field $U(z)$ (for example, gravity) switches on and it acts on the particles and leads to their sedimentation. When the transient processes are completed the system achieves its *equilibrium* state with uniform distribution of *temperature and chemical potential* and simultaneously with nonuniform distribution of grain concentration $n(z)$ along the axis z. The diffusion flux owing to the gradient of concentration is balanced by the opposite flux initiating by the one-particle regular force $\mathbf{F}_{\text{reg}}=-\nabla U$. Following Einstein and Batchelor [27], we imagine that each particle undergoes the influence of two compensating forces—the regular force $\mathbf{F}_{\text{reg}}$ and the driving (thermodynamic) force of diffusion, $\mathbf{F}_D=-\mathbf{F}_{\text{reg}}$. The explicit form of $\mathbf{F}_D$ is obvious from the condition of chemical equilibrium of grains in the external potential U:

$$\mu_{\text{field}} = \mu + U = \text{const}, \tag{2}$$

where μ_{field} and μ are the chemical potential of grains in one-particle field and in the field absence, respectively. Then the closed form for the driving force $\mathbf{F}_D$ of diffusion is

$$\mathbf{F}_D = -\nabla\mu. \tag{3}$$

The relation concludes the problem of determining the driving force of diffusion [26,27]. It asserts that the driving force of diffusion is fully determined by *the equilibrium properties* of the system. Of course, this remarkable result does not mean that the diffusion itself is an equilibrium phenomenon. Indeed, according to the general theory of the irreversible processes [3], the diffusion velocity $\mathbf{v}_D$ of particles

$$\mathbf{v}_D = b\mathbf{F}_D \tag{4}$$

is proportional to the driving force $\mathbf{F}_D$ and the particle mobility b, which is *kinetic in nature property*. Therefore, the significance of result (3) is due to fact that it establishes (i) the explicit form of the driving force of diffusion and (ii) its relation to the equilibrium thermodynamics.

The situation with *thermal diffusion* is much more complicated. The point is that instead of the conditions of thermal ($T=\text{const}$) and chemical equilibrium (2) now we have only the significantly weaker condition of mechanical equilibrium $p=\text{const}$, where p is the pressure in the system. Thus, the mentioned elegant treatment fails and we cannot determine the driving force of thermal diffusion $\mathbf{F}_T$ in such a compact and explicit form as thermodynamic force of diffusion $\mathbf{F}_D$ in Eq. (3). However the problem of determination of the driving force of thermal diffusion has a solution at least in its general form. The most surprising thing is that this formal solution has been found as early as 50 years ago by Bearman and Kirkwood in Ref. [28]. Their work was significantly ahead of its time and now it is absolutely forgotten. We consider the main conclusions of the Bearman-Kirkwood theory in Sec. III.

III. BEARMAN-KIRKWOOD APPROACH TO THE PROBLEM

Let us first introduce the specific notation used below. We consider a two-component liquid mixture. Let m_α and n_α be the molecule mass and number density of component α, respectively. The potential $U_{\alpha\beta}(r)$ of interaction of molecules of sort α and β is assumed to be central.

The important point of the Bearman-Kirkwood approach is the concept of the *partial pressure* p_α of component α. In equilibrium the partial pressure is determined by the relation [28]

$$p_\alpha = n_\alpha k_B T - \frac{2\pi n_\alpha}{3}\sum_{\beta=1}^{2} n_\beta \int r^3 U'_{\alpha\beta}(r) g_{\alpha\beta}(r)\,dr, \tag{5}$$

where k_B is Boltzmann constant, the prime denotes the derivative over r, and $g_{\alpha\beta}(r)$ is the equilibrium pair correlation function. The quantity (5) might be considered as the pressure exerted on the wall by the particles of one sort if the particles of second sort are suddenly stopped. Obviously, the sum of both partial pressures is just the equilibrium pressure in the system

$$p = p_1 + p_2. \tag{6}$$

Now we are ready to formulate the basic result of the statistical mechanical theory [28]. According to Bearman and Kirkwood the general form of the thermodiffusional driving force $\mathbf{F}_T^{(\alpha)}$ acting on the particles of sort α is the sum of equilibrium $\mathbf{F}_{\text{eq}}^{(\alpha)}$ and nonequilibrium $\mathbf{F}_{\text{noneq}}^{(\alpha)}$ terms:

$$\mathbf{F}_T^{(\alpha)} = \mathbf{F}_{\text{eq}}^{(\alpha)} + \mathbf{F}_{\text{noneq}}^{(\alpha)}. \tag{7}$$

The word "equilibrium" means that the term $\mathbf{F}_{\text{eq}}^{(\alpha)}$ is determined only by the *equilibrium properties* of the system. The term can be written in closed form as [28]

$$\mathbf{F}_{\text{eq}}^{(\alpha)} = -\frac{1}{n_\alpha}\left(\frac{\partial p_\alpha}{\partial T}\right)_{p,w}\nabla T. \tag{8}$$

Thus the equilibrium part of the driving force is proportional to the gradient of the partial pressure taken at fixed values of the *pressure* (the condition of mechanical equilibrium) and *weight fraction* of components (the condition of absence of usual diffusion in the system). We note that in the original work of Bearman and Kirkwood the relation for $\mathbf{F}_{\mathrm{eq}}^{(\alpha)}$ is given erroneously (see Eq. (5.6) in Ref. [28]), namely, the derivative over temperature is taken at constant values of p and the number density n_β of second component of mixture. There are a number of ways to prove the fallacy of the result. The explicit way is critical reproduction of the awkward calculations of Bearman and Kirkwood. However simpler general arguments exist. Indeed, describing the diffusive mass transport in a binary liquid mixture the relevant conjugate thermodynamic variables are the pressure, temperature, and mass fraction of one of components [3]. In contrast to our expression (8) the Bearman-Kirkwood formula does not satisfy this property. The additional argument of correctness of Eq. (8) will be given in Sec. IV.

Let us return to the analysis of the equilibrium part of the driving force $\mathbf{F}_{\mathrm{eq}}^{(\alpha)}$. If we take into account the condition of mechanical equilibrium $p=p_1+p_2=\mathrm{const}$, we find the relation between the thermodiffusional driving forces acting on the particles of both sorts

$$n_1\mathbf{F}_{\mathrm{eq}}^{(1)}+n_2\mathbf{F}_{\mathrm{eq}}^{(2)}=\mathbf{0}. \tag{9}$$

The physical meaning of this expression is simple. It means that the full force acting on the ensemble of particles is zero. In other words, the center of mass of the system is at rest and the components of the mixture take part into their relative motion.

Thus, the general form of the equilibrium part of the driving force of thermal diffusion is known: it is a universal, closed, and explicit one. At the same time, there is no definite prescription for the nonequilibrium part $\mathbf{F}_{\mathrm{noneq}}^{(\alpha)}$. The term depends on a number of details of the system, for example, what kind of mixture do we consider—gas or liquid, what are the characteristic time scales and so on. In short, the term should be provided by the consecutive kinetic theory. This is a sophisticated problem on its own. Because of the nonuniversal character of the nonequilibrium part $\mathbf{F}_{\mathrm{noneq}}^{(\alpha)}$, its investigation seems to be premature before studying the contribution of the equilibrium term $\mathbf{F}_{\mathrm{eq}}^{(\alpha)}$. This is why we omit the nonequilibrium term on the whole and consider only the equilibrium contribution to the driving force. [We expect the dominant role of the last quantity also because of analogy of the problem with the considered case of usual diffusion (see Sec. II)]. As we will see below, this simplified approach leads to a surprisingly well description of the Soret effect. It enables an understanding of the basic mechanisms of the phenomenon and describing qualitatively and sometimes quantitatively the abundance of data on the Soret coefficient S_T. In general, the significance of the nonequilibrium omitted term could be judged by *a posteriori* comparison of the results with the experiment. As we will see, the nonequilibrium term proves to be of secondary importance for the case of benzene-cyclohexane mixtures considered in Sec. VIII.

Finalizing the formulation of our approach to the problem, we make an assumption supplementary to that mentioned above. We limit ourselves to the treatment of the *diluted* mixture only. The component 1 is supposed to be a low-concentrated one and subsequently called *the solute*. The high-concentrated component 2 forms *the solvent* of binary mixture. The special case of diluted mixtures allows us to use below all the power of modern solvation theory in our study of the problem. Since the component 1 is chosen, one can define the main aim of the paper. It is a determination of the Soret coefficient of nonpolar solute dissolved in the sea of nonpolar solvent.

IV. SORET COEFFICIENT: GENERAL RELATIONS

Let us derive the general relation for the Soret coefficient. As long as the concentration of solute is negligible, the solvent could be considered immovable. The solute particles experience the action of thermodiffusional driving force $\mathbf{F}_1$ and move via solvent with the velocity $\mathbf{v}_1=b\mathbf{F}_1$, where the particle mobility b is connected with the diffusion coefficient by the Einstein relation $D=bk_BT$ valid for the diluted solutions [27]. Taking into account the definition of the density ρ of mixture and the weight fraction w of solute

$$\rho=n_1m_1+n_2m_2, \quad w=n_1m_1/\rho, \tag{10}$$

we find the thermodiffusional mass flow

$$\mathbf{j}_T=n_1m_1\mathbf{v}_1=\rho wD\mathbf{F}_1/k_BT. \tag{11}$$

The comparison with Eqs. (1) and (8) leads to the general result for the Soret coefficient:

$$S_T=\frac{1}{n_1k_BT}\left(\frac{\partial p_1}{\partial T}\right)_{p,w\to 0}. \tag{12}$$

We use first the relation for a particular mixture of two *ideal gases*. The partial pressure of component 1 is $p_1=n_1k_BT=xp$, where $x=n_1/(n_1+n_2)$ is the mole fraction of solute. Since the conditions $w=\mathrm{const}$ and $x=\mathrm{const}$ are equivalent, it gives a zero value for the Soret coefficient, $S_T=0$. Physically, the result is clear. Indeed, in the ideal mixture, the gas molecules do not "see" each other and thus cannot be separated. This is a direct consequence of our formula (8). We note that usage of the erroneous expression by Bearman and Kirkwood would result in a nonzero value of S_T. This is just the additional argument of correctness of Eq. (8) we mentioned in Sec. III.

In the case of liquid mixtures, the elegant general result is a practically useless one. The point is that the partial pressure entering in Eq. (12) is not an experimentally determined quantity. Therefore we have to define it theoretically. This will be the subject of following investigation.

Summarizing the section we indicate two other ways to perform Eq. (12), which will be used later. First, we define *the compressibility factor* Z of pure liquid as the ratio of pressure to its ideal gas value, $Z=p/nk_BT$. Generalizing now the relation for the case of mixture, one can write the partial pressure p_1 in the form

$$p_1=n_1k_BTZ_{12}, \tag{13}$$

where the quantity Z_{12} can be called the compressibility factor of solute in solvent. Obviously, in our case of negligible solute concentration, Z_{12} does not depend on n_1. The condition $w=\mathrm{const}$ gives the relation between the gradients of number density of solute and solvent particles, $\nabla n_1/n_1=\nabla n_2/n_2$. Substitution of two last expressions into Eq. (12)

allows to perform the Soret coefficient without any memory about the concentration of solute

$$S_T = \frac{1}{n_2 T}\left[\frac{\partial(n_2 T Z_{12})}{\partial T}\right]_p. \tag{14}$$

Finally, we use the relation for pure solvent $p=p_2=n_2 k_B T Z_2$, where Z_2 is the compressibility factor of solvent. It is clear that derivative of the expression with additional condition $p=\text{const}$ is zero. Subtracting this value from Eq. (14) leads to the third and practically useful representation of S_T,

$$S_T = \frac{1}{n_2 T}\left[\frac{\partial(n_2 T\{Z_{12}-Z_2\})}{\partial T}\right]_p. \tag{15}$$

The expressions (12), (14), and (15) are three alternative forms for S_T which obviously follow on from the formalism of the equilibrium thermodiffusional driving force. In Sec. V we give the ways of determining the partial pressure and compressibility factor of liquid mixture.

V. PERTURBATION THEORY FOR PURE LIQUIDS AND MIXTURES

We start with considering the case of pure substances. Molecules of nonpolar liquids interact via the dispersion forces, which are traditionally written in the form of the Lennard-Jones (LJ) potential

$$U(r) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6]. \tag{16}$$

Two parameters determine the potential: the characteristic length r_0 and energy ϵ. To describe the LJ system the reference hard-sphere (HS) fluid modeling the intermolecular repulsions is usually chosen. The attractions are treated as perturbation within the framework of the Barker-Henderson [29] or the Andersen-Weeks-Chandler [30] formalisms. Both theories prescribe a peculiar way of determination of the HS diameter d. As noted in Ref. [31], the LJ characteristic size of *molecules* is only effective length of the molecular repulsive core and depends on the way of definition. Thus in practice, instead of determination of the HS diameter d via the previously unknown LJ size r_0 the opposite procedure is used: d is obtained first from some thermodynamic liquid properties and then the LJ parameter r_0 is calculated as an effective length of soft repulsions [31]. The same strategy might be applied also when determining the energy parameter ϵ from some auxiliary quantity connected simply with the experimental data.

We perform the mentioned procedure using the generalized vdW equation of state [32,33]

$$Z \equiv p/nk_B T = Z_{\text{HS}}(\eta) - \eta a, \tag{17}$$

i.e., the compressibility factor of liquid is a sum of the compressibility factor Z_{HS} of the reference HS system and the attraction forces term, $\eta=\pi n d^3/6$ is a packing fraction. The HS diameter d and van der Waals constant a are assumed to be temperature dependent, $d=d(T)$ and $a=a(T)$. The latter quantity is written often in the form $a=a_{\text{vdW}}/k_B T$ [31–34]. Since however a_{vdW} depends on temperature, it is useful to include the thermal energy into definition of new dimensionless constant a. The compressibility factor of hard spheres is well described by the Carnahan-Starling relation [35]

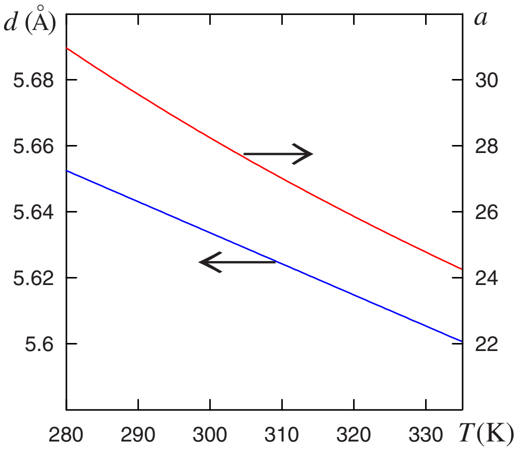

FIG. 1. (Color online) The hard-sphere diameter d and the van der Waals constant a of cyclohexane as a function of temperature. The values of d are given in angstroms.

$$Z_{\text{HS}}(\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{18}$$

Similarly to Eq. (16), relation (17) has two parameters: the characteristic length d and energy a. However in contrast to r_0 and ϵ, they both can be easily expressed via experimentally observable variables—the molar volume V_m and the isothermal compressibility $\beta_T=-(1/V)(\partial V/\partial p)_T$ [31,33]:

$$a = [Z_{\text{HS}}(\eta) - Z_{\text{exp}}]/\eta, \quad Z_{\text{exp}} = pV_m/RT, \tag{19}$$

$$\beta_T^{-1} = nk_B T[\eta Z'_{\text{HS}}(\eta) - Z_{\text{HS}}(\eta) + 2Z_{\text{exp}}]. \tag{20}$$

Here R is a gas constant and the experimental value Z_{exp} of compressibility factor is taken at normal condition $p=1$ atm. As our immediate aim is a determination of $d=d(T)$ and $a=a(T)$ it would be strongly desirable to have the detailed data on temperature dependencies of the molar volume $V_m(T)$ and the isothermal compressibility $\beta_T(T)$. Fortunately, these data are currently available [36]. Cerdeirina *et al.* [36] measured with very high accuracy the number of characteristics (density, isobaric and isothermal compressibilities, thermal expansivity, and others) of many nonpolar liquids. It is important that the results are given within the wide temperature interval 288–333 K with the step 1 K.

An example of the typical temperature behavior of both quantities is shown in Fig. 1 for the case of cyclohexane. As seen, the parameters $d(T)$ and $a(T)$ are weakly nonlinear decreasing functions. Additionally, we found also the packing fraction $\eta(T)$ and temperature derivative of all the functions, $d'(T)$, $a'(T)$, and $\eta'(T)$.

Further, we generalize the equation to the case of mixtures. The starting point here is expression (5) for partial pressure. After the transformation to the reference system, the repulsive part of the interaction potential derivative is written as [30]

$$U'_{12}(r) \to -k_B T \delta(r - d_{12}), \tag{21}$$

where $\delta(x)$ is the delta-function and d_{12} is the solute-solvent HS diameter. Following Ref. [31], we choose it in the additive form $d_{12}=(d_1+d_2)/2$ so as it has a meaning of contact value of distance between hard spheres with diameters d_1 and d_2. Substituting Eq. (21) into Eq. (5) and integrating gives the HS contribution to the partial pressure. The attractive part of p_1 apparently follows from Eq. (5) [37]. Combining both contributions we finally have

$$p_1 = n_1 k_B T\left[1 + \frac{2\pi}{3} n_2 d_{12}^3 g_{12}^{\mathrm{HS}}(d_{12}) - \frac{\pi}{6} n_2 d_{12}^3 a_{12}\right]. \tag{22}$$

Here $g_{12}^{\mathrm{HS}}(d_{12})$ is the contact value of the HS solute-solvent radial distribution function and $a_{12}=a_{12}(T)$ is the vdW constant of solute-solvent attraction. Thus for the compressibility factor Z_{12} [see Eq. (13)] of solute one finds

$$Z_{12} = 1 + 4\eta\sigma^3 g_{12}^{\mathrm{HS}}(d_{12}) - \eta\sigma^3 a_{12}, \tag{23}$$

where $\eta=\pi n_2 d_2^3/6$ is the packing fraction of pure solvent and $\sigma=(1+d_1/d_2)/2$. At first glance, since the vdW constant $a_{12}(T)$ of cross interaction is not determined yet, the temperature-dependent parameter σ^3 could be combined with a_{12}. However the following physical argument prohibits this formal procedure. The point is that according to the simplified considerations [34,37] the vdW constant a_{12} of solute-solvent attraction is proportional just to the product $\epsilon_{12} d_{12}^3$ of the Lennard-Jones cross-interaction parameter and the solute-solvent HS diameter. In its turn, ϵ_{12} is often approximated by the combining rule in the Lorentz-Berthelot form $\epsilon_{12} \to (\epsilon_1 \epsilon_2)^{1/2}$. The rule is very useful as an effective way of qualitative (and sometimes quantitative) consideration of the problem. We can use successfully the combining rule also for the vdW constant a_{12} only avoiding its merge with σ^3. This is why the attractive part of the interaction has been done in the form of Eqs. (22) and (23).

So, the partial pressure p_1 and the compressibility factor Z_{12} of solute are expressed via two parameters—the contact value $g_{12}^{\mathrm{HS}}(d_{12})$ of the correlation function and the vdW constant a_{12} of solute-solvent interactions. The former is well approximated by the analytical formula from the Boublik-Mansoori-Carnahan-Starling-Leland equation of state for HS mixtures [38,39]

$$g_{12}^{\mathrm{HS}}(d_{12}) = \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2}\frac{\gamma}{\gamma+1} + \frac{2\eta^2}{(1-\eta)^3}\left(\frac{\gamma}{\gamma+1}\right)^2, \tag{24}$$

where $\gamma=d_1/d_2$. We note that in special case of equal sized solute and solvent, $\gamma=1$, the repulsive contribution $Z_{12}^{\mathrm{HS}}=1+4\eta\sigma^3 g_{12}^{\mathrm{HS}}(d_{12})$ to the compressibility factor reduces it to pure liquid value (18). As for determination of the vdW constant a_{12} an additional investigation is required. We consider the issue in Sec. VI.

VI. CROSS-INTERACTION CONSTANT AND THE SOLVATION THEORY

We have seen above how the vdW constant a is related to the properties of pure liquid. It is quite clear that in order to define the vdW constant a_{12} of solute-solvent interactions we should use some property characterizing liquid *mixture*. The appropriate candidate for the property is the excess of volume V^E which is a difference of volume of mixture and its additive value. To establish the explicit link between a_{12} and V^E we remind the readers the basic steps of the solvation theory developed in the papers by Pierotti [37] and Ben-Amotz and co-workers [40].

First we make the notation used more precise. As before, the components 1 and 2 of the mixture are the solute and solvent, respectively. The vdW constant $a_{22} \equiv a_2$ describes the attraction of solvent molecules. As a mixture is assumed to be diluted its packing fraction η, isothermal compressibility $\beta_T(T)$, and thermal expansion coefficient α_p coincide with that for pure solvent. Now we write the chemical potential μ_1 of solute extracting its ideal gas value *at the same density*

$$\mu_1 = \mu_1^* + k_B T \ln\left(\frac{N_1}{V}\Lambda_1^3 q_1^{-1}\right), \tag{25}$$

where N_1 is the number of solute molecules, Λ is the de Broglie wavelength, and q_1 is the internal partition function of a single solute molecule. The last quantity is supposed to be dependent on temperature only as well as Λ. The first term on the right-hand side of Eq. (25) has a sense of the reversible work required to introduce one solute molecule into a solvent [37]. The process of introducing the solute is divided into two steps: the formation of a cavity in the solvent and then the introduction of solute into the cavity. The former step requires the work against the solute-solvent repulsions whereas the second one is due to interparticle attractions [31,37,40]. Thus

$$\mu_1 = \mu_1^{\mathrm{HS}} + \mu_1^{\mathrm{at}} + k_B T \ln\left(\frac{N_1}{V}\Lambda_1^3 q_1^{-1}\right). \tag{26}$$

Analogically to the case of the partial pressure (22) the chemical potential μ_1^{HS} of cavity formation is expressed from the Boublik-Mansoori-Carnahan-Starling-Leland equation of state for HS mixtures [38,39]

$$\frac{\mu_1^{\mathrm{HS}}}{k_B T} = \frac{2\eta\gamma^3}{(1-\eta)^3} + \frac{3\eta\gamma^2}{(1-\eta)^2} + \frac{3\eta\gamma(-\gamma^2+\gamma+1)}{1-\eta} + (-2\gamma^3+3\gamma^2-1)\ln(1-\eta). \tag{27}$$

The explicit form of the attractive contribution is obvious

$$\mu_1^{\mathrm{at}} = -2\eta\sigma^3 a_{12} k_B T. \tag{28}$$

We use now the thermodynamic relation for the *partial volume* $\bar{v}_1$ of solute molecule in solvent $\bar{v}_1=(\partial\mu_1/\partial p)_{T,N1,N2}$. Then we have

$$\bar{v}_1 = \left[\eta\frac{\partial(\mu_1^{\mathrm{HS}}/k_B T)}{\partial\eta} - 2\eta\sigma^3 a_{12} + 1\right] k_B T \beta_T. \tag{29}$$

The relation establishes the connection between the cross-interaction constant a_{12} and the partial volume $\bar{v}_1$ of solute in solvent. The latter could be expressed via experimentally measured parameters. Let us consider the point in more detail.

It is well known that the volume of mixture V does not coincide with its additive value $xV_1+(1-x)V_2$, where x is a mole fraction of component 1; V_1 and V_2 are the volumes of pure substances. Their difference

$$V^E = V - xV_1 - (1-x)V_2 \tag{30}$$

is called the excess volume [41]. The parameter characterizes the property of liquid mixture and might be positive as well as negative depending on the nature of compounds. It is determined from densitometric measurements. The observed values of V^E are fitted usually by the Redlich-Kister polynomials [41]

$$V^E = x(1-x)\sum_{i=0}^{g} A_i(1-2x)^i, \tag{31}$$

which allows calculation of the coefficients A_i. In general, the partial volumes $\bar{v}_1$ and $\bar{v}_2$ of components depend nontrivially on the molar fraction x. However the case of diluted solution is simpler: the partial volume $\bar{v}_2$ of solvent coincides with that for pure liquid, $\bar{v}_2 = V_2/N_2$, whereas the partial volume $\bar{v}_1$ of solute deviates most of all from its pure liquid value v_1,

$$\bar{v}_1 = \frac{V_1 + \delta V_1}{N_1} = v_1 + \delta v_1, \tag{32}$$

and the "defect" of molar volume δV_1 equals to x derivative of the volume excess [41]

$$\delta V_1 = \left(\frac{\partial V^E}{\partial x}\right)_{x\to 0} = \sum_{i=0}^{g} A_i. \tag{33}$$

Expressions (30)–(33) complete the determination of vdW constant a_{12} via the measured quantities.

We formulated above the approach of evaluation of the parameters of pure substances and their mixtures like the hard-sphere diameters d_1, d_2, and d_{12} and van der Waals constants a_1, a_2, and a_{12}. We remind readers that all these quantities are temperature dependent. Therefore, to calculate the Soret coefficient according to Eqs. (12), (14), and (15) the values of their temperature derivatives are needed. Moreover, it is necessary to know also $\beta_T'(T)$ and $\eta'(T)$—the temperature derivatives of solvent compressibility and packing fraction, respectively. There are a number of ways to define the parameters. First, they can be inferred from the polynomial fitting to measured values. For example, the compressibility $\beta_T(T)$ is well described by the polynomial of second order over the powers $T-T_0$, where T_0 is some reference temperature. Second, it might use the analytical relations for the derivatives. So, differentiating Eqs. (19) and (29) over T leads to explicit expressions for $a_1'(T)$, $a_2'(T)$, and $a_{12}'(T)$. We do not quote these formulas due to their evidence and unhandiness.

VII. CHEMICAL CONTRIBUTION TO THE SORET EFFECT

Let us revert now to an analysis of general relation (15) which performs the Soret coefficient via the difference of compressibility factors Z_{12} and Z_2 of solute and solvent, respectively. According to Eq. (23) it contains the repulsive and attractive terms. The terms do not include the masses and the moments of inertia of molecules and thus form the *chemical contribution* to the Soret effect [6]. In other words, the chemical contribution follows from the *interparticle interactions*. Therefore, the Soret coefficient S_T itself proves to be a result of *balance* of forces of both types. In the hypothetical binary mixture where molecules have the same size, $d_1 = d_2$, and interact via the same interparticle potential, $a_2 = a_{12}$, this balance becomes the *complete equality*. The Soret coefficient of such a system is equal to zero because molecules of both sorts cannot discriminate each other similarly to the case of ideal gas mixture considered in Sec. IV. In general, the balance is not complete and one of two physical mechanisms—repulsion and attraction—prevails.

It would be desirable to understand which sign of S_T does a separate action of repulsive and attractive forces lead to. The next qualitative picture allows us to imagine the trend of repulsions. The steric interactions try to push the molecules out of the more dense (cold) region into warmer layers of fluid. Particles of both sorts strive to being there and thus have to compete with each other. The particles with larger interparticle interactions gain and move indeed to the warmer region. Obviously, these are the molecules with larger size. So, the stronger repulsive interactions are responsible for a negative contribution to the Soret coefficient. On the contrary the attractive interactions lead just to opposite tendency—they force the particles with stronger interactions to move toward the cold region [42]. For a solute this takes place when cross-interaction parameter $\sigma^3 a_{12}$ [see below Eq. (35)] prevails over interactions a_2 of solvent molecules. Thus the repulsive interactions rival with attractive ones as usual and the actual magnitude and the sign of the Soret coefficient depends on the *relation* between their contributions, $S_T = S_T^{\mathrm{HS}} + S_T^{\mathrm{at}}$. It is worth noting that the larger the molecules the stronger simultaneously both types of interaction [43]. It means that their balance might be quite a delicate quantity which is smaller in absolute value than the contributions taken separately.

The explicit form of both contributions is

$$S_{\mathrm{T}}^{\mathrm{HS}} = \frac{4}{n_2 T}\left[\frac{\partial(n_2 T\eta\{\sigma^3 g_{12}^{\mathrm{HS}}(d_{12}) - g_{22}^{\mathrm{HS}}(d_2)\})}{\partial T}\right]_p, \tag{34}$$

and

$$S_T^{\mathrm{at}} = -\frac{1}{n_2 T}\left[\frac{\partial(n_2 T\eta\{\sigma^3 a_{12} - a_2\})}{\partial T}\right]_p. \tag{35}$$

We intend now to compare our result with the data of numerical experiments. There are a lot of publications on the subject [5,42,44,45]. However, the majority of them are not unanimous and often contradict each other [44] or the data quoted are not enough for comparison [42,45]. The best candidate for the comparison might be numerical experiments of the HS mixture because of minimal set of molecular parameters governing thermal diffusion in such a system. Unfortunately, the data for the Soret coefficient of the HS mixture are very rare in the literature [46,47]. The results of Erpen-

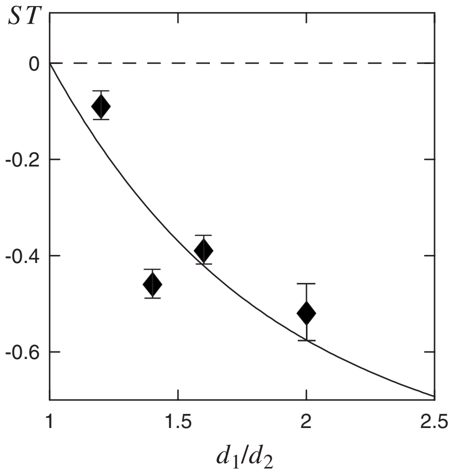

FIG. 2. Thermal diffusion factor ST as a function of diameter ratio for equimolar mixture of hard spheres for $\eta=0.209$. Diamonds are the data from Ref. [47]. The line is a result of linear fitting of $1/S$ upon extreme points $1/S^{\mathrm{HS}}(x=0)$ and $1/S^{\mathrm{HS}}(x=1)$.

beck [46] were found for HS system with the mass ratio of components $m_1/m_2=10$ and $m_1/m_2=33$ and thus are not appropriate for our needs. Some data of recent paper [47] have been obtained for *equimolar* mixture of hard spheres of equal masses. To use them we adopted the linear dependence of the inverse value of the Soret coefficient on the mole fraction [47]

$$S^{\mathrm{HS}}(x=1/2) \approx \frac{2S^{\mathrm{HS}}(x=0)S^{\mathrm{HS}}(x=1)}{S^{\mathrm{HS}}(x=0)+S^{\mathrm{HS}}(x=1)}. \qquad (36)$$

The limiting values $S^{\mathrm{HS}}(x=0)$ and $S^{\mathrm{HS}}(x=1)$ were determined according to Eq. (34). The dependence of the thermal diffusion factor, ST, on the diameter ratio is shown in Fig. 2 for the packing fraction $\eta=0.209$. As seen, the theoretical results are in good agreement with the simulation data. In Sec. VIII we consider in detail the steric and dispersion contributions to the Soret coefficient for the particular case of benzene-cyclohexane mixture.

VIII. SORET EFFECT IN BENZENE-CYCLOHEXANE MIXTURE

In this section we apply the proposed theory for a special case of benzene-cyclohexane mixture—the standard reference system for thermodynamic measurements. This is due to the fact that properties of pure components and the excess volume of mixture are known with high precision [36,48–53]. Furthermore, the Soret coefficient of benzene-cyclohexane system is well determined and reveals a physically interesting behavior—changing sign at a mole fraction of benzene $x\approx 0.8$ [6,54,55]. First we define the properties of pure substances.

A. Properties of pure liquids

We use the temperature dependence of molar volume $V_m(T)$ and the isothermal compressibility $\beta_T(T)$ as input parameters measured in Refs. [36,48] for benzene and cyclohexane, respectively. The hard-sphere diameter $d(T)$, packing fraction $\eta(T)$, and van der Waals constant $a(T)$ were determined with the help of Eqs. (18)–(20). The typical behavior of two parameters as a function of temperature is shown in Fig. 1 for the case of cyclohexane. The calculated values of parameters are given in Table I at $T=25$ °C. Owing to obvious similarity of benzene and cyclohexane molecules the parameters prove to be very close to each other.

TABLE I. Packing fraction η, hard-sphere diameter d, van der Waals constant a, thermal expansion coefficient α_p, and compressibility β_T of pure substances at $T=25$ °C.

Liquid	η	d (Å)	a	α_p (kK^{-1})	β_T (TPa^{-1})
C_6H_6	0.515	5.27	28.0	1.23[a]	973[a]
C_6H_{12}	0.519	5.64	28.5	1.22[b]	1131[b]

[a] Data from Ref. [48].

[b] Data from Ref. [36].

Next we found the derivatives $\eta'(T)$, $d'(T)$, and $a'(T)$. The defined dependencies $d(T)$, $d'(T)$, $\eta(T)$, and $\eta'(T)$ were used to calculate the thermal expansion coefficient $\alpha_p = -(\partial \ln n/\partial T)_p$ as a function of T. The comparison of calculated values $\alpha_{p,\mathrm{calc}}$ with the measured ones $\alpha_{p,\mathrm{exp}}$ [36] reveals the very high agreement of both results: the relative deviation $\alpha_{p,\mathrm{calc}}/\alpha_{p,\mathrm{exp}}-1$ does not exceed 0.25%. For example, for cyclohexane at $T=60$ °C both magnitudes are $\alpha_{p,\mathrm{calc}} = 1.324\times 10^{-3}\ \mathrm{K}^{-1}$ and $\alpha_{p,\mathrm{exp}}=1.327\times 10^{-3}\ \mathrm{K}^{-1}$. The property testifies to the intrinsic self-consistency of the perturbation theory and the van der Waals Eq. (17). The calculated values of derivatives taken at $T=25$ °C are given in Table II.

B. Properties of benzene-cyclohexane mixture

The main input parameter now is a "defect" of molar volume δV_1, i.e., the difference between the partial molar volume of solute in solvent and its pure liquid value. There is an extensive bibliography devoted to measuring δV_1 [49–53]. In our opinion, the most precise measurements were fulfilled in Ref. [52] where the values $\delta V_1=2.73\ \mathrm{cm}^3/\mathrm{mol}$ and $\delta V_2=2.56\ \mathrm{cm}^3/\mathrm{mol}$ have been found at $T=25$ °C for infinite dilution of benzene in cyclohexane and cyclohexane in benzene, respectively. The corresponding vdW constants a_{12} and a_{21} are calculated from Eq. (29). This way we get the almost identical estimations $a_{12}=27.2$ and $a_{21}=27.3$. They prove to be noticeably smaller than their mean-geometrical value $a_{\mathrm{mg}}=(a_1a_2)^{1/2}=28.2$. The decrease in cross-interaction constant is physically obvious because the volume of mix-

TABLE II. Temperature derivatives of packing fraction η', hard-sphere diameter d', van der Waals constant a', and compressibility β_T' of pure substances at $T=25$ °C.

Liquid	η'/η (kK^{-1})	d'/d (kK^{-1})	a' (K^{-1})	β_T'/β_T (kK^{-1})
C_6H_6	−1.63	−0.134	−0.117	7.87
C_6H_{12}	−1.71	−0.165	−0.128	8.49

TABLE III. Defect of molar solute volume δV, cross-interaction van der Waals constant a, its value at $\delta V=0$ and temperature derivatives a' and $\delta V'$. All the values are given at $T=25$ °C.

Mixture	δV (cm^3/mol)	a	a ($\delta v=0$)	a' (K^{-1})	$\delta V'/\delta V$ (kK^{-1})
C_6H_6 (1) in C_6H_{12} (2)	2.73	27.2	28.2	−0.113	1.77
C_6H_{12} (2) in C_6H_6 (1)	2.56	27.3	28.2	−0.114	1.51

ture is larger than its additive value. The relative variations in molar volume $\delta V_1/V_1$ and cross-interaction constant $a_{12}/a_{\text{mg}}-1$ have close magnitudes.

We describe now the striking property revealed when the hypothetical benzene-cyclohexane mixture with *zero value of the "defect" of volume* is considered. Substituting $\delta V_1=0$ in Eq. (29) reduces the cross-interaction constants *just to their mean-geometrical value*, $a_{12}(\delta V_1=0)=a_{21}(\delta V_2=0)=a_{\text{mg}}$. We point out that the equality is satisfied with very high precision better than 0.06%. It is important that the property is not specific only for the benzene-cyclohexane mixture. For example, adding toluene does not change the property dramatically: it is fulfilled now for toluene-benzene and toluene-cyclohexane pairs with slightly worse accuracy of 0.09% and 0.25%, respectively. We use the property in Sec. IX where the simplified relation for the Soret coefficient is given.

It was mentioned above that equation for a'_{12} is obtained by differentiating Eq. (29) over temperature. The quantity $\delta V'_1 \equiv \partial(\delta V_1)/\partial T$ is required calculating a'_{12}. The quantity is not well defined in experiment parameter. Indeed, the majority of works on excess thermodynamic properties of benzene-cyclohexane system deals with the fixed standard temperature $T=25$ °C (see detailed review in Ref. [53]). The data performed at different temperatures can be found significantly rarely [49–52,56] and often contradict each other. The situation is not surprising because the parameter $\partial(\delta V_{1,2})/\partial T$ is the second derivative [see Eq. (33)] of the hardly measured volume excess V^E taken at infinite dilution of solute. To estimate it we used again the most reliable data for $\delta V_{1,2}$ found in Ref. [52] for four values of temperature—$T=25$, 30, 35, and 40 °C. Assuming the linear dependence $\delta V_1(T)$ we get $\partial(\delta V_1)/\partial T = 0.00483\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$. We note that the value well correlates to the estimation $0.00382\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ given in Ref. [51] but it is two and half time smaller that the value $0.0115\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ which can be deduced from data of Ref. [56]. Analogically for the case of cyclohexane as a solute we have $\partial(\delta V_2)/\partial T=0.00387\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$. It is interesting that it overestimates by 2.5 times the result $0.00184\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ of Kumaran and Benson [51] and is very close to the value $0.00406\ \text{cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ found from Ref. [56].

The calculated values of $a'_{12}=-0.113\ \text{K}^{-1}$ and $a'_{21}=-0.114\ \text{K}^{-1}$ prove to be very close to each other, but notably smaller than derivative of the mean-geometrical value $[(a_1a_2)^{1/2}]'=-0.123\ \text{K}^{-1}$. All main data for benzene-cyclohexane mixture are collected in Table III. Substituting the parameters into Eq. (14) or Eq. (15) yields the Soret coefficient $S_{T,1}=-0.00369\ \text{K}^{-1}$ of benzene in cyclohexane and the Soret coefficient $S_{T,2}=-0.00399\ \text{K}^{-1}$ of cyclohexane in benzene. We compare them with the results of Wittko and Köhler [55,57,58] that determined the chemical contribution from the data measured for the different isotopically substituted mixtures. Figure 3 shows our result in comparison with the data [58]. The theoretical curve 2 is a second-order polynomial fit with the same curvature as the "experimental" curve 1. As seen, the theoretical curve catches the main features of the Soret coefficient behavior. They are the change in sign of S_T taking place with the growth of benzene concentration and the correct order of magnitude of the effect, $|S_T| \sim 0.001\ \text{K}^{-1}$. Moreover, the value of the Soret coefficient $S_{T,1}$ of benzene in cyclohexane is in reasonable agreement with the experimental result $S^{\text{exp}}_{T,1}=-0.00291\ \text{K}^{-1}$. At the same time, the calculated value of the Soret coefficient of cyclohexane in benzene overestimates twice its measured value.

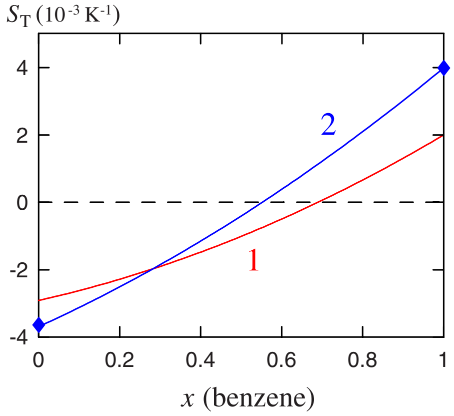

FIG. 3. (Color online) The chemical contribution to the Soret coefficient of benzene/cyclohexane at $T=25$ °C. Line 1 refers to the data from Ref. [58]. Diamonds are the result of present work. Line 2 is a polynomial fit to the result.

In Table IV we present the values of the Soret coefficient for diluted benzene/cyclohexane mixtures as well as the separate contributions of steric and dispersion forces. The signs of all contributions are in accordance with the qualitative picture considered in Sec. VII. Indeed, the cyclohexane molecule is larger than the benzene one (see Table I). Thus the repulsive interactions constrain the former to move into the warmer layer. This is why the sign of S_T^{HS} is negative for the mixture cyclohexane in benzene (mixture II) and positive for the case of benzene in cyclohexane (mixture I). The contribution of attractive forces depends on the value of parameter $\sigma^3 a_{12}-a_2$. Using the data of Table I we find the values −3.9 and 2.3 for the mixtures I and II, respectively. This signifies that dispersion forces cause a movement of cyclo-

TABLE IV. Repulsive and attractive contributions to the Soret coefficient S_T. All values are given in kK^{-1} for benzene-cyclohexane mixtures at $T=25$ °C.

Mixture	S_T^{HS}	S_T^{at}	S_T
C_6H_6 (1) in C_6H_{12} (2)	8.99	−12.68	−3.69
C_6H_{12} (2) in C_6H_6 (1)	−9.57	5.58	−3.99

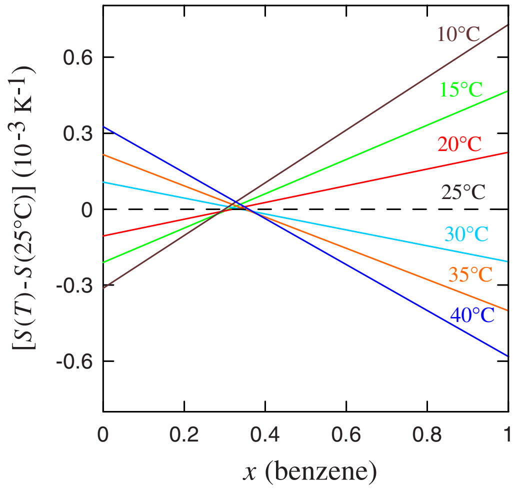

FIG. 4. (Color online) The chemical contribution to the Soret coefficient of benzene/cyclohexane mixture at different temperatures relative to its value at $T=25$ °C. Curves are linear fit upon extreme points $x=0$ and $x=1$.

hexane to colder side. It provides the negative sign of S_T^{at} for mixture I and its positiveness in the case of mixture II. The absolute values of repulsive and attractive contributions to the Soret coefficient prove to be 2–3 times higher than its summary result. This is in accordance with our expectations mentioned in Sec. VII.

Besides the Soret coefficient our theory reasonably describes its temperature dependence. The relative deviations of S_T from its reference value $S_T(25\ °\text{C})$ are shown in Fig. 4 for six different temperatures between 10 and 40 °C. When plotting the curves we have used the linear fit upon extreme points $x=0$ and $x=1$. The graph renders properly the behavior of S_T in experiment [57,58]. We indicate three common features of theoretical and experimental results. First, all lines intersect approximately at one point. Second, curves are arranged in "correct" order—the higher the temperature the smaller the absolute value of the Soret coefficient of benzene in benzene/cyclohexane mixture. Finally, curves are arranged almost equidistantly at any fixed value of mole fraction x. The quantitative agreement between theory and experiment data however is worse. The intersection point in Fig. 4 $x=0.33$ is shifted to a region of low concentration in comparison with result $x=0.72$ of Ref. [57]. We note that the latter quantity is a mole fraction of benzene corresponding to the mole fraction $1-x=0.28$ of cyclohexane. The analogous "inverse" result takes place in the case of temperature derivative of the Soret coefficient. So, we find the values 0.021×10^{-3} K^{-2} and 0.043×10^{-3} K^{-2} for dS_T/dT of benzene in cyclohexane and cyclohexane in benzene, respectively. Corresponding experimental data are 0.035×10^{-3} K^{-2} and 0.024×10^{-3} K^{-2} [57]. There are no doubts that the mentioned mismatch is a direct consequence of the doubly overestimated value of the Soret coefficient of cyclohexane in benzene (see Fig. 3). The possible reasons of the result are discussed in Sec. IX.

IX. DISCUSSION

We consider now the observation mentioned in paragraph B of Sec. VIII that in the hypothetical benzene-cyclohexane mixture with zero value of the "defect" of volume the cross-interaction vdW constant equals to the mean-geometrical value, $a_{12}(\delta V_1=0)=a_{21}(\delta V_2=0)=a_{\text{mg}}$. Mathematically, this can be written in the form similar to Eq. (29)

$$v_1 \approx \left[\eta\frac{\partial(\mu_1^{\text{HS}}/k_BT)}{\partial\eta} - 2\eta\sigma^3 a_{\text{mg}} + 1\right]k_BT\beta_T. \qquad (37)$$

We note that the relation is not an identity and it is fulfilled only approximately. Nevertheless, as we emphasized before, Eq. (37) is satisfied with very high precision better than 0.06% for benzene/cycloxexane mixture. If we successively add to the pair of substances first toluene and then hexane, we could register the growth of inaccuracy of Eq. (37) correspondingly to 0.25% and 2.3%. The last number is comparable in magnitude with the relative value of the defect of volume $\delta V_1/V_1$ and should be considered as inappropriate when using Eq. (37). The reason behind the growth of inaccuracy in the series benzene+cyclohexane, +toluene, +hexane is clear. It is due to an increase of molecule nonsphericity [59] whereas the theory developed here relates to the case of spherical solute and solvent particles. Strictly speaking, our theory and Eq. (37) are applicable or become unsuitable simultaneously.

With the help of Eq. (37) we can find a very compact relation for the Soret coefficient. Indeed, let us consider the *hypothetical* solute whose molecules possess the same hard-sphere diameter as the particles of real solute do but differ from them by the mean-geometrical value $a_{\text{mg}}=(a_1a_2)^{1/2}$ of cross-interaction constant with solvent. Let Z_{mg} be the compressibility factor of this hypothetical solute. Then adding and subtracting Z_{mg} from Z_{12} in Eq. (14) we obtain

$$S_T = S_T^{\text{mg}} + \frac{1}{n_2T}\left[\frac{\partial(n_2T\{Z_{12}-Z_{\text{mg}}\})}{\partial T}\right]_p, \qquad (38)$$

where S_T^{mg} is the Soret coefficient of the hypothetical mixture. Substitution of Eqs. (23), (29), and (37) and differentiation over temperature finally yield

$$S_T = S_T^{\text{mg}} + S_T^E = S_T^{\text{mg}} - \frac{\delta V_1}{2RT\beta_T}\left[\alpha_p + \frac{\beta_T'}{\beta_T} - \frac{\delta V_1'}{\delta V_1}\right]. \qquad (39)$$

Therefore the Soret coefficient of solute is composed of two terms. One of them is the Soret coefficient S_T^{mg} of the hypothetical system; it is determined *solely* by the properties of *pure* liquids. Second term S_T^E is owing to *excess* properties of mixture. It is interesting that the microscopic parameters such as the hard-sphere diameters do not enter at all into the relation for S_T^E, which is expressed via the defect of solute molar volume δV_1, its temperature derivative $\delta V_1'$, and the solvent properties β_T, β_T', and α_p.

So, there are different ways to decompose the Soret coefficient. The decomposition in Eqs. (34) and (35) has been done according to the nature of intermolecular forces. As seen from Table IV, the repulsive and attractive contributions prove to be one and the same order. The property is not typical of only the benzene/cyclohexane system and takes place in any nonpolar fluids. It means that the decomposition [Eqs. (34) and (35)] is quite a formal and noninformative one. A different physical approach is used in Eq. (39). Both terms entering the equation differ by magnitude of *the system volume*. The volume of the hypothetical system is an *additive* quantity what is equivalent to zero value of the volume excess. On the contrary, the second contribution S_T^E is proportional to the volume excess δV_1 of solute. The contribution becomes tangible roughly at $\delta V_1 \sim 1$ cm^3/mol corresponding to dimensionless value $\delta V_1 / V_{1,2} \sim 1\%$. In the benzene/cyclohexane system, the ratio achieves 3% as follows from the data in Table III and the term S_T^E prevails. Indeed, substituting the parameters of Tables II and III leads to results $S_{T,1}^E = -3.87$ kK^{-1} and $S_{T,2}^E = -4.03$ kK^{-1} for benzene in cyclohexane and cyclohexane in benzene, respectively. The values are very close to that calculated for the Soret coefficient (see the last column of Table IV) implying the negligible contribution of first term in Eq. (39). In their pioneering work, Story and Turner [54] were the first who suggested an important role of volume change mixing in the Soret effect. As we have demonstrated, an intimate connection of the Soret coefficient with the mixture excess volume appears in our approach in natural and transparent way.

Let us summarize the main results of the paper. Using the representations of Bearman and Kirkwood, we have developed the theory of thermodiffusion in a molecular nonpolar liquid mixture. It was assumed that the Soret effect is due to that part of driving force which is defined solely by the equilibrium thermodynamic quantities. It has been shown that modification of the original Bearman-Kirkwood relation for the driving force is required. The corrected formula was used to obtain the explicit general relation between the Soret coefficient and the partial pressure of one of mixture components. The partial pressure and compressibility factor of liquid mixture have been determined within the framework of perturbation theory where the hard-sphere fluid was chosen as reference system and dispersion interactions are considered as perturbation. The hard-sphere diameters and the van der Waals constants of pure liquids were expressed via measured quantities—the molar volumes and isothermal compressibilities taken at different temperatures. The solvation theory has been used to relate the vdW constant of cross interactions with the volume change on mixing the components. This way, two physically different representations for the chemical contribution to the Soret effect were derived. The theoretical predictions proved to be in reasonable agreement with the data for benzene-cyclohexane mixture: the calculated values of S_T have correct order and change sign at some fraction of benzene. A quantitative agreement of theoretical and experimental results is revealed also for temperature dependence of the Soret coefficient.

All these properties confirm the main idea of the paper that the gradient of partial pressure (equilibrium part of the driving force) is an important mechanism of thermodiffusional motion. The pertinent question is whether the quantitative mismatch of the theoretical predictions and data is a consequence of another uncharted mechanism or it is a result of the inevitably approximated character of the theory. Unfortunately, an answer lies beyond the scope of the present work and separate investigation is required. As was mentioned, our theory has been developed for the case of spherical particles. Due to the fast rotational motion, the platelike benzene and cyclohexane molecules are considered traditionally as quasispherical ones as contrary to alkanes [31–33,43]. Nevertheless, there is an opposite point of view on benzene and cyclohexane molecules as nonspherical particles [59]. We hope to clarify the role of nonsphericity of real molecules later.

Here we applied the developed theory only for benzene-cyclohexane system and did not consider any other mixture. There are a number of reasons for that. First, the benzene-cyclohexane system is a standard well-studied reference mixture. To calculate the Soret coefficient according to Eq. (39) it has to know such evasive variables as volume excess δV_1 and its temperature derivative $\delta V_1'$. For majority of mixtures these parameters are not available or defined inaccurately. Second, there are only four mixtures where the chemical contribution to the Soret effect is determined experimentally [57,58]. Unfortunately, three of them are not appropriate for comparison because of polar (water, ethanol, dibromohexane) or nonspherical (hexane, dibromohexane) molecules. The fourth mixture is just the benzene-cyclohexane system. Finally, the direct comparison with the available data for S_T is meaningless since the chemical contribution often proves to be of secondary importance in the phenomenon. In fact there is an additional contribution to the Soret effect which does not reduce to interparticle interactions and has the dynamic nature. The contribution has been observed in isotopic mixtures and after the paper of Debuschewitz and Köhler [6] known as isotopic one. In our opinion, this is an unsuccessful term because the contribution takes place in both isotopic and nonisotopic mixtures. The isotopic contribution by itself is the main subject of our next paper.

ACKNOWLEDGMENTS

The author is grateful to W. Köhler for many fruitful discussions. This work was supported by the DFG (SFB 481) and by Grant No. 07-01-96037 of the Russian Foundation for Basic Research.

---

[1] C. Ludwig, Sitzber. Akad. Wiss. Wien **20**, 539 (1856).
[2] C. Soret, Arch. Geneve **3**, 48 (1879).
[3] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
[4] M. E. Schimpf and J. C. Giddings, J. Polym. Sci., Part B: Polym. Phys. **27**, 1317 (1989).
[5] S. Wiegand, J. Phys.: Condens. Matter **16**, R357 (2004).
[6] C. Debuschewitz and W. Köhler, Phys. Rev. Lett. **87**, 055901 (2001).
[7] R. Piazza and A. Guarino, Phys. Rev. Lett. **88**, 208302 (2002).
[8] S. Iacopini and R. Piazza, Europhys. Lett. **63**, 247 (2003).
[9] R. Rusconi, L. Isa, and R. Piazza, J. Opt. Soc. Am. B **21**, 605

(2004).

[10] B. Hoffmann, W. Köhler, and M. Krekhova, J. Chem. Phys. **118**, 3237 (2003).

[11] E. Blums, Eur. Phys. J. E **15**, 271 (2004).

[12] D. Jung and M. Lücke, Phys. Rev. Lett. **89**, 054502 (2002).

[13] C. Fütterer and M. Lücke, Phys. Rev. E **65**, 036315 (2002).

[14] M. I. Shliomis and M. Souhar, Europhys. Lett. **49**, 55 (2000).

[15] R. Cerbino, A. Vailati, and M. Giglio, Phys. Rev. E **66**, 055301(R) (2002).

[16] M. I. Shliomis and B. L. Smorodin, Phys. Rev. E **71**, 036312 (2005).

[17] D. Braun and A. Libchaber, Phys. Rev. Lett. **89**, 188103 (2002).

[18] S. Duhr, S. Arduini, and D. Braun, Eur. Phys. J. E **15**, 277 (2004).

[19] R. W. Schmitt, Sci. Am. (Int. Ed.) **272** (5), 70 (1995).

[20] F. H. Busse, *Mantle Convection: Plate Tectonics and Global Dynamics*, edited by W. Peltier (Gordon and Breach, London, 1989), p. 23.

[21] R. Piazza and A. Parola, J. Phys.: Condens. Matter **20**, 153102 (2008).

[22] K. I. Morozov, Zh. Eksp. Teor. Fiz. **115**, 1721 (1999); [JETP **88**, 944 (1999)].

[23] K. I. Morozov, *Thermal Nonequilibrium Phenomena in Fluid Mixtures*, Lecture Notes in Physics Vol. 584, edited by W. Köhler and S. Wiegand (Springer-Verlag, Berlin, 2002), pp. 38–60.

[24] A. Parola and R. Piazza, Eur. Phys. J. E **15**, 255 (2004).

[25] S. Fayolle, T. Bickel, and A. Würger, Phys. Rev. E **77**, 041404 (2008).

[26] A. Einstein, Ann. Phys. **322**, 549 (1905).

[27] G. K. Batchelor, J. Fluid Mech. **74**, 1 (1976).

[28] R. J. Bearman and J. G. Kirkwood, J. Chem. Phys. **28**, 136 (1958).

[29] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[30] H. C. Andersen, D. Chandler, and J. D. Weeks, Adv. Chem. Phys. **34**, 105 (1976).

[31] D. V. Matyushov and R. Schmid, J. Chem. Phys. **104**, 8627 (1996).

[32] D. Ben-Amotz and D. R. Herschbach, J. Phys. Chem. **94**, 1038 (1990).

[33] D. Ben-Amotz and K. G. Willis, J. Phys. Chem. **97**, 7736 (1993).

[34] R. Schmid and D. V. Matyushov, J. Phys. Chem. **99**, 2393 (1995).

[35] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[36] C. A. Cerdeirina, C. A. Tovar, D. Gonzalez-Salgado, E. Carballo, and L. Romani, Phys. Chem. Chem. Phys. **3**, 5230 (2001).

[37] R. A. Pierotti, Chem. Rev. **76**, 717 (1976).

[38] T. Boublik, J. Chem. Phys. **53**, 471 (1970).

[39] G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, J. Chem. Phys. **54**, 1523 (1971).

[40] L. E. S. de Souza, A. Stamatopoulou, and D. Ben-Amotz, J. Chem. Phys. **100**, 1456 (1994); L. E. S. de Souza and D. Ben-Amotz, *ibid.* **101**, 9858 (1994).

[41] C. R. Reid, J. M. Prauznitz, and B. E. Poling, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1987).

[42] P.-A. Artola and B. Rousseau, Phys. Rev. Lett. **98**, 125901 (2007).

[43] J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, San Diego, 1992).

[44] P. Bordat, D. Reith, and F. Müller-Plathe, J. Chem. Phys. **115**, 8978 (2001).

[45] E. Leonardi, B. D'Aguanno, and C. Angeli, J. Chem. Phys. **128**, 054507 (2008).

[46] J. J. Erpenbeck, Phys. Rev. A **39**, 4718 (1989); J. J. Erpenbeck, *ibid.* **45**, 2298 (1992); J. J. Erpenbeck, Phys. Rev. E **48**, 223 (1993).

[47] S. Yeganegi and M. Zolfaghari, Fluid Phase Equilib. **243**, 161 (2006).

[48] J. M. Pardo, D. Gonzalez-Salgado, C. A. Tovar, C. A. Cerdeirina, E. Carballo, and L. Romani, Can. J. Chem. **80**, 370 (2002).

[49] E. Aicart, G. Tardajos, and M. Diaz Pena, J. Chem. Thermodyn. **12**, 1085 (1980).

[50] M. Takenaka, R. Tanaka, and S. Murakami, J. Chem. Thermodyn. **12**, 849 (1980).

[51] M. K. Kumaran and G. C. Benson, J. Chem. Thermodyn. **16**, 183 (1984).

[52] A. Arimoto, H. Ogawa, and S. Murakami, Thermochim. Acta **163**, 191 (1990).

[53] B. D. Smith, O. Muthu, A. Dewan, and M. Gierlach, J. Phys. Chem. Ref. Data **11**, 1151 (1982).

[54] M. J. Story and J. C. R. Turner, Trans. Faraday Soc. **65**, 349 (1969).

[55] G. Wittko and W. Köhler, J. Chem. Phys. **123**, 014506 (2005).

[56] M. K. Dutta-Choudhury, G. Dessauges, and W. A. Van Hook, J. Phys. Chem. **86**, 4068 (1982).

[57] G. Wittko and W. Köhler, Europhys. Lett. **78**, 46007 (2007).

[58] G. A. Wittko, Ph.D. thesis, Universität Bayreuth, Bayreuth, 2007.

[59] T. Boublik, J. Phys. Chem. B **109**, 19437 (2005).