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Theory for solubility in static systems

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A theory for the solubility of small particles in static structures has been developed. The distribution function of the solute in a frozen solid has been derived in analytical form for the quantum and the quasiclassical cases. The solubility at infinitesimal gas pressure (Henry's constant) as well as the pressure dependence of the solute concentration at elevated pressures has been found from the statistical equilibrium between the solute in the static matrix and the ideal-gas phase. The distribution function of a solute containing different particles has been evaluated in closed form. An application of the theory to the sorption of methane in the computed structures of glassy polycarbonate has resulted in a satisfactory agreement with experimental data.

INTRODUCTION

The solubility of small atoms or molecules in solids is of interest both from a fundamental and a practical point of view. Separation of gaseous mixtures (e.g., air separation, hydrogen isotope separation, etc.), the solubility of boron and carbon in metallic alloys, or deuterium solubility in palladium are just some of the relevant examples.

The solubility of the smallest molecules can be treated as a limiting case where one might conjecture that it is tolerable to neglect a structural relaxation in the host matrix. This makes it possible to describe the solubility as a statistical equilibrium between solute particles and the frozen static structure.

In general, a sorption process leads to some structural relaxations in the solid matrix. Nevertheless, even here the static approach can be useful as a first approximation to estimate the behavior and properties of a solute.

It is the goal of this paper to establish the fundamental relationships governing the statistical behavior of small solute atoms and molecules in frozen matrices, i.e., to evaluate the distribution function for the solute gas in a static host matrix.

GAS DISSOLVED IN A MATRIX AS SPATIAL FERMI GAS

Basic concepts

We consider here solids as sets of atoms, frozen in the positions of detailed mechanical equilibrium (they may constitute a metastable configuration), i.e., we will deal with a static model that does not take into consideration the thermal motion of atoms. From this point of view a solid structure is specified by a list of coordinates of atoms that constitute the body under consideration.

Let us consider the potential energy $U(x,y,z)$ that describes the interaction between a structureless solute particle at position (x,y,z) and the atoms of a frozen structure. The real trajectories of solute particles in a frozen structure are not trivial, but an important feature of this movement can be elucidated explicitly: a solute particle should reside a large fraction of time in the vicinity of the minima of the potential energy $U(x,y,z)$. These minima are expected to be spatially separated by a space in which the probability of finding a solute particle is considerably lower. Let us define here the sites for a solute particle in a frozen structure as the vicinity of the local minima of the potential energy $U(x,y,z)$.

We assume that the solubility in static host matrices obeys the following two principles: (i) the solid structure remains "frozen," i.e., the static description of the solid by a list of coordinates is not changed by the presence of the solute particles; (ii) no more than one solute molecule is able to occupy a site at one time.

Assumption (ii) has the effect of replacing the "real" potential of interaction between any solute particles by a geometrical principle, which is analogous to the well-known Pauli principle for electrons. This principle leads to a system with statistics of the Fermi-Dirac type and we define here an ensemble of particles of solute obeying this principle as a "spatial Fermi gas."

Statistics of the spatial Fermi gas

Let a unit volume of the medium consist of K sites. Consider now the ensemble consisting of L ($\gg 1$) images of this unit volume. The macroscopic state of the spatial Fermi gas in this ensemble may be described as follows.[1] Let us distribute all sites in the ensemble among groups, each containing one and the same site from every image. Let the groups of sites be numbered by j ($j=1,2,\ldots,K$) and let N_j denote the number of sites in group j that are occupied by solute particles at a given time. The set of numbers N_j completely describes the macroscopic (in the general case, nonequilibrium) state of the gas.

The free (Helmholtz) energy A of a given macroscopic state of the gas is

$$A=\langle E\rangle-TS\ , \tag{1}$$

where T is the temperature and S and $\langle E\rangle$ are the entropy and the mean energy of the macroscopic state, respectively. To find the value of $\langle E\rangle$ we neglect any interaction between solute particles at different sites so that the mean energy $\langle E \rangle$ of a given macroscopic state of the gas is just the sum of the mean energies of solute particles at site j, $\langle \varepsilon_j \rangle$, collected over all the sites that are occupied by the solute particles at a given time. The free energy of the macroscopic state of the gas can now be written as

$$A = \sum_{j=1}^{K} N_j \langle \varepsilon_j \rangle - TS \ . \tag{2}$$

The total entropy of the gas, S, can be considered as being made up of two independent parts. The first one, S_1, is associated with the indeterminacy of the positions of the solute particles at the sites and can be written as

$$S_1 = \sum_{j=1}^{K} N_j s_j \ , \tag{3}$$

where s_j is the entropy of a solute particle residing at site j. The second term, the communal entropy S_2, has its origin in the indistinguishability of the different microscopic realizations of a given macroscopic state. To calculate the communal entropy we should determine the number of microscopic ways in which a given macroscopic state can be realized. For the spatial Fermi gas this number is just the number of ways of selecting N_j out of L states, i.e., the number of combinations of L things, N_j at a time. Thus the communal entropy S_2 of the gas is

$$S_2 = k \sum_{j=1}^{K} \ln \left[\frac{L!}{N_j!(L-N_j)!} \right] , \tag{4}$$

where k is the Boltzmann constant. Since the numbers L and N_j are supposed to be large, we can use Stirling's approximation, $\ln N! \approx N \ln(N/e)$, and find

$$S_2 = \sum_{j=1}^{K} [L \ln L - N_j \ln N_j - (L-N_j)\ln(L-N_j)] \ . \tag{5}$$

The free (Helmholtz) energy A of the macroscopic state of the dissolved gas can be written as

$$A = \sum_{j=1}^{K} N_j(\langle \varepsilon_j \rangle - Ts_j) - TS_2 \ . \tag{6}$$

The term in the parentheses is just the free energy a_j of a solute particle occupying site j. Hence we can rewrite Eq. (6) as

$$A = \sum_{j=1}^{K} N_j a_j - TS_2 \ . \tag{7}$$

At equilibrium the free energy of the gas should be at a minimum, subject to the subsidiary conditions

$$\sum_{j=1}^{K} N_j = N \ , \tag{8}$$

where N is the total number of molecules of the gas. The method of Lagrange multipliers gives the following set of equations for N_j:

$$\frac{\delta}{\delta N_j}(A + \alpha N) = 0, \quad j = 1,2,..,K \ , \tag{9}$$

where α is a constant. By combining Eqs. (5), (7), (8), and (9), we find

$$a_j + \alpha + kT \ln[N_j/(L-N_j)] = 0, \quad j = 1,2,\ldots,K \ . \tag{10}$$

To find the undetermined multiplier α we write Eq. (9) as a relation between differentials:

$$dA + \alpha dN = 0 \tag{11}$$

and compare this expression with the differential free energy at constant volume and temperature:

$$dA = \mu dN \ , \tag{12}$$

where μ is the chemical potential of the spatial Fermi gas. By solving the set of equations (10), one finds that the equilibrium mean number $\langle n_j \rangle_{\text{eq}}$ of solute molecules at site j is given by

$$\langle n_j \rangle_{\text{eq}} \equiv \frac{\langle N_j \rangle_{\text{eq}}}{L} = \frac{1}{e^{(a_j-\mu)/kT}+1} \ , \tag{13}$$

where $\langle \ \rangle_{\text{eq}}$ indicates the equilibrium values. Formula (13) gives the equilibrium distribution function for a dissolved gas obeying Fermi statistics. When $\exp((a_j-\mu)/kT) \gg 1$, the distribution function approaches the Boltzmann distribution function, as should be expected.

The normalizing condition for the distribution function (13) is

$$\sum_{j=1}^{K} \frac{1}{e^{(a_j-\mu)/kT}+1} = c \ , \tag{14}$$

where c is the concentration of the solute, i.e., the total number of solute molecules per unit volume. Equation (14) relates the concentration c, the temperature T, and the chemical potential μ at constant volume V [a consequence of the "static" assumption (i)] and can be considered as the equation of state for the spatial Fermi gas. The spectrum of a_j values has its origin in the microscopic details of the particular system under consideration and can be determined when the energy levels of a solute molecule at any site j are known:

$$a_j = -kT \ln \sum_{s} e^{-E_s^{(j)}/kT} \ , \tag{15}$$

where s numbers the energy levels $E_s^{(j)}$ of a solute particle being localized at site j.

In the limiting case of low temperature, only the levels with the lowest energies are important and one can use the harmonic approximation to determine values of a_j. In this case the potential energy $U(x,y,z)$ of a solute particle localized in the vicinity of the bottom of site j is approximated by the form

$$U(\Delta x_1, \Delta x_2, \Delta x_3) = U_0^{(j)} + \tfrac{1}{2} \sum_{i,l} k_{il}^{(j)} \Delta x_i \Delta x_l \ , \tag{16}$$

where $U_0^{(j)}$ denotes the potential energy of a solute particle at the bottom of site j, Δx_i $(i = 1,2,3)$ are the components of the displacement vector with the origin at the bottom of site j, and $k_{il}^{(j)}$ is the Hessian matrix evaluated at the bottom of site j:

$$k_{il}^{(j)}=\frac{\partial^2 U}{\partial x_i \partial x_l} . \tag{17}$$

The free energy a_j of a solute particle at site j is then

$$a_j=\varepsilon_j+kT\sum_r \ln(1-e^{-h\nu_r^{(j)}/T}) , \tag{18}$$

where ε_j is the energy of a solute particle executing "zero-point" vibrations at site j, h is the Planck constant, and $\nu_r^{(j)}$ $(r=1,2,3)$ are the frequencies determining the energy levels $E_s^{(j)}$ of a solute particle oscillating at site j,

$$E_s^{(j)}=\sum_r h\nu_r^{(j)}(n_r+\tfrac{1}{2}) , \tag{19}$$

where n_r $(r=1,2,3)$ are non-negative integers.

In the limiting case of high temperatures one can use the quasiclassical approximation[2] to calculate the partition function Q_j of a solute particle at site j:

$$\begin{aligned} Q_j&=\frac{1}{h^3}\int\int dp\, dq\, e^{-p^2/2mkT-U(x,y,z)/kT} \\ &=\left[\frac{2\pi mkT}{h^2}\right]^{3/2}\int_{V_j} e^{-U(x,y,z)/kT}dV , \end{aligned} \tag{20}$$

where $\mathbf{p}=(p_x,p_y,p_z)$ is the momentum of a solute molecule, $dp\, dq$ denotes the volume element in phase space, V_j denotes the volume of site j, $U(x,y,z)$ is the potential energy of a solute molecule at the position (x,y,z), and m is the mass of a solute molecule. The spectrum of a_j values can be calculated then in accordance with

$$a_j=-kT\ln Q_j . \tag{21}$$

It is a condition for the quasiclassical approximation to be valid that the energy intervals in the vibrational structure of solute molecule oscillations at the sites should be small compared with the thermal energy. To estimate the validity of this condition for a specific system under consideration one can compare the frequencies of the normal vibrations, $\nu_s^{(j)}$, calculated in the harmonic approximation and the thermal energy. If the relation $h\nu_s^{(j)} \ll kT$ holds for the normal modes, then we can consider this fact as an indication of applicability of the quasiclassical approximation.

To calculate the spectrum of a_j values by means of a suitable approximation noted above, it is necessary to specify the system of interest. For a symmetry of crystals the spectrum of a_j values has only a few components and, in principle, it seems to be possible to evaluate this spectrum in analytical form. For disordered systems it is atomistic computer modeling that provides a unique tool to evaluate this spectrum and an example of this will be presented in the last part of this paper.

PHASE EQUILIBRIUM BETWEEN THE IDEAL GAS AND THE SPATIAL FERMI GAS

Consider the spatial Fermi gas as introduced above in contact with the ideal gas of the same molecules, at temperature T and pressure P. At equilibrium the chemical potentials of these two gases must have the same value, μ. The chemical potential of the ideal gas is[1]

$$\mu=kT\ln\left[\frac{P}{kT}\left[\frac{h^2}{2\pi mkT}\right]^{3/2}\right] , \tag{22}$$

where m is the mass of a molecule and h is the Planck constant. If we assume that the internal degrees of freedom of the ideal-gas molecules and those dissolved in the solid matrix are the same, it suffices to substitute Eqs. (20), (21), and (22) into (13) to find (in the quasiclassical case) the equilibrium number of solute molecules at site j at temperature T and the ideal-gas pressure P:

$$\langle n_j\rangle_{\text{eq}}=\frac{P}{\dfrac{kT}{Z_j}+P} , \tag{23}$$

where Z_j is the spatial (configurational) part of the partition function Q_j:

$$Z_j=\int_{V_j} e^{-U(x,y,z)/kT}dV . \tag{24}$$

The equilibrium concentration c of the solute can be obtained now as the sum over the equilibrium numbers of solute molecules for every site j per unit volume,

$$c\equiv\sum_{j=1}^{K}\langle n_j\rangle_{\text{eq}}=\sum_{j=1}^{K}\frac{P}{\dfrac{kT}{Z_j}+P} , \tag{25}$$

where K is the total number of the sites in a unit volume, as defined above. The corresponding relation for the quantum case states

$$c=\sum_{j=1}^{K}\frac{P}{\dfrac{(2\pi mkT)^{3/2}kT}{h^3 Q_j}+P}, \quad Q_j=\sum_s e^{-E_j^{(s)}/kT} , \tag{26}$$

where the summation over s is made over all quantum levels of a solute at site j. Equations (25) and (26) can be written in a unique manner:

$$c=\sum_{j=1}^{K}\frac{b_j P}{1+b_j P} , \tag{27}$$

where the constant b_j characterizes the sorption ability of site j.

THE SORPTION ISOTHERM

Equation (27) is a description of the sorption isotherm. It provides the total dissolved concentration at any pressure, subject of course to the assumptions noted above. Its usefulness lies in the fact that for any temperature T the local classical configuration partition function Z_j or the quantum energy levels $E_j^{(s)}$ can be evaluated for each site j, once the structure under consideration is specified in detail and the interaction energy $U(x,y,z)$ is known for a guest molecule as a function of its position (x,y,z) in the host matrix. If this is done, the solute concentration c can be evaluated for any particular pressure P.

Let us now consider the sorption isotherm in Eq. (27)

in the limit of low pressures P. For small P we can neglect the term b_jP in the denominator of Eq. (27) and find

$$c = P\sum_{j=1}^{K} b_j = HP \ , \qquad (28)$$

where H is a constant of the system. Expression (28) indicates that in the limit of small pressure the spatial Fermi gas obeys Henry's law, i.e., the concentration of the weak solution is proportional to the ideal-gas pressure. In the quasiclassical case, Henry's constant H is the volume integral over the entire structure:

$$H = \frac{1}{kTV}\int_V e^{-U(x,y,z)/kT} dV \ , \qquad (29)$$

where V is the volume of the solid body. In the quantum case, the corresponding expression for Henry's constant is (γ denotes the solute energy levels in a unit volume)

$$H = \frac{h^3}{kT(2\pi mkT)^{3/2}} \sum_{\gamma} e^{-E_\gamma/kT} . \qquad (30)$$

At elevated pressure the dependence of the solute concentration on the ideal-gas pressure [see Eq. (27)] can be represented as a sum of linear terms, b_jP (for sites j with $b_jP \ll 1$), and "Langmuir-like" terms, $b_jP/(1+b_jP)$ (for sites j where the term b_jP is comparable to or larger than unity). If a system consists only of "linear" sites and a set of identical "Langmuir" sites, the well-known "dual-mode-sorption" model[3] is obtained:

$$c = k_D P + C_H \frac{b_H P}{1+b_H P} \ , \qquad (31)$$

where k_D, C_H, and b_H are the constants. This form is widely used in practical applications[4] as a convenient functional form for fitting experimental data.

From the phenomenological point of view, the dual-mode-sorption model just reflects the fact that the sorption isotherms cannot separately be fitted either by Henry's or a Langmuir isotherm. In this sense, the form (31) contains three adjustable parameters (k_D, C_H, b_H) and usually allows one to fit experimental data on the gas solubility in solids in a quantitative manner.

It is fairly often implied that the dual-mode-sorption model has a physical basis in two distinct mechanisms of gas solubility in solids. The first one is assumed to be associated with a "liquidlike" solubility, while the second one is due to gas solubility in some "preexisting holes" in a solid structure.[4] Hardly any direct physical evidence can be found for the validity of this way of thinking.

To check the microscopic basis of this approach for the gas solubility in static structure, one can analyze the spectrum of b_j values [see Eqs. (27) and (31)]. If the dual-mode-sorption model is meaningful for this case, then the value b_H should stand out as a part of the spectrum of b_j values, bringing a substantial contribution to the total solubility of a gas.

We shall numerically investigate a shape of this spectrum for the methane solubility in the computed structures of glassy bisphenol-A-polycarbonate in the last part of this paper.

SPATIAL FERMI GAS CONTAINING DIFFERENT PARTICLES; GAS MIXTURES

Let us consider again the ensemble consisting of L images of a unit system and containing $L \times K$ sites. Suppose now that the spatial Fermi gas consists of particles of M different kinds. Let $N_j^{(i)}$ be the number of particles of kind i in group j, N_j be the total number of particles in group j, and $N^{(i)}$ be the total number of the particles of kind i in the ensemble. We assume that *no more than one* solute particle of any kind can simultaneously occupy any site in a frozen structure of solids. The problem here is that, generally speaking, the locations of local minima of potential energy $U(x,y,z)$ for different solute particles might not coincide. But, in practice, there should be a correlation between the minima for similar solute particles simply due to the fact that a frozen solid matrix has to impose strong geometrical limitations on the location of solute particles in solids. We shall suppose below that there is an unambiguous correlation between the locations of the potential-energy minima for different solute particles.

In calculating the communal entropy S_2 for the mixture of solute particles, the essential feature is that the number of combinations of L things N_j at a time should be divided not by $N_j!$ as for a gas containing identical particles [see formula (4)], but by the product $N_j^{(1)}! \cdots N_j^{(M)}!$ of the factorials of the numbers of particles of all components of the gas in group j:

$$S_2 = k\sum_{j=1}^{K} \ln\left[\frac{L!}{N_j^{(1)}! \cdots N_j^{(M)}!(L-N_j)!}\right] \ , \qquad (32)$$

where K is the number of sites in a unit volume. By using Stirling's approximate formula for the factorials in (32), we have

$$S_2 = k\sum_{j=1}^{K} [L\ln L - N_j^{(1)}\ln N_j^{(1)} - \cdots - N_j^{(M)}\ln N_j^{(M)} - (L-N_j)\ln(L-N_j)] \ . \qquad (33)$$

The free energy A of the macroscopic state of the gas can now be written as

$$A = \sum_{j=1}^{K} (a_j^{(1)}N_j^{(1)} + \cdots + a_j^{(M)}N_j^{(M)}) - TS_2 \ , \qquad (34)$$

where $a_j^{(i)}$ is the free energy of a particle of kind i residing at site j. From the condition for this expression to be a minimum under the condition of a constant number of particles $N^{(i)}$ of every kind i, we have

$$\frac{\delta}{\delta N_j^{(i)}}(A - \mu^{(1)}N^{()} - \cdots - \mu^{(M)}N^{(M)}) = 0 \ ,$$

$$j = 1, \ldots, K, \quad i = 1, \ldots, M \ , \qquad (35)$$

where $\mu^{(i)}$ is the chemical potential of particles of kind i. The corresponding set of equations for the equilibrium distribution functions for the components of the gas is

$$n_j^{(1)}+\cdots+n_j^{(i)}(1+e^{(a_j^{(i)}-\mu^{(i)})/kT})+\cdots+n_j^{(M)}=1\ ,$$

$$j=1,\ldots,K,\quad i=1,\ldots,M\ , \tag{36}$$

where $n_j^{(i)}$ is the mean occupancy of site j by the particles of kind i. The solution of this set of $K\times M$ equations gives the equilibrium occupancy $\langle n_j^{(i)}\rangle_{\text{eq}}$ of site j by the particles of kind i:

$$\langle n_j^{(i)}\rangle_{\text{eq}}=\frac{e^{(\mu^{(i)}-a_j^{(i)})/kT}}{1+\sum_{m=1}^{M}e^{(\mu^{(i)}-a_j^{(m)})/kT}}\ ,$$

$$j=1,\ldots,K,\quad i=1,\ldots,M\ . \tag{37}$$

The equilibrium concentrations $c^{(i)}$ of the particles of kind i can now be calculated as

$$c^{(i)}=\sum_{j=1}^{K}\langle n_j^{(i)}\rangle_{\text{eq}},\quad i=1,\ldots,M\ , \tag{38}$$

where the values of $\langle n_j^{(i)}\rangle_{\text{eq}}$ are given by formula (37). This set of equations implicitly determines the chemical potentials $\mu^{(i)}$ of the components of the spatial Fermi gas as a function of temperature T and partial solute concentrations $c^{(i)}$ and can be viewed as the "equation of state" for a spatial Fermi gas containing different particles.

Let us consider now the phase equilibrium of a spatial Fermi gas with a mixture of the ideal gases. We shall use here the quasiclassical approximation [Eqs. (20) and (21)] to calculate the free energies $a_j^{(i)}$. Collecting formulas (20)–(22) and (37), we obtain the following final expressions for the equilibrium distribution functions of the components of the spatial Fermi gas in contact with the mixture of the ideal gases:

$$\langle n_j^{(i)}\rangle_{\text{eq}}=\frac{Z_j^{(i)}P^{(i)}}{kT+Z_j^{(1)}P^{(1)}+\cdots+Z_j^{(M)}P^{(M)}}\,,$$

$$j=1,\ldots,K,\quad i=1,\ldots,M\ , \tag{39}$$

where $Z_j^{(i)}$ is the configurational part of the partition function of a particle of kind i at site j and $P^{(i)}$ is the partial pressure of component i. The equilibrium solute concentration $c^{(i)}$ of the component i can now be found by the formula

$$c^{(i)}=P^{(i)}\sum_{j=1}^{K}\frac{Z_j^{(i)}}{kT+Z_j^{(1)}P^{(1)}+\cdots+Z_j^{(L)}P^{(L)}}\ ,$$

$$i=1,\ldots,M\ . \tag{40}$$

Equation (40) states that at elevated pressures the solubilities of the components of the spatial Fermi gas are not independent and the partial pressure $P^{(i)}$ does not determine in a unique manner the appropriate concentration $c^{(i)}$. This means that it is necessary to specify the partial pressures of all components to predict the concentration of a solute of interest.

In the limiting case of low partial pressures of all components of a gas, we can neglect the terms $Z_j^{(i)}P^{(i)}$ in the denominator of Eq. (40) and find

$$c^{(i)}=\frac{P^{(i)}}{kTV}\int_V e^{-U^{(i)}(x,y,z)/kT}dV\ , \tag{41}$$

where V is the volume of the solid body under consideration and $U^{(i)}(x,y,z)$ is the potential energy of the interaction between a solute particle of kind i being at a point with coordinates (x,y,z) and the atoms of a solid matrix. In this case the solubilities of the components are independent and it becomes possible to use Henry's law for any kind of solute particle.

AN APPLICATION: METHANE IN BISPHENOL-A-POLYCARBONATE

Recently,[5,6] the computed structures of glassy polycarbonate of 4,4′-isopropylidenediphenol (bisphenol-A-polycarbonate, PC) have been produced at a density of 1.20 g cm^{-3} (corresponding to a well-relaxed glass at ambient temperature and a pressure of 1 bar) by minimization of the total potential energy of the polymeric chain in a cell with a spatially periodic continuation condition. The microstructures consisted of a chain of seventeen repeat units (485 atoms) and occupied a cube with edges of 18.44-Å length. Twelve such atomistically explicit microstructures of PC were the basis of the calculations reported here.

Methane is traditionally considered as a polyatomic molecule that could most reasonably be represented as a spherically symmetric one.[7] If we suppose further that the internal degrees of freedom of a methane molecule can be considered as independent of the dissolution process, then it becomes possible to use directly our current theory to evaluate the sorption isotherm. Reliable experimental data[8] are also available for the methane solubility in the glassy polycarbonate in a pressure range of 0–60 bar and we choose the sorption of methane in the glassy polycarbonate to illustrate a possible application of the theory developed above.

The interaction potentials

We suppose that the Lenard-Jones 6-12 function can be used to describe the potential energy of the interaction, $U_k(R)$, between a methane molecule and the host atom of type k at the separation R:

$$U_k(R)=-4\epsilon_k\left[\left[\frac{\sigma_k}{R}\right]^6-\left[\frac{\sigma_k}{R}\right]^{12}\right]\,, \tag{42}$$

where ε_k and σ_k are the parameters of the interaction. The most traditional combining rules[7] were used to estimate these parameters:

$$\sigma_k=\frac{\sigma_{kk}+\sigma_M}{2},\quad \epsilon_k=\sqrt{\epsilon_{kk}\epsilon_M}(1-k_M)\ , \tag{43}$$

where the parameters for the interaction of two like atoms in the polymeric matrix, ϵ_{kk} and σ_{kk}, were taken as provided with the structures of PC (see Table I), the methane-methane interaction parameters, $\epsilon_M/k=144$ K and $\sigma_M=3.80$ Å, were taken from Ref. 9, and the adjustable parameter k_M quantifies the deviations from the

TABLE I. Interaction parameters between species of bisphenol-A-polycarbonate.

Species	σ (Å)	ϵ/k (K)
Carbon (in phenylene)	3.30	54.2
Carbon (in aliphatic structure)	3.03	59.2
Carbon (in C=O)	3.03	90.1
Oxygen (in C=O)	2.67	127.5
Oxygen (in C—O—C)	2.67	97.0
Hydrogen	2.14	61.6
Methyl—pseudospherical	3.39	94.4

pure geometric mean rule ($k_M=0$), which is known[7] to tend to overestimate the strength of the interaction between unlike molecules.

Simulation procedure

As a calculation procedure we used an orthogonal equispaced net of 10^7 points with 0.085-Å intervals for every static structure. At the grid points the potential energy $U(x,y,z)$ of the interaction between the methane molecule and all atoms of the frozen PC structure was calculated. The bottoms of the sites were found as points on the grid at which the potential energy $U(x,y,z)$ is less than the one at the 26 surrounding grid points. These 26 points lie on the surface of the cube surrounding the tested point, where the edge length of the cube equals the double-grid interval. The frequencies of the normal vibrations, $\nu_r^{(j)}$ [see Eq. (19)] were calculated at the bottom of sites j as

$$\nu_r^{(j)}=\frac{1}{2\pi}\left[\frac{k_r^{(j)}}{m}\right]^{1/2}, \tag{44}$$

where m is the mass of the methane molecule, $k_r^{(j)}$ are the eigenvalues of the Hessian matrix, $k_{il}^{(j)}$, governing the solute oscillations at site j in the harmonic approximation

$$k_{il}^{(j)}=-24\sum_\alpha \frac{\epsilon_\alpha}{R_\alpha^2}\left[\left[\frac{\sigma_\alpha}{R_\alpha}\right]^6\left[8\frac{x_i x_l}{R_\alpha^2}-\delta_{il}\right]\right. \\ \left. -2\left[\frac{\sigma_\alpha}{R_\alpha}\right]^{12}\left[14\frac{x_i x_l}{R_\alpha^2}-\delta_{il}\right]\right], \tag{45}$$

where $\mathbf{R}_\alpha=(x_1,x_2,x_3)$ is the distance between the bottom of a site under consideration and atom α of the host structure, δ_{il} is the Kronecker tensor, and the summation is made over all atoms.

It was found that a condition $h\nu_r^{(j)}<0.3kT$ holds for the sites that bring a contribution to the methane solubility and we conclude that the quasiclassical approximation is here a suitable one. To compute the sorption isotherm in the quasiclassical case, it is necessary [see Eqs. (24) and (25)] to perform the numerical integration in the limits of sites j. To reveal the borders of sites j, the steepest-descent path is chosen from every point of the net which, by necessity, will terminate in one of the local potential-energy minima. In this way a unique assignment of all points of the net to sites j has been accomplished. The calculation of Z_j values is then straightforward.

All computations were carried out at the temperature $T=300$ K.

Deviations from the ideal state

At elevated pressures the deviations from the ideal state can become important. This can result in the impossibility of using the ideal-gas expression for the chemical potential μ [see Eq. (22)]. It is the fugacity of a gas that quantifies these deviations.[1] The fugacity P^* is the pressure at which an actual gas has the same chemical potential μ as the ideal gas at pressure P. Since the energy of the interaction, $U_M(R)$, of two methane molecules at the distance R is assumed to be known, we can estimate the deviations from the ideal state in a quantitative manner:[1]

$$P^*=P\left[1+\frac{BP}{kT}\right],\quad B=2\pi\int_0^\infty(1-e^{-U_M(R)/kT})R^2dR\ , \tag{46}$$

where B is the second virial coefficient.

We shall correct below the deviations from the ideal state by using the fugacity P^* instead of the actual gas pressure $P\,[(P-P^*)/P\approx 0.08$ at $P=50$ bar] for the evaluation of the sorption isotherms [see Eq. (25)].

The computed isotherm

Figure 1 presents the calculated solubility of methane in the computed structures of PC together with experimental results by Moll.[8] The considerable variation in the individual isotherms reveals the heterogeneous nature

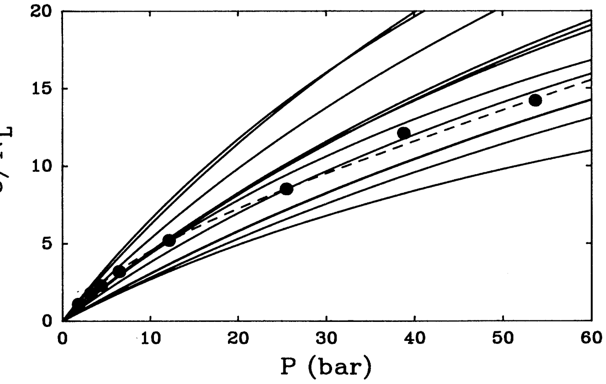

FIG. 1. Methane solubility in glassy polycarbonate. N_L denotes the number of molecules of the ideal gas in 1 cm^3 at $T=300$ K and $P=1$ bar. The solid lines represent the sorption isotherms computed with $k_M=0.56$ for twelve computed structures of PC. Solid circles represent the experimental data on the methane sorption in glassy PC of Moll (Ref. 8). The dashed line is the result of fitting (Ref. 8) with the "dual-mode-sorption" model [see Eq. (31)] with $k_D/N_L=0.18$ bar^{-1}. $C_H/N_L=5.56$, and $b_H=0.095$ bar^{-1}.

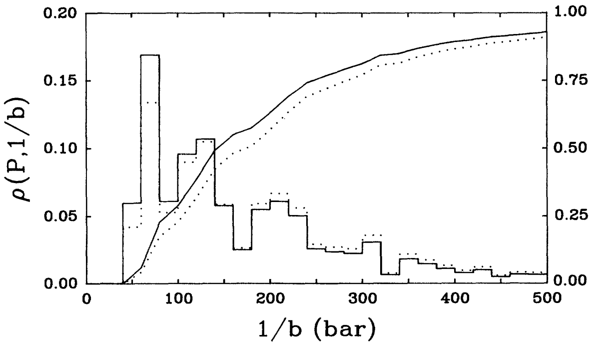

FIG. 2. The distribution functions $\rho(P,1/b)$ for the methane solubility in the computed structure of glassy PC. The corresponding integral distribution functions are also shown (right side of the plot). Solid lines represent the distribution functions computed at a pressure of 1 bar; dotted lines represent the distribution functions computed at a pressure of 50 bar.

of the computed structures and can be put down to the finite size of the simulated cell. The computed isotherms are rather sensitive to the value of the adjustable parameter k_M (the computed methane solubility drops by more than one order of magnitude when k_M changes from zero to 0.5). An agreement with experimental data can be achieved with k_M lying in the range 0.5–0.6, which is in acceptable agreement with the range 0.2–0.5, which was experimentally determined for the interaction between helium and the heavier noble gases.[7]

Figure 1 shows that the computed isotherms have the proper functional form at elevated pressures. This fact convinces us that the Fermi statistics for the solute is indeed a physically correct approximation to quantify the departure of the sorption isotherms from Henry's law.

Let us consider the normalized distribution function

$$\rho(P,1/b)=\frac{1}{c(P)}\frac{dc}{d(1/b)}\ , \tag{47}$$

where dc denotes the contribution brought to the total gas solubility, $c(P)$, by the sites with a value of $1/b_j$ lying in infinitesimal intervals between $1/b$ and $1/b+d(1/b)$. The computed distribution functions (see Fig. 2) highlight the components in the range of 50–500 bar, while the dual-mode-sorption model predicts (see Fig. 1) that the sites with the values of $1/b_j \approx 10$ bar are of special importance for the methane solubility in glassy PC. By taking into account the simple phenomenological nature of the dual-mode-sorption model, one should admit here that the agreement is rather satisfactory. In other words, the dual-mode-sorption model might be considered as a reasonable model for the methane solubility in computed structures of glassy PC although the distribution of sites is of a form that does not render it amenable to a quantitative reduction to the shape predicted by the dual-mode-sorption model.

CONCLUSIONS

A theory for the solubility in static structures has been presented. This theory is based on the statistics describing a gas dissolved in a matrix with sites that can be occupied by at most one solute molecule (a so-called spatial Fermi gas). The general thermodynamic relations, such as the equilibrium distribution function, the free energy, the pressure dependence of the concentration of solute being in contact with the ideal-gas phase, etc., have been evaluated in closed form for a spatial Fermi gas containing identical particles as well as different ones. The theory has been applied to the methane solubility in atomistically described computed matrices of amorphous polycarbonate.

The success of the theory in yielding the correct order of magnitude and the proper functional form of the sorption isotherm with an acceptable value of the adjustable interaction parameter is indeed somewhat surprising if one realizes that the theory does not account for the thermal vibrations in the solid matrix and swelling of the matrix, which might become significant at the elevated pressures. However, the apparent success of the presented, simple model seems to indicate that such a refinement is currently not called for.

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