

# Deformability of Adsorbents during Adsorption and Principles of the Thermodynamics of Solid-Phase Systems

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**Abstract**—A microscopic theory of adsorption, based on a discrete continuum lattice gas model for noninert (including deformable) adsorbents that change their lattice parameters during adsorption, is presented. Cases of the complete and partial equilibrium states of the adsorbent are considered. In the former, the adsorbent consists of coexisting solid and vapor phases of adsorbent components, and the adsorbate is a mobile component of the vapor phase with an arbitrary density (up to that of the liquid adsorbate phase). The adsorptive transitioning to the bound state changes the state of the near-surface region of the adsorbent. In the latter, there are no equilibrium components of the adsorbent between the solid and vapor phases. The adsorbent state is shown to be determined by its prehistory, rather than set by chemical potentials of vapor of its components. Relations between the microscopic theory and thermodynamic interpretations are discussed: (1) adsorption on an open surface, (2) two-dimensional stratification of the adsorbate mobile phase on an open homogeneous surface, (3) small microcrystals in vacuum and the gas phase, and (4) adsorption in porous systems.

**Keywords:** adsorption, thermodynamics of solids, microscopic theory, lattice gas model, non-inert adsorbents, surface tension, lattice deformation

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## INTRODUCTION

In describing adsorption processes, the thermodynamic methods developed by Gibbs [1] have traditionally been used for interpreting experimental results. In thermodynamics, the field of solid bodies remains the one most open, so it has been continuously debated and gradually refined over the last century [2–20]. In the theory of adsorption, one work in which the adsorbent was assumed to be inert has long been considered fundamental [4]. This statement has gradually been challenged because of other experimental works [21–48]. The problem of considering adsorbent deformability during adsorption relates the state of the adsorbate's physicochemical properties to changes in the adsorbent's mechanical state. A transition from the adsorptive to the bound state changes that of the adsorbent's near-surface region. If the adsorbent is deformed, it cannot be considered absolutely inert, and we must consider how a change in adsorbate density alters the elastic characteristics of a solid adsorbent and its vibrational spectrum. Generally speaking, greater changes occur in the adsorbent that alter its surface composition and structure.

In adsorption experiments, the adsorbent can be in the state of complete or partial internal chemical equilibrium. In the first case, the densities of the elements coexisting with elements in vapor correspond to the

equilibrium state of the adsorbent when there is no adsorbate. This state is basic (standard) with respect to the adsorption process: all thermodynamic states of the system must be counted from it. In the second case, there is no equilibrium of adsorbent components between the solid and vapor phases. The adsorbent state is not determined by the chemical potentials of vapor phases of its components. The adsorptive concentration is usually much higher than the vapor concentrations of adsorbent elements, so both adsorbent and adsorbate can be considered immiscible phases, even if adsorption occurs inside the system of adsorbent pores. (The absorption process is associated with the embedding of adsorptive atoms/molecules into the incorporation and substitution sublattices of the adsorbent, and this system is regarded as mixable.) Adsorption on the nonequilibrium deformable adsorbent can also change the state of its near-surface region. In chemisorption, this is due to the comparable binding energies between atoms of a solid and the adsorbent–adsorbate relationship [49–52]. To a lesser extent, this is also possible for physical adsorption. The adsorbent nonequilibrium state in the experiment is either virtually frozen and determined by its prehistory, or it evolves and must be described by kinetic equations. For instance, the diffusion exchange of components between the adsorbent bulk and its near-surface region is observed. The diffusion evolution of

systems was considered in [53–55], but these equations are not discussed here.

This work presents the microscopic theory of adsorption on noninert adsorbents, deformable and otherwise, which reflects the results from theoretical works on the describing solid-phase systems using the discrete-continuum lattice gas model (LGM) [54–61]. One difference between describing deformable adsorbents and the rigid ones considered earlier is the need to consider the adsorbate and adsorbent properties identically, even though the energies of adsorbate–adsorbate interaction and interaction between adsorbent atoms can differ substantially (up to one order of magnitude), while the relaxation times of the adsorbate mobile phase and the slow phase of adsorbent atoms can differ by more than ten orders of magnitude (which underlies the approximation in [4]). Equations are presented that describe both adsorbate and deformable adsorbent behavior, first in states of full equilibrium and then in partial equilibrium. This allows discussion of ways to apply equations [54–61] to typical problems of the theory of adsorption with regard to adsorbent noninertness and its boundaries: (1) adsorption on an open surface (vacuum, vapor, liquid); (2) two-dimensional vapor–liquid stratification on an open homogeneous surface; (3) small microcrystals and adsorption on them; and (4) microporous systems filled with an adsorbate.

#### Initial Positions [54–61]

Let us consider a multicomponent mixture of  $s$  particle types (more exactly,  $s$  is the number of occupancy states of some site  $f$ , which equals the number of the types of molecules ( $s - 1$ ) and vacancies  $i = V$  in the mixture). The complete set of equations contains ones for bulk phase states and the region of transition between the phases. To illustrate how the half-spaces of solid and liquid regions join with each other and close the complete set of equations, we shall limit ourselves to considering interactions  $z$  of nearest neighbors and the case of a layered structure of the interface between coexisting and immiscible phases (including distinctions in the numbers of particle types in different half-spaces):  $z = \sum_{p=q-1}^{q+1} z_{qp}$ , where  $z_{qp}$  is the number of neighboring sites of a layer:  $p = q, q \pm 1$ . If the coexisting layering solid–mobile phase (vapor or liquid) phases are considered, the number of components in the system is  $s$ . The number of components in the adsorbent is  $s_2$ , and the number of components in the mobile phase is  $s_1$ . Hence, the maximum number of system components  $s = s_1 + s_2$ .

The parameters of the theory are those of the pair potential functions of interactions between the components. Lateral interactions of the  $ij$  components are described by the Mie potential

$$\varepsilon_{qp}^{ij} = 4\varepsilon_{qp}^{ij0} \{(\sigma_{ij}/r_{qp}^{ij})^n - (\sigma_{ij}/r_{qp}^{ij})^m\},$$

where  $r_{fg}^{ij}$  are the distances between the  $i$  and  $j$  particles at different  $f$  and  $g$  sites;  $\varepsilon_{qp}^{ij0}$  and  $\sigma_{ij}$  are the pair potential parameters,  $n$  and  $m$  are the Mie potential parameters ( $n = 12$  and  $m = 6$  correspond to the Lennard–Jones (LD) potential). Interactions between particles with vacancies are equal to zero:  $\varepsilon_{qp}^{iV} = \varepsilon_{qp}^{Vj} = \varepsilon_{qp}^{VV}$ .

Layer concentration distributions are determined by local concentrations  $\theta_q^i$  characterizing the probabilities of layer site  $q$  being occupied by particle  $i$ ;  $1 \leq i \leq s_q$ ,  $s_q$  is the number of components in layer  $q$ ;  $1 \leq q \leq t$ ,  $t$  is the number of monolayers in the transition region of the interface,  $\sum_{i=1}^{s_q} \theta_q^i = 1$ ; and pair functions  $\theta_{qp}^{ij}$  characterizing the probability of components  $i$  and  $j$  being at the nearest sites of  $q$  and  $p$  monolayers;  $p = q, q \pm 1$ . Normalizing relations for the pair functions of components have the form

$$\sum_{i=1}^{s_q} \theta_{qp}^{ij} = \theta_p^j, \quad \sum_{j=1}^{s_p} \theta_{qp}^{ij} = \theta_q^i.$$

The  $\theta_q^i$  value is the local numerical density of particles  $i$  at the  $q$  layer site. For the entire system,  $\theta_i = N_i/M$  determines the concentration of component  $i$  (where  $N_i$  is the number of  $i$ -type particles, and  $M$  is the number of sites). Its relationship with generally accepted concentration  $n_i$  (the number of  $i$ -type particles in the unit volume) is written as  $\theta_i = n_i v_0$ , where  $v_0$  is the average site volume.

If there is an equilibrium distribution of system components over space, functions  $\theta_{qp}^{ij}$  obey the quasi-chemical approximation (QCA) equation used in theory [54–61] and in this work:

$$\theta_{qp}^{ii} \theta_{qp}^{jj} = \theta_{qp}^{ij} \theta_{qp}^{ji} \exp\{\beta[\varepsilon_{qp}^{ii} + \varepsilon_{qp}^{jj} - \varepsilon_{qp}^{ij} - \varepsilon_{qp}^{ji}]\}; \quad (1)$$

otherwise, the evolution of pair functions must be calculated using kinetic equations [62–64].

In the microscopic theory, it is enough to know the potential interaction functions of components in order to obtain the equations of state of the adsorbent bulk phase and the mobile phase consisting of the vapor of the adsorbent and adsorptive elements [54–56, 59–61]. The adsorbate layers are numbered from the first surface monolayer ( $q = 1$ ) to the mobile phase bulk; the number of layers in the transition region is denoted as  $t_{\text{mob}}$ . The adsorbent layers are numbered from its planar surface into its bulk. The  $q$  index, which changes from 1 (the adsorbent surface layer) to  $t_{\text{sol}}$  (the layer corresponding to the volume of the adsorbent phase), is maintained for numbering the adsorbent layers in the backward direction. The layer with  $q = 0$  formally corresponds to the plane between the first layers of each of the phases. The index “sol” corresponds to the half-space of the adsorbent phase, and

the index “mob” corresponds to the half-space of the adsorbate phase. If the adsorbent is inert, it is enough to determine its surface composition and structure to formulate surface potential  $U_q^i$  and calculate its potential relief and force constants for local vibrations [57]. If the adsorbent is not inert, adsorption or the external pressure of the unadsorbed mobile phase affects the state of surface atoms, altering bond lengths  $\lambda_{qp}^{ij}$  (where  $\lambda_{qp}^{ij}$  is the distance between the  $i$  and  $j$  atoms at the sites of layers  $q$  and  $p$ ) between the near-surface atoms inside a transition region with width  $t_{\text{sol}}$ . Knowing partial contributions  $\lambda_{qp}^{ij}$  from the neighboring pairs of molecules  $ij$  and the character of the spatial distribution of components  $\theta_{qp}^{ij}$ , we can calculate the average lattice constant:  $\lambda_{qp} = \sum_{ij} \lambda_{qp}^{ij} \theta_{qp}^{ij}$ .

Let  $V$  be the volume of a system consisting of  $M$  particles, including vacancies:  $V = \bar{v}_q^0 M$ , and  $\bar{v}_q^0 = v_0$  is the average cell volume of the system. We designate the local cell volume with number  $q$  via  $v_q^0 = \gamma_s \lambda_{qq}^2 [\lambda_{qq-1} + \lambda_{qq+1}] / 2$ , where  $\gamma_s$  is the form factor. It is related to the total system volume  $V$  through the numbers of pairs of bound  $f$  and  $g$  sites as

$$V(\{\lambda_{qp}\}) = \sum_{f=1}^M v_f = \gamma_s \sum_{f=1}^M \prod_{\sigma} \lambda_{f,\sigma}, \quad (2)$$

$$\lambda_{f,\sigma} = [\lambda_{ff-1,\sigma} + \lambda_{ff+1,\sigma}] / 2,$$

where  $ff \pm 1, \sigma$  corresponds to the neighboring sites in the direction of axis  $\sigma = x, y, z$ ; the average bond lengths between sites  $\lambda_{ff \pm 1, \sigma}$  correspond to the nearest neighbors determining cell volumes  $v_f$  with number  $f$ . The lattice symmetry determines the transition from the numbers of neighboring sites  $f \pm 1, \sigma$  to number  $z_{qp}$  and site types  $p = q$ , with  $q \pm 1$  corresponding to different monolayers. Weight volume fractions  $F_q^{(m,s)} = 1/t_{m,s}$ , where  $t_{m,s}$  is the number of monolayers in the subsystem ( $\sum_{q=1}^{t_{m,s}} F_q^{(m,s)} = 1$ ) characterizing the fraction of  $q$  type sites, correspond to heterogeneous layers of each of the phases. If a full system is considered, a separate phase layer is normalized to the value  $F_q = 1/(t_{\text{mob}} + t_{\text{sol}})$ .

### Local Partial Equilibrium Isotherms

Local partial concentrations  $\theta_q^i(P_i)$  of  $i$  components at the sites of layer  $q$  are functions of the total ensemble of partial pressures  $\{P_i\}$ ,  $1 \leq i \leq (s_{\text{mob}} - 1)$ , and are determined at set of partial pressures  $\{P_i\}$  from the equality condition of the chemical potential between adsorbate  $i$  in the considered lattice system and the thermostat ( $1 \leq q \leq t_{\text{mob}}$ ), and between the

atoms of a solid mixture and the thermostat ( $1 \leq q \leq t_{\text{sol}}$ ),  $\{P_i\}$ ,  $1 \leq i \leq (s_{\text{sol}} - 1)$ . The states of adsorbate and adsorbent site occupancy are identically characterized by the local retention coefficients of components  $i$  (in adsorption, these are local partial Henry coefficients). The total occupancy of the system as a function of external pressure  $\{P_j\}$  is written in the form of weighted summands from the local partial isotherms for each monolayer of the adsorbate and the adsorbent, which have the form [60–63]

$$\theta_i(\{P_j\}) = \sum_{q=1}^{t_{\text{mob,sol}}} F_q \theta_q^i(\{P_j\}), \quad (3)$$

$$\exp(\beta \mu_q^{is}) = \beta v_q^0 \exp(\beta U_q^i) P_i = \theta_q^i \Lambda_q^i / \theta_q^s,$$

where  $\mu_q^{is} = \mu_q^i(\text{con}) - \mu_q^s(\text{con})$  is the difference between the configurational components of chemical potentials of component  $i$  and the vacancy that determines the local equilibrium at the site of layer  $q$ ;  $\Lambda_q^i$  is the function of nonideality with allowance for lateral interactions  $\varepsilon_{qp}^{ij}$  between particles at neighboring sites of layer  $p$  ( $q, q \pm 1$ ) and particle  $i$  in layer  $q$ . It reflects the effect the neighbors of component  $i$  at the site in layer  $q$  have on its internal motions. For the mobile phase,

$$\Lambda_q^i = \prod_{p=q-1}^{q+1} \sum_{\mathbf{k}(qp)} \int_{\lambda_{qp}^{-b_{qp}^-}}^{\lambda_{qp}^{+b_{qp}^+}} \frac{\theta_q^i(\mathbf{k}(qp), \{\lambda_{qp}\}) S(\lambda_{qp}) d\lambda_{qp}}{Q_q^i(\mathbf{k}(qp), \{\lambda_{qp}\})}$$

for the adsorbent,

$$\Lambda_q^i = \prod_{p=q-1}^{q+1} \sum_{\mathbf{k}(qp)} \frac{\theta_q^i(\mathbf{k}(qp), \{\lambda_{qp}\})}{Q_q^i(\mathbf{k}(qp), \{\lambda_{qp}\})}$$

To enumerate all configurations of mixture components, we introduce contracted notation as the sum over  $\mathbf{k}(qp)$ :

$$\sum_{\mathbf{k}(qp)} \equiv \sum_{k_{qp}^{i1}=0}^{z_{qp}} \sum_{k_{qp}^{i2}=0}^{z_{qp}-k_{qp}^{i1}} \dots \sum_{k_{qp}^{is-1}=0}^{z_{qp}-k_{qp}^{i*}} \dots$$

Here,  $k_{qp}^{i*} = \sum_{j=1}^{s-2} k_{qp}^{ij}$ ;  $k_{qp}^{ij}$  denotes a set  $k_{qp}^{ij}$  of particles  $j$  at a site in layer  $p$ , the values of which vary since  $0 \leq k_{qp}^{ij} \leq z_{qp}$  near the central particle of type  $i$  in layer  $q$ ;  $\{k_{qp}^{ij}\}$  denotes a complete set of numbers  $k_{qp}^{ij}$ . In QCA, function  $\theta_q^i(\mathbf{k}(qp), \{\lambda_{qp}\})$  is written as

$$\theta_q^i(\mathbf{k}(qp), \{\lambda_{qp}\}) = \prod_{j=1}^s C_{z_{qp}}^{\{k_{qp}^{ij}\}} [t_{qp}^{ij} \exp(-\beta \varepsilon_{qp}^{ij})]^{k_{qp}^{ij}},$$

where  $C_{z_{qp}}^{\{k_{qp}^{ij}\}} = z_{qp}! / \prod_{j=1}^s k_{qp}^{ij}!$  is the number of combinations characterizing the statistical weight of a configuration with given number of bonds  $k_{qp}^{ij}$ . For the

number of neighboring vacancies, we have  $k_{qp}^{iV} = z_{qp} - \sum_{j=1}^{s-1} k_{qp}^{ij}$ . Functions  $t_{qp}^{ij} = \theta_{qp}^{ij}/\theta_q^i$  are the conventional probability of a  $j$ -type particle being at a site in layer  $p$  near an  $i$ -type particle in layer  $q$ . In functions  $\Lambda_q^i$ , designations are introduced for  $Q_q^i(\mathbf{k}(qp), \{\lambda_{qp}\})$  (the statistical sum of internal motions of component  $i$  at a site in layer  $q$  is  $Q_q^i(\mathbf{k}(qp), \{\lambda_{qp}\}) = Q_{q,tr}^i(\mathbf{k}(qp), \lambda_{qp}) Q_{q,vib}^i(\mathbf{k}(qp), \{\lambda_{qp}\})$  for a fluid (see [59] for details) and  $Q_q^i(\mathbf{k}(qp), \{\lambda_{qp}\}) = Q_{q,vib}^i(\mathbf{k}(qp), \{\lambda_{qp}\})$  for a solid. The distinctions between the internal motions of component  $i$  at a site in layer  $q$  reflects the existence of two branches of isotherms for the chemical potential of the component in different phases [56]. The distinctions between a solid and a fluid are apparent in the procedures for averaging over the vibrations and displacements of the centers of mass with functions  $S(\lambda_{qp})$ , where  $\lambda_{qp}$  is the distance between the centers of cells in neighboring layers  $q$  and  $p$  (see [59, 65]).

In the equilibrium state of the adsorbent,  $U_q^i = 0$  for local isotherms in formulas (3) because the potential interaction functions of adsorbent and adsorbate atoms  $\varphi_{ij(s)}(q) = \varepsilon_{qs}^{ij}(r)$  are reflected in the functions of nonideality.

### Free Energies of Layered Systems

Free energy  $F$  of a multicomponent mixture consists of three summands,  $F = F_{\text{lat}} + F_{\text{vib}} + F_{\text{tr}} =$

$$E_q^i = \sum_{p=q-1}^{q+1} \sum_{\mathbf{k}(qp)} \sum_{j=1}^{s-1} \int_{\lambda_{qp}-b_{qp}}^{\lambda_{qp}+b_{qp}} \varepsilon_{qp}^{ij}(\lambda_{qp}) k_{qp}^{ij} \Lambda_{qp}^i(\{k_{qp}^{ij}(\lambda_{qp})\}) S_n(\lambda_{qp}) d\lambda_{qp}^i. \quad (5)$$

Here, the cluster distribution functions of contributions are used:

$$\Lambda_{qp}^i(\{k_{qp}^{ij}\}) = C_{z_{qp}}^{\{k_{qp}^{ij}\}} \prod_{j=1}^s [t_{qp}^{ij}]^{k_{qp}^{ij}};$$

the other designations are introduced above. The expression for entropy through the cluster distribution is written as

$$S_q^{(2)} = \frac{k_B}{2} \times \sum_{p=q-1}^{q+1} \sum_{\mathbf{k}(qp)} \sum_{i,j=1}^s \int_{r_{qp}-b_{qp}}^{r_{qp}+b_{qp}} \theta_q^i [k_{qp}^{ij} \ln \theta_{qp}^{ij}(\mathbf{k}(qp)) \Lambda_{qp}^i(\{k_{qp}^{ij}\}) - \ln(\theta_q^i \theta_p^j) \Lambda_{qp}^{i*}(\{k_{qp}^{ij}\})] S(\lambda_{qp}^i) d\lambda_{qp}^i. \quad (6)$$

$\sum_{q=1}^t F_q \Psi_q(F_q^{\text{lat}} + F_q^{\text{vib}} + F_q^{\text{tr}})$ , describing lattice contributions  $F_{\text{lat}}$  from interparticle interaction and the contributions from the vibrational  $F_{\text{vib}}$  and translational  $F_{\text{tr}}$  (none for the adsorbent) motions of components in each layer in the transitional region. Function  $\Psi_q = v_q^0/\bar{v}_q^0$  explicitly reflects the local change in lattice lengths. The potential energy and entropy of heterogeneous layers in  $F_q^{\text{lat}} = E_q^{\text{pot}} - TS_q^{\text{lat}}$  have the form

$$E_q^{\text{pot}} = \sum_{i=1}^{s-1} \theta_q^i (U_q^i + E_q^i/2), \quad S_q^{\text{lat}} = S_q^{(1)} + S_q^{(2)}, \quad (4)$$

$$S_q^{(1)} = k_B \sum_{i=1}^s \theta_q^i \ln \theta_q^i,$$

where  $U_q^i$  is the energy of component  $i$  in layer  $q$  in the adsorbent field [57, 63];  $S_q^{(1)}$  and  $S_q^{(2)}$  are the single- and double-particle contributions to entropy; and  $t$  is the number of monolayers in the transition region of the interface. Here and below, the sum over particle types in  $E_q^{\text{pot}}$  excludes the zero summands from vacancies, while the entropy contains statistical weights reflecting the existence of vacancies. The contributions from lateral interactions to  $E_q^i$  for components  $i$  at sites of layer  $q$  are described by the expressions for the adsorbent and the mobile phase, which have identical structures:

The structure of the  $S_2$  contribution is such that pair functions  $\theta_{qp}^{ij}$  and  $\Lambda_{qp}^i(\{k_{qp}^{ij}\})$  belong to the correlated particle distribution over lattice sites, and  $\Lambda_{qp}^{i*}(\{k(\alpha)\})$  corresponds to random particle distribution  $\Lambda_{qp}^{i*}(\{k(\alpha)\}) = C_{z_{qp}}^{\{k_{qp}^{ij}\}} \prod_{j=1}^s [t_{qp}^{ij}]^{k_{qp}^{ij}}$ .

Vibrational contribution  $F_{\text{vib}}$  to the free energy of heterogeneous mixtures of the adsorbent and the mobile phase is written as

$$F_q^{\text{vib}} = -kT \sum_{i=1}^{s-1} \theta_q^i \sum_{p=q-1}^{q+1} z_{qp} \times \sum_{\mathbf{k}(qp)} \Lambda_q^i(\{k_{qp}^{ij}\}) \ln Q_{q,vib}^i(\mathbf{k}(qp), \{\lambda_{qp}^i\}), \quad (7)$$

$$\begin{aligned}
 F_q^{\text{vib}} &= -kT \sum_{i=1}^{s-1} \theta_q^i \sum_{p=q-1}^{q+1} z_{qp} \\
 &\times \sum_{\mathbf{k}(qp)} \sum_{j=1}^{s-1} \int_{r_{qp}-b_{qp}^-}^{r_{qp}+b_{qp}^+} \Lambda_q^i(\{k_{qp}^{ij}\}) \\
 &\times \ln Q_{q,\text{vib}}^i(\mathbf{k}(qp), \{\lambda_{qp}^{ij}\}) S_n(\lambda_{qp}^{ij}) d\lambda_{qp}^{ij},
 \end{aligned} \quad (8)$$

where the  $\mathbf{k}(qp)$  index determines the state of the nearest neighbor of type  $1 \leq j \leq s$  around the central particle  $i$  in layer  $q$ . Integration in (8) is therefore performed over corresponding displacements  $\lambda_{qp}^{ij}$ , as in formula (5). The frequency of vibrational motion is calculated for a fixed arrangement of all neighbors  $\{\lambda_{qp}^{ij}(\rho)\}$  [56, 59].

The free energy of the translational motion of molecules of the mobile phase is

$$\begin{aligned}
 F_q^{\text{tr}} &= -kT \sum_{i=1}^{s-1} \theta_q^i \sum_{p=q-1}^{q+1} \sum_{\mathbf{k}(qp)} \sum_{j=1}^{s-1} \\
 &\times \int_{r_{qp}-b_{qp}^-}^{r_{qp}+b_{qp}^+} \Lambda_q^i(\{k_{qp}^{ij}\}) \ln Q_{q,\text{tr}}^i(\mathbf{k}(qp), \lambda_{qp}^{ij}) S_n(\lambda_{qp}^{ij}) d\lambda_{qp}^{ij},
 \end{aligned} \quad (9)$$

where the statistical sum of the translational motion, function  $Q_{q,\text{tr}}^i(\mathbf{k}(qp), \lambda_{qp}^{ij})$ , depends on variables containing variable lengths between mixture components  $\lambda_{qp}^{ij}$ ,  $p = q, q \pm 1$  (for details see [59]). Equations (4)–(8) are written analogously for a solid and the mobile phase. Loss of the translational degree of freedom by particles in the mobile phase of the adsorbent results in disintegration, as mentioned above for the function of nonideality in formula (3) [59]. Equations (4)–(9) differ from the expressions in [59] because of the transition to a more detailed description of the distribution of neighbor pairs  $ij$  in  $\lambda_{qp}^{ij}$ , with respect to average cell sizes  $\lambda_{qp}$ . Note that it is generally necessary to consider the effect vibrational motion has on a change in lateral interaction parameters, in the form [56, 63]

$$\begin{aligned}
 &\tilde{\xi}_{qp}^{ij}(\mathbf{k}(qp)) \\
 &= \int_{\lambda_{qp}^{ij}-b}^{\lambda_{qp}^{ij}+b} \varepsilon_{qp}^{ij}(\mathbf{k}(qp)) \xi_{\chi} \theta_{qp}^{ij}(\mathbf{k}(qp)) \xi_{\chi} S_{qp}^{ij}(\xi_{\chi}) d\xi_{\chi} / \theta_{qp}^{ij},
 \end{aligned}$$

where the averaging procedure depends on the calculations for the vibrational spectrum. Even in the simplest case of considering the motion of the central particle in a field of stationary neighbors, we find that anharmonic effects must be considered. Renormalized  $\tilde{\xi}_{qp}^{ij}$  value must be included in all expressions written above in formulas (4)–(9) and those used below.

### Local Mechanical Equilibria

The presented expressions for equilibrium free energy  $F(\{\lambda_{qp}^{ij}\})$  of an adsorbate–adsorbent system are used to find bond length sets  $\{\lambda_{qp}^{ij}\}$  from the microscopic conditions for the local mechanical equilibrium of all particles in a system at constant temperature  $T$  [60, 61]:

$$\begin{aligned}
 \frac{\partial F}{\partial v_q} &= \sum_{p=q-1}^{q+1} z_{qp} \sum_{ij} \frac{\partial F}{\partial \lambda_{qp}^{ij}} \frac{\partial \lambda_{qp}^{ij}}{\partial v_q} \\
 &= \sum_{p=q-1}^{q+1} z_{qp} \sum_{ij} F_{qp}^{ij} \frac{\partial \lambda_{qp}^{ij}}{\partial v_q} = -P_q,
 \end{aligned} \quad (10)$$

where  $F_{qp}^{ij} = \partial F / \partial \lambda_{qp}^{ij}$ ,  $P_q$  is the local mechanical pressure in a cell of layer  $q$  with respect to a change in the number of vacancies due to the deformation of cell  $q$  in the system and the isothermal exchange of different types of particles with a reservoir. The microscopic Gibbs–Duhem equation [60, 61] yields the expression

$$P_q = \int_0^{\theta_q} \frac{1}{v_q} \sum_{i=1}^{s-1} \theta_q^i d(\mu_q^{is}), \quad (11)$$

where  $\mu_q^{is}$  is the difference between the configurational components of the chemical potentials of component  $i$  and a vacancy, which is expressed by Eq. (3) of the local partial isotherm. The upper limit of integration in (11) is the full occupancy density ( $\theta_q = \sum_{i=1}^{s-1} \theta_q^i$ ) of the local cell  $q$ . In the equilibrium state, integration over density can be performed using isothermal bonds in any order until we reach both total occupancy  $\theta_q$  and partial occupancy  $\theta_q^i$  that correspond to this equilibrium state at given chemical potentials  $\mu_q^{is}$ ,  $1 \leq i \leq s-1$ , depending on the partial pressure of component  $i$  in thermostat  $P_i^0$  (in an ideal gas). The cell volumes corresponding to the current  $\theta_i$  value,  $1 \leq i \leq s-1$ , vary according to (2) with changes in the degree of lattice occupancy. The expression for  $P_q$  can be written in analogy with (10) as

$$P_q = \sum_{p=q-1}^{q+1} z_{qp} P_{qp} = \sum_{p=q-1}^{q+1} z_{qp} \sum_{ij} P_{qp}^{ij},$$

which gives equations for bond lengths  $\{\lambda_{qp}^{ij}\}$ :

$$\begin{aligned}
 F_{qp}^{ij} \frac{\partial \lambda_{qp}^{ij}}{\partial v_q} &= -P_{qp}^{ij} = -\beta^{-1} \int_0^{\theta_q} \frac{1}{v_q} \\
 &\times \left[ \Delta_{ij} \theta_q^i \frac{d(\ln(\theta_q^i / \theta_q^s))}{d\theta_q} + \frac{d \ln \Lambda_q^i}{d\lambda_{qp}^{ij}} \frac{d\lambda_{qp}^{ij}}{d\theta_q} \right] d\theta_q.
 \end{aligned} \quad (12)$$

The number of Eqs. (12) coincides with the number of unknown bond lengths  $\lambda_{qp}^{ij}$ . Ways of simplifying the calculation of  $\lambda_{qp}^{ij}$  were discussed in [60].

### Surface Tension

Knowledge of the local components of a pressure tensor allows the calculation of surface tension. The determination of the surface tension of a spherical droplet is generally ambiguous [6, 66–68], so different values of surface tension  $\sigma_r$  are obtained, depending on the choice of the reference line of tension  $\rho_r$ . For planar boundaries, however, this ambiguity is removed. The surface tension for planar and spherical interfaces is expressed as

$$\sigma_r = \frac{1}{F_{\rho_r}} \left[ \sum_{q \leq \rho_r} F_q (P_1^\alpha - P_q^T) + \sum_{q > \rho_r} F_q (P_\kappa^\beta - P_q^T) \right], \quad (13)$$

where  $F_q = N_q/M$  is the fraction of monolayer  $q$  sites,  $M = \sum_{q=R+1}^{R+k-1} M_q$ ;  $M_q$  is the number of sites in layer  $q$ ; and  $M$  is a number of all sites in the transitional region, from  $q = 2$  to  $\kappa - 1$ . For the planar boundary in Eq. (13), layer weights  $F_q$  are reduced, and the known Becker equation is obtained [68].

For a layered structure on planar (and spherical curved) boundaries, we move to mean forces

$$F_q^\alpha = \sum_{p=1}^t z_{qp} \sum_{ij} F_{qp}^{ij} c_{qp}^\alpha \cos^2(qp, \alpha) \frac{\partial \lambda_{qp}^{ij}}{\partial v_q},$$

where  $c_{qp}^\alpha$  denotes the coefficients corresponding to the macroscopic symmetry of the system, which are related to the dimensionality of the system space  $d$  ( $d = 2$  or  $3$ ) and the average components of pressure tensor  $P_q^\alpha = \sum_{p=1}^t z_{qp} \sum_{ij} c_{qp}^\alpha \cos^2(qp, \alpha) P_{qp}^{ij}$  [60, 61];  $(qp, \alpha)$  denotes the angle between direction  $\alpha$  ( $\alpha = N$  and  $T$  correspond to the normal and tangential components of the local pressure tensor in layer  $q$  of a planar or spherical surface) and the direction of the bond between sites in layers  $q$  and  $p$ . The average local pressure is related to the pressure tensor components by routine macroscopic expression  $P_q = [P_q^N + (d-1)P_q^T]/d$ . (For a three-dimensional near-surface region of the adsorbent,  $c_{qp}^T = 3/4$  and  $c_{qp}^N = 3/2$ .)

All of the above expressions are self-consistent equations describing the distributions of mixture components in the near-surface adsorbate–adsorbent region, and bond lengths between all components of immiscible and coexisting equilibrium phases.

### Nonequilibrium Adsorbents

For the nonequilibrium adsorbent in the expressions for local isotherms (3),  $U_q^i \neq 0$ . If a planar surface is chemically homogeneous, all sites of one monolayer belong to the same type. Upon moving away from the surface, the effect of the surface potential diminishes as

$U_q^i = \varphi_{is}(q) = \varepsilon_{is} [(\sigma_{is}/\rho_{qs})^{n_s} - (\sigma_{is}/\rho_{qs})^{m_s}]$  for an averaged potential function of type  $(n_s - m_s)$ ;  $\varepsilon_{is}$  and  $\sigma_{is}$  are the parameters of the molecule–wall potential,  $n_s = 10$  or  $9$ , and  $m_s = 4$  or  $3$ , respectively [57, 63].

Here,  $\rho_{qs} = \sum_{n=0}^{q-1} \lambda_{n,n+1}$ ; and  $\rho_q$  is the distance between a molecule in layer  $q$  and the nearest surface.

If the adsorbent consists of different types of atoms,  $U_q^i$  is the sum of potential contributions:

$$U_q^i = \sum_{j \in s} \varphi_{ij(s)}(q) = \sum_{j \in s} \varepsilon_{ij(s)} [(\sigma_{ij(s)}/\rho_{qs})^{12} - (\sigma_{ij(s)}/\rho_{qs})^6],$$

where  $\varepsilon_{ij(s)}$  and  $\sigma_{ij(s)}$  are the parameters of the LD potential between adsorbate  $i$  in layer  $q$  and atom  $j(s)$  of the adsorbent: these are atom–atom LD interactions before averaging over layers or the half-space [63, 69–71].

For a nonequilibrium adsorbent, the distribution of its components can be determined at current time  $t$  by functions  $\theta_q^i(t)$  and  $\theta_{qp}^{ij}(t)$  for  $1 \leq i, j \leq (s_{\text{sol}} - 1)$ . These distributions along the normal to the solid surface can differ due to the values  $\theta_{s_{\text{sol}}}^i(t) \equiv \theta_i(t)$  corresponding to the homogeneous bulk phase of a solid, and

$$\theta_{s_{\text{sol}}}^{ij}(t) \equiv \theta_{ij}(t) \text{ for } 1 \leq i, j \leq (s_{\text{sol}} - 1).$$

Equation (1) for pair functions and Gibbs–Duhem equation (11) cannot be applied to the adsorbent nonequilibrium state, so we must use the expressions for local stresses obtained for nonequilibrium conditions in order to calculate the mechanical equilibria [54]. The form of the expression for pressure tensor components  $P_{kn}$  [54] depends on the type of phase.

For a solid (number of components  $s_1$ ),

$$P_{kn}(q) = - \frac{\lambda_{q_k p_n} \partial E_q}{\gamma_s v_q^0 \partial \lambda_{q_k p_n}}, \quad (14)$$

$$E_q = \left\langle \sum_{p=q-1}^{q+1} z_{qp} \sum_{i,j=1}^{s_p-1} \theta_{qp}^{ij} \varepsilon_{qp}^{ij} \right\rangle;$$

for the mobile phase (number of components  $s_2$ ),

$$P_{kn}(q) = \frac{\theta_q k T_q}{V_q^0} - \frac{1}{V_q^0} \left\langle \sum_{p=q-1}^{q+1} z_{qp} \sum_{i,j=1}^{s_p-1} \theta_{qk,p}^{ij} r_{qnp}^{ij} \frac{\partial \langle \varepsilon_{qp}^{ij}(r) \rangle_\tau}{\partial r_{qk,p}^{ij}} \right\rangle, \quad (15)$$

where  $s_p = s_1$  if  $p$  corresponds to the mobile phase, and  $s_p = s_2$  if  $p$  corresponds to the adsorbent. The  $l_{\text{sol}}l_{\text{mob}}$  bond has different numbers of components in layers  $l_{\text{sol}}$  and  $l_{\text{mob}}$ .

Internal energy  $E_q$  is implicitly related to vibrational spectrum  $\omega(\{r_{fg}^{ij}\})$  for particle arrangement  $\{r_{fg}^{ij}\}$ , so any procedure for varying distances between the particles requires recalculation of the vibrational spectrum for different particle arrangements. At long times when there is an equilibrium frequency distribution (but not the components) of a solid (i.e., when there is an isothermal state of the vibrational subsystem), the local contribution from vibrations to the free Helmholtz energy of the system must be taken into account:  $\langle E_q \rangle_\tau \equiv E_q^{\text{lat}} + F_q^{\text{vib}}$ . In both cases, determining the particle coordinates means determining the system's volume [54].

In the equilibrium state, expressions (14) and (15) transform into the above Gibbs–Duhem equations for the respective phases. For the bulk phase, Eq. (15) transforms into the familiar Irving–Kirkwood equation [66, 72], but it cannot be applied to a surface monolayer ( $q = 1$ ) for localized adsorption, or for any solid phase. For a surface monolayer, Eq. (15) is rewritten as  $P_{q=1}^{N,T} = P_{q=1}^{N,T}(1) + P_{q=1}^{N,T}(2)$ , where the first summand reflects the contribution from mobile components (their number is  $s_1$ ), and the second is the contribution from stationary adsorbent components (their number is  $s_2$ ), determined by different types of lateral interactions with the respective neighbors [54]. The same distinction is observed in all of the above formulas that contain the  $l_{\text{sol}}l_{\text{mob}}$  bond between the adsorbate and the adsorbent.

For a nonequilibrium adsorbent, expression  $F(t)$  for the free energy is a nonequilibrium analog of the equilibrium free energy for a given moment  $t$  [64]. The same analogs are introduced for other thermodynamic Gibbs potentials  $G$ , entropy  $S$ , internal energy  $U = E_{\text{lat}} + E_{\text{vib}} + E_{\text{tr}}$  ( $E_{\text{lat}} = \sum_q E_q^{\text{pot}}$ ; the two latter contributions refer to the internal energy of vibrational and translational motions). A mobile subsystem is always in an equilibrium distribution, but it is adjusted to the established nonequilibrium adsorbent state. Formulas for functions  $F(t)$ ,  $G(t)$ ,  $S(t)$ , and  $U(t)$  are similarly expressed through the local concentrations  $\theta_q^i(t)$  and pair functions  $\theta_{qp}^{ij}(t)$ , regardless of whether they are equilibrium or nonequilibrium [64]. Functions  $\theta_q^i(t)$

and  $\theta_{qp}^{ij}(t)$  must be governed by kinetic equations of the processes that form an adsorbent by a given time. Through them, we can calculate the respective non-equilibrium analogs of surface tension as an excess value of surface free energy  $\sigma(t)$ , depending on time. Being functions of time, these characteristics transform into the limiting values of equilibrium surface tension for long periods of time. A similar way of introducing dynamic surface tension was used for measurements in liquids at short periods of time after the creation of a new surface [66, 73].

### Solid–Mobile Phase Interfaces

Let us consider situations describing the derived equations. The half-spaces are related to the solid and the mobile phase via the  $l_{\text{sol}}l_{\text{mob}}$  bonds.

(1) For ordinary solid–mobile phase equilibria, concentration profiles  $\theta_q^i$  are calculated using equations of the equilibrium distribution of components in the transitional region. Through them, the equilibrium surface tension  $\sigma$  (13) is found;  $s = s_1 = s_2$ , because all characteristics are thermodynamic functions as in a normal vapor–liquid system. The width of the transitional region consists of two subregions,  $t_{\text{sol}}$  and  $t_{\text{mob}}$ .

(2) Adding an adsorptive to the bulk mobile phase alters distribution  $\theta_q^i$ ,  $1 \leq q \leq t_{\text{mob}}$ , since number of components  $s_1$  increases but number  $s_2$  is retained;  $s = s_1$ . A change in the mobile phase state alters the state of the adsorbent's transitional region (the concentration profile and width  $t_{\text{sol}}$ ). Equations (13) also allow us to find  $\sigma$ . The second case is an analog of the stratification of liquid systems when one of the liquid phase components is insoluble in another.

(3) The adsorbent nonequilibrium state when there is no adsorptive is established by its bulk distribution at this time using functions  $\theta_i(t)$  and  $\theta_{ij}(t)$  (for simplicity, we let them be homogeneous in volume), obtained by solving the kinetic equations in [62, 66] for a mechanically stable adsorbent. Functions  $\theta_q^i(t)$  and  $\theta_{qp}^{ij}(t)$ ,  $1 \leq q \leq t_{\text{sol}}$ , can differ near a surface, depending on the way the surface is created. The mobile phase state is characterized by the pressures of the components of its own adsorbent elements, or there is no mobile phase (there is a vacuum):  $s = s_1 = s_2$ . The distributions of functions  $\theta_q^i$  and  $\theta_{qp}^{ij}$ ,  $1 \leq q \leq t_{\text{mob}}$ , of the mobile phase are equilibrium distributions. Adsorbent noninertness is observed, since the adsorption of its own vapor can alter its mechanical states relative to the vacuum; this in turn affects the mobile phase state (which depends on whether the adsorbent is or is not inert). Using formula (13), we can calculate surface tension  $\sigma(t)$  of the system with respect to its mobile bulk phase, and vol-

ume distributions  $\theta_i(t)$  and  $\theta_j(t)$  of adsorbent components when there is a noninert wall:  $t = t_{\text{mob}} + t_{\text{sol}}$ . When the adsorbent serves as an inert rigid wall on which adsorption of its own elements occurs, surface tension  $\sigma(t)$  is calculated with respect to its two bulk phases in the absence of wall deformation effects [74].

(4) This situation differs from the third by the presence of an absorptive, just as the second and first situations differ. For the solid phase, everything remains as it was in the third case, while the number of components increases for the mobile phase:  $s = s_1 + s_2$ . Both equilibrium distribution functions  $\theta_q^i$  and  $\theta_{qp}^{ij}$ ,  $1 \leq q \leq t_{\text{mob}}$ , and surface tensions  $\sigma$  change relative to the bulk phase when there is a noninert wall. An adsorbent is noninert when the adsorption of its own vapor and the adsorptive can alter its mechanical states, relative to a vacuum and the adsorption of own vapor; this in turn also affects the mobile phase state. If the adsorbent serves as an inert rigid wall, surface tension  $\sigma(t)$  is calculated with respect to the bulk phase in the absence of wall deformation effects [74].

The traditional use of surface tension or internal energy  $U^s(t)$  (where upper index  $s$  corresponds to excess surface functions [66]) as a new characteristic of the interface that differs from surface tension  $\sigma(t)$  in formula (13) was an attempt to express specific features of surface formation under nonequilibrium conditions. (It is explicitly mentioned in the definition of nonequilibrium analogs of thermodynamic potentials.) Since  $F^s(t) = U^s(t) - TS^s(t)$ , with the corresponding choice of the separating surface we have  $F^s(t) = \sigma(t)A(t)$  (where  $A(t)$  is the surface area). It can be seen that the adsorbent distinctions between  $U^s(t)$  and  $\sigma(t)$  are due to considering the vibrational contributions to entropy (this is done for  $\sigma(t)$  but not for  $U^s(t)$ ). The nonequilibrium analogs of thermodynamic potentials are thus stricter concepts than Gibbs' proposal to use  $U^s(t) \equiv \gamma$  values; they not only reflect the essence of adsorbent nonequilibrium states but also allow strict calculation of these characteristics through the kinetic equations in [62, 64].

The above four situations of introducing different  $\sigma$  and  $\sigma(t)$  correspond to the free adsorbent boundary, but without an external mechanical load. The inclusion of an external mechanical load complicates the situation, since an additional factor emerges that affects the component distributions both inside a solid and on its surface, and thus the mobile phase distributions relative to a mechanically perturbed adsorbent.

The introduction of nonequilibrium analogs of thermodynamic potentials requires refinement of the concept of creating a new surface under the effect of mechanical loads, which is currently far from clear. Refinements are needed for the  $\sigma(t)$  value corresponding to the surface that forms after removing an applied load or during the action of an external load. It must also be specified whether the surface is formed from

the solid phase bulk (e.g., by chipping) or by applying a load to an already existing surface. We then have two different situations. In the first, if the surface does not relax to the initial surface area after the load is removed, we are dealing with an analog of plastic deformation and must indicate what changes occurred in the solid to describe them. In the second, we must clarify the type and way of creating contact interaction during mechanical loading. Different variants are possible here, starting from direct perturbations of the neighboring solids (or neighboring phases) to indirect perturbations at the remote ends of a crystal when deformation interaction propagates through the crystal lattice over the volume and the surface. Each nonequilibrium process is characterized by its own kinetic scheme and specific features of the dynamics, which must reflect microscopic models. Otherwise, the process cannot be defined under the action of mechanical perturbations. These complications are thus due to the need to specify the new process of surface creation at the microlevel [75]. This problem has virtually not been considered so far. In addition, the question of the size of the created surface, which applies only to the simplest ideal (planar, spherical) geometries, is also problematic. Different rough surfaces emerge at any more or less real mechanical perturbation, and estimating the surface area for these is a separate problem.

### *Heterogeneous Monolayers*

A layered model of a region of interface transition consisting of a mixture of mobile components and solid solutions was presented above; we considered how concentration profiles of components  $\theta_q^i$  and bond lengths  $\lambda_{qp}^{ij}$  are involved with one another in different monolayers, depending on the mobility of solid phase components. Below, we discuss the structure of equations of similar adsorption problems when this means of description is insufficient (the distribution of components inside a layer becomes heterogeneous). The simplest example of this is the two-dimensional stratification of an adsorbate on the open surface of an adsorbent. The densities of the rarefied and dense phases of the adsorbate in one monolayer differ here. Another example of heterogeneous monolayers is the surfaces of isolated single crystals as small bodies and the case of adsorption on a single crystal, which are described by more complex distributions of components than the layered distributions of surface macrosystems. Finally, a more complex case of a heterogeneous system is adsorption inside a porous adsorbent system when different heterogeneous distributions of the adsorbent material encompass a large number of monolayers, and the distribution of adsorbate inside these is heterogeneous.



*Two-dimensional Stratification  
of an Adsorbate on an Open Surface*

Let us consider a system in which adsorbed vapor and liquid are in chemical equilibrium with gas in a three-dimensional volume. A characteristic feature of the two-dimensional ( $d = 2$ ) stratification of an adsorbate is the formation of a vapor–liquid interface in a system with linear tension, which is physically similar to the droplet surface tension in the volume of a macroscopic system. Depending on the size of the dense phase, the linear tension can correspond to an adsorbate macroscopic phase with a linear structure of the transition region, or to a small dense phase of the adsorbate ( $d = 2$  is a droplet), and can have a curved structure of the transitional region (for a homogeneous surface, this structure is round). In considering any noninertness of the adsorbent, we must reflect the effect the adsorbate phase state (vapor or droplet) has on the degree of adsorbent perturbation from the phase density, and the effect the variable adsorbate density inside the two-dimensional transitional region has on the adsorbent’s noninertness [61]. These features are reflected by the sequence of bonds in the microscopic version of the Gibbs–Duhem equation that describes the change in pressure in a system under study. Upon minor deformations of a homogeneous adsorbent, the macroscopic symmetry of a planar droplet can be used in the first approximation. (The situation becomes more complex for a heterogeneous surface and depends on the character of the distribution of solid components in the surface layer of the adsorbent [61].)

A set of sites in the surface monolayer of the adsorbate is divided into two types of two-dimensionally homogeneous dense and rarefied phases, and into sets  $N_1^{(q)}$  of sites of the transitional region of a two-dimensional droplet [61]. Here, the lower index in  $N_1^{(q)}$  corresponds to the surface layer of the mobile phase, while the upper index denotes the layers of transitional region  $d = 2$  of the droplet,  $1 \leq q \leq \kappa$ , where  $\kappa$  is the number of circumferences in the transitional region of the droplet. The fraction of the surface under droplet  $d = 2$  is clearly defined by its radius  $R$ . (In this section, designations  $R$  and  $\kappa$  are maintained for droplet  $d = 2$ , and for an ordinary droplet in the bulk.) Hence, the full set of equations for the concentration profiles of mobile phase components consists of  $(s_1 - 1)\kappa$  equations, and the concentration profiles of the adsorbent consist of  $(s_2 - 1)\kappa t_{\text{sol}}$  equations instead of the characteristics of one monolayer, as mentioned above. In the first approximation, number of monolayers  $t_{\text{sol}}$  that the adsorbate influences is retained. This value is determined by the maximum  $t_{\text{sol}}$  value below the vaporous or liquid adsorbate. Equations for bond lengths  $\lambda_{qp}^{ij}$  are reformulated in a similar manner: they relate all mobile phase components in the transitional region between the vaporous and liquid adsorbate both

normal to the tension line and in the tangential direction inside the surface plane. For the solid phase, the sequence of bonds  $\lambda_{qp}^{ij}$  from the adsorbent external surface to depth  $t_{\text{sol}}$  of monolayers must be considered with regard to the radial symmetry in this cylinder. For the problem under study, it is worth emphasizing that the equations for bond lengths  $\lambda_{qp}^{ij}$  are based on Eqs. (14) in both mobile phases on the localized adsorption and adsorbent, rather than Irving–Kirkwood equations (15), due to the need to consider the direct interaction between the adsorbate and the substrate, and the vibrational motions of the adsorbate.

*Microcrystals*

The structures of an isolated microcrystal were described in [59] (particle interactions at distances  $R_{\text{lat}}$  for a more general case), and the same principle is used in considering adsorption on microcrystals. For these, we cannot use representations of macroscopic faces or their properties associated with the layered distribution of solid components normal to a surface. We must move to a discrete description of the arrangement of atoms in the interface plane relative to the boundary edges. Atoms at different distances from the edges have different properties and must be specified according to this principle.

The above formulated set of bonds for the nearest neighbors in near-surface region  $z_{qp}$  changes to  $z_{qp}(x, y)$ , making them dependent not only on the distance from the central region, but also the  $(x, y)$  coordinates along the surface of each face. This increases the number of types of centers in the near-surface monolayers, which raising the dimensionality of the set of Eqs. (3). As for the remainder, the set of equations for local occupancies (3) retains its structure. The concept of quasi-averages [56] regardless of the displacement of components greatly simplifies the procedure for calculating the functions of nonideality and thermodynamics; however, it retains the averaging procedure over vibrations. In QCA, the function of nonideality in Eq. (3) is rewritten as

$$\Lambda_q^i = \prod_{p=q-1}^{q+1} \sum_{k_{qp}^{i1}=0}^{z_{qp}(x,y)} \sum_{k_{qp}^{i2}=0}^{z_{qp}(x,y)-k_{qp}^{i1}} \cdots \sum_{k_{qp}^{is-1}=0}^{z_{qp}(x,y)-k_{qp}^{i1}-k_{qp}^{i2}-\dots-k_{qp}^{is-2}} \prod_{j=1}^s C_{z_{qp}(x,y)}^{\{k_{qp}^{ij}\}} [t_{fg}^{ij} \exp(-\beta \varepsilon_{fg}^{ij})]^{k_{fg}^{ij}} \times \frac{1}{Q_{q,\text{vib}}^i(\mathbf{k})}, \quad (16)$$

where  $C_{z_{qp}(x,y)}^{\{k_{qp}^{ij}\}} = z_{qp}(x,y)! / \prod_{j=1}^s k_{qp}^{ij}!$  is the number of combinations of the polynomial distribution for types  $s$ . The meaning of  $k_{qp}^{ij}$  remains unchanged, although the values of sites  $q$  and  $p$  increase. Symbol  $\mathbf{k}$  denotes the complete spectrum of atom and vacancy

distributions in a crystal. For the crystal volume, the number of vacancies inside cluster  $K$  does not exceed 2–3. In the transitional region of a rough crystal, the number of vacancies can be the same as in a fluid. Expressions for free energy (4)–(7) and local pressure (14) can be correspondingly rewritten. Upon moving to polylayer adsorption on single crystal faces, the number of site types above the face planes grows inside the adsorbent–adsorbate transitional region for which the surface potential is valid.

The same principle is also used in considering equations for bond lengths (12): the isolation of near-edge regions increases their number. It follows from the system of bond linkage according to the microscopic Gibbs–Duhem equation that as the size of a crystal shrinks, we must consider the contributions from edge and vertex atoms; however, in the planar face regions near the edges in the transitional regions (both normal to and along the face plane) the contributions to the thermodynamic characteristics in all atoms are altered too, due to changes caused by edge effects. This leads to the dependence of the surface tension of any face on its size and the type of the neighboring face. Gibbs mentioned the latter in [1], but it was ignored in subsequent works (it is missing in particular from Wolf's rule concerning the macroscopic faces of anisotropic crystals, rather than small microcrystals), although it is implicitly present in the general formulation of the Gibbs–Curie principle.

The four situations described above for macroscopic adsorbent–adsorbate interfaces retain their meaning, but now all adsorbent faces are related by the general conditions of chemical and mechanical equilibria. Analysis of the stability of these systems is especially important for possible processes of the structural rearrangement of the adsorbent during chemisorption. For a nonequilibrium adsorbent, the adsorbate effect occurs in exactly the same way as in situation 4.

It is normally assumed that equilibrium almost always exists for small bodies. As was shown by analyzing the relaxation times of the leveling of labeled atoms inside solid spheres with different radii [76–78], decelerations can be observed for long periods that exceed even the normal experimental times for nanosized samples. The effect of the time factor therefore cannot be excluded, even for small microcrystals.

### Porous Adsorbent Systems

An important example of a heterogeneous distribution of an adsorbent's components is the existence of a porous system inside it. According to [55, 63, 79, 80], the model of a porous body is two-phase: adsorbate–adsorbent interaction belongs to molecular level  $\lambda$  (the characteristic size of the adsorbate), and the description of pore distributions over the adsorbent grain volume and intergrain contacts belongs to supramolecular level  $L$  ( $L \gg \lambda$ ). The structure of a porous material

determines the relationship between the pore volumes and their near-wall regions, since the same amount of the adsorbate causes different deformations due to contact with the surface. Analysis shows that pores must have limited volumes in all three dimensions to ensure mechanical stability. On the other hand, the total surface must be large for the effect of perturbation inside the adsorbent to a depth of about  $t_{\text{sol}}$  monolayers to be noticeable with respect to the total adsorbent volume. The theory should include a model of contact interactions in the grain/microcrystal ensemble of which the real adsorbent consists. Contact interactions are associated with interaction forces between the grains and grain sizes; this determines the depth of grain deformation, which governs mechanical changes in the linear sizes of a sample. On the other hand, grain size is directly related to adsorbate–adsorbent interactions. Experimental measurements of changes  $\Delta L(\theta)$  in the linear size of a deformable sample with changes  $\theta$  in the amount of adsorbed material in this case have a molecular interpretation. A microscopic theory based on two-level models is being formulated [55, [63], 79, 80], though theoretical representations of contact interactions are now well developed for macroscopic systems [81–86].

The bonding energy of the adsorbate in a confined pore is expressed through atom–atom potentials as  $Q_{q,f} = \int_{\Omega} 4\epsilon_{Aj(s)} [(\sigma_{Aj(s)}/r)^{12} - (\sigma_{Aj(s)}/r)^6] n_s dV$ , where  $n_s$  is the particle distribution density in the adsorbent volume [63]; potential  $V_s$  of an adsorbate particle for interaction with atoms of a solid element can be expressed by an integral over the volume of a solid ( $\Omega = V_s$ ) using LD potentials;  $\rho$  is the distance from site  $f$  of solid part  $dV$ ;  $s$  corresponds to the adsorbent, and  $j$  is the atom interacting with adsorbate A. For the slit-like part of a pore with width  $H$ , the energy of interaction between adsorbate  $i$  is written as  $Q_q^i = \varphi_{is}(q) + \varphi_{is}(H - q + 1)$ , where  $\varphi_{is}(q)$  is defined above [69–71]. The adsorbate distribution is additionally affected by the potential of the opposite wall:  $1 \leq q \leq H$ .

The above equations consider the cooperative behavior of the adsorbate–adsorbent system at all degrees of occupancy. Let us discuss the distinction between a deformable adsorbent and a rigid one, which can be important for narrow pores at small  $\theta$  because of the combined effect of long-range potentials of walls when the potentials overlap, and the adsorbate plays a role of a bonding link. It is well known [69–71] that the potential of interaction between an adsorbate and a surface has a minimum near  $\lambda_1 = 1.2\sigma_{ss}$  that virtually vanishes at distances of  $2.5\text{--}3.0\sigma_{ss}$ . If the distance between the walls is short ( $\sim 2\text{--}3\lambda$ ), the adsorbate is in the middle between both walls, and its contribution to determining the bond lengths of the system reduces the distance between the opposite walls. If the pore width is  $\sim 4\text{--}6\lambda$ , the adsor-

bate is attracted to one of the walls; the second wall attracts it too, but this attraction is transferred to the first wall. This effect seems to increase the potential length of the walls by  $\lambda$ . When  $H$  is increased, the effect drops rapidly. The main contribution to a change in the force of interaction between the opposite walls comes from pores with sizes not exceeding  $\sim 6$  monolayers. For distances greater than 6 monolayers, a further increase does not enhance the direct action of the walls. The latter, however, does not correspond to the indirect effect of walls through the dense adsorbate phase, which is apparent when pore occupancy is nearly complete, or to the subsequent direct effect on wall deformation. Rather, it is due to repulsive forces between the rigid spheres of the adsorbate. If the system is highly irregular and has relatively large mechanical moduli, a reduction in grain size can be negligible for low adsorbate densities.

#### The Used Method

The approach in [54, 60] allows simultaneous operation with both changes in the composition of a solid body and the lengths of bonds between all pairs of components directly associated with their specific volume. This approach was derived in analogy with ordinary vapor–liquid solutions, in which the effects of partial volumes of components play an important role. All derivations in microscopic theory are known to be based on the potential interaction functions between components. When the potential functions of interparticle interaction are known, Newtonian equations are introduced for each atom, allowing us to write the equations for the microscopic motion of atoms in a complex lattice of a given symmetry [87–92]. Expressions are thus found for the vibrational spectrum of a system, its mechanical moduli, and the local pressures, depending on the mass and local environment of the atom under study at any nonequilibrium distribution of neighboring atoms. In equilibrium, these expressions become the local equations of state for the bulk phase. The general procedure for these derivations has long been known and is not repeated here [87–92].

The traditional approach in the theory of elasticity deals with atomic displacements rather than specific volumes of components. In it, the role of equations of state is played by the bulk moduli of elasticity. Expressions for these moduli are also derived through potential functions [87–92]. In this respect, the initial forms of Hamiltonians are fully equivalent in both [87–92] and the LGM [54–61]. Differences emerge at the stage of expanding the potential energy in terms of small displacements (i.e., the transition to displacement terms in the classical approach and operating with specific bond lengths in the LGM).

In dealing with specific volumes, the authors of [54, 60], arrived at an alternative interpretation of the description of deformations in crystals with regard to

microscopic distributions of mixture components, which allow reflection of their spatial distributions with allowance for defects and/or a wide range of structural heterogeneities. Calculated bond lengths  $\{\lambda_{fg}^{ij}\}$  between components  $i$  and  $j$  at lattice sites  $f$  and  $g$  are related to the local site volumes  $v_f^0$ . The curly brackets denote the complete set of component pairs  $1 \leq i, j \leq s - 1$ , where  $s - 1$  is the number of mixture components;  $s$  is the number of site occupancy states, including vacancies; and the latter  $s$  corresponds to them. Values  $v_f^0$  of the specific cell volumes are directly related through  $\{\lambda_{fg}^{ij}\}$  to rigid sphere parameters in Mie-type potential functions  $\varepsilon_{fg}^{ij}$  (or similar pair potentials).

The lattice symmetry and type of displacement are considered in the expansion of the potential function to find elastic coefficients and vibrational spectra when deriving equations for local pressures and bond values  $\{\lambda_{fg}^{ij}\}$ . The calculations are performed using current sets of  $\{\lambda_{fg}^{ij}\}$  values with no connection to an initial reference or any other state. Local interpretation of the system instead of a macroscopic one formally allows us to avoid restrictions on small deformations [81, 88], which do not always occur at interfaces. Macroscopic characteristics of the system are obtained when a successive connection of sites described by pair functions  $\theta_{fg}^{ij}$  is considered. Deformation characteristics are determined from the difference between calculations for the current crystal states and the initial state with  $\{\lambda_{fg}^{ij}\}_0$  values found for the reference states (or reference systems). In the reference states,  $\{\lambda_{fg}^{ij}\}_0$  values are found from the given type of the lattice symmetry and potential function by minimizing the potential energy (the free energy at  $T = 0$  K). This determines both the unit cell constant and the  $\lambda_{fg}^{ij}$  values inside a unit cell, which depend on the nature of quantum-chemical relations in the crystal.

The convenience of the new approach lies in the possibility of deriving *direct* expressions for thermodynamic potentials. For the Gibbs potential, our interpretation of the elasticity theory results in the expression  $G = F + P(V - V_0)$ , where  $F$  is the free energy,  $V$  is the current volume, and  $V_0$  is the initial undeformable volume, instead of the traditional thermodynamic expression  $G = F + PV$  [81]. The expression for the chemical potential within deformation potentials requires a transition from displacements to strain (through Hooke's equation) [90], while the expression for the chemical potential associated with the product of the local pressure and the specific volume is immediately obtained using this approach.

## CONCLUSIONS

Our microscopic theory can be applied to a much wider range of situations than the traditional thermodynamic Gibbs interpretation for ideally elastic deformation. It reflects the rearrangement of near-surface regions of adsorbents and relates any states of a body's deformation with atomic–molecular processes at both intermediate times for small chemical changes during an experiment and long times once all chemical changes have already occurred. The restriction according to which the vapor pressures of characteristic elements are much lower than the adsorbate vapor pressure is eliminated. This is important for series of oxides, hydrides, and other nonstoichiometric compounds with highly volatile components.

It has been shown that the existing thermodynamics of adsorbents and most solids is based on replacing nonequilibrium relationships with equilibrium ones. Under these conditions, we cannot use equations of caloric and thermal states to describe solids. Nonequilibrium bodies can be described by nonequilibrium analogs of equilibrium characteristics/potentials (the nonequilibrium analogs themselves are described by kinetic equations) that depend on the way these bodies are formed. For nonequilibrium analogs, however, the fundamental thermodynamic principle of the independence of thermodynamic functions from the way of transitioning from the initial to the final state is not observed [1]. The microscopic approach eliminates different thermodynamic failures and ensures explicit consideration of the nonequilibrium state of a solid in the form of passive forces [1], directed values [20], abstract internal variables [93], and so on.

The theory of elasticity [81, 94] focuses on external mechanical loads, while the study of physicochemical systems traditionally concerns systems without external loads [95–98]. The mechanical equilibrium of a system without an external load means compensation for the internal strain on any plane inside the body and its interfaces with any external mobile or solid phase. At the microscopic level, the transition to considering mechanical loads requires specification of the interaction between the solid being studied and the external bodies transmitting the mechanical load (e.g., during the formation of contact interactions in tribology) [75]. Gibbs' statement about the need to consider the degree of deformation of a solid [1] in a solid–mobile phase interface is not enough for a correct analysis of most solid-phase systems. Subsequent works did not provide a strict analysis of this statement, and the concept of the chemical nonequilibrium of a solid and the mechanical strain distributions determined by this factor are now often confused with the concept of the local mechanical stability of a system or a mechanical equilibrium that is always present in crystals.

The transition to the strictly statistical description of adsorbent nonequilibrium states allows us to relate

thermodynamic derivations to other measurements: structural, kinetic, mechanochemical, and so on.

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