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An integrated model for adsorption-induced strain in microporous solids

Samir H. Mushrif, Alejandro D. Rey*

Department of Chemical Engineering, McGill University, 3610 University Street, Montréal, Québec, Canada H3A 2B2

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Dedicated to Prof. Morton M. Denn on the occasion of his 70th birthday

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ABSTRACT

Deformation of porous materials during adsorption of gases, driven by physico- or chemo-mechanical couplings, is an experimentally observed phenomenon of importance to adsorption science and engineering. Experiments show that microporous adsorbents exhibit compression and dilation at different stages of the adsorption process. A new integrated model based on the thermodynamics of porous continua (assumed to be linear, isotropic and poroelastic) and statistical thermodynamics is developed to calculate the adsorption-induced strain in a microporous adsorbent. A relationship between the strain induced in the adsorbent and the equilibrium thermodynamic properties of the adsorbed gas is established. Experimental data of CO_2 adsorption-induced strain in microporous activated carbon adsorbents (Yakovlev, V.Y., Fomkin, A.A., Tvardovskii, A.V., Sinitsyn, V.A., 2005. Carbon dioxide adsorption on the microporous ACC carbon adsorbent. Russian Chemical Bulletin, International Edition 54, 1373–1377) is used to fit the model parameters and to validate the model. Assuming that the initial contraction in a microporous adsorbent is caused due to an attractive interaction between the adsorbed gas and the adsorbent, we demonstrate that there also exists a repulsive interaction amongst the adsorbed gas molecules and that this repulsive interaction can be correlated to the adsorption-induced strain. The proposed correlation can be extended to take into account the adsorbate–adsorbent attractive interaction in order to offer an undisputed and complete explanation of the adsorption-induced strain in microporous adsorbents.

1. Introduction

Adsorption is a phenomenon in which a solid surface with unbalanced forces, when exposed to a gas, bonds (physically in physisorption or chemically in chemisorption) to the gas molecules. The solid substrate is referred to as the adsorbent whereas the gas phase is the adsorbate. The solid adsorbent is usually a porous medium and the pores are classified as micropores (<20 Å), mesopores (20–50 Å), and macropores (>50 Å) (Everett, 1972). Adsorbents like alumina, silica, activated carbon, activated carbon fibers, zeolite, to name a few, are extensively used in separation and purification processes where physisorption takes place inside the pores and adsorption is analyzed as a volume phenomenon (Do, 1998). In the chemical industry, 90% of the chemicals are manufactured using catalytic processes (Masel, 1996) where adsorption is also studied as a 2-D surface phenomenon. Depending upon the pore size, the type of adsorption, and the underlying physics either approach is used to describe adsorption equilibria and kinetics.

Given the environmental, industrial, and chemical importance of adsorption, extensive experimental and theoretical research has been done in the field adsorption science and the review article by Dąbrowski (2001) critically summarizes the key developments. Most of these studies consider that an adsorbent is thermodynamically inert and it only contributes in inducing an external force field on the adsorbate. This assumption reduces the adsorption process to a thermodynamic phenomenon without any mechanics. However, the adsorbent may not be an inert component during the process of adsorption and this was first shown by Meehan (1927) when a dimensional change was observed in charcoal due to CO_2 adsorption. Wiig and Juhola (1949) and Haines and McIntosh (1947) also observed dimensional changes in carbonaceous adsorbents upon adsorption and more recently Levine (1996), Yakovlev et al. (2003, 2005), Day et al. (2008), and Cui et al. (2007) have also shown that dimensional changes take place in porous adsorbents during gas physisorption. Deformation and surface stresses are also caused during chemisorption and those have been experimentally observed by Packard and Webb (1988), Grossmann et al. (1994, 1996), and Gsell et al. (1998), to name a few.

Since an adsorbent cannot be inert during the process of adsorption, adsorption properties are bound to be affected due to the dimensional changes occurring in the solid. The degree of deformation can be as large as 50% (Reichenauer and Scherer, 2000) or as small as 0.1% (Yakovlev et al., 2005), but even a relatively small deformation can cause a substantial impact on the experimentally

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* Corresponding author. Tel.: +1 514 398 4196; fax: +1 514 398 6678.
E-mail address: alejandro.rey@mcgill.ca (A.D. Rey).

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determined equilibrium thermodynamic characteristics of the adsorption system (Yakovlev et al., 2003). For example, Kharitonov et al. (2001) showed that the differential molar isosteric heat of adsorption (CO_2-activated carbon system) increased in the initial adsorption region and the authors suggested that it was due to the contribution of energy from the adsorption deformation phenomenon. Yakovlev et al. (2005) further confirmed this fact by experimentally observing CO_2 adsorption-induced strain in a similar adsorbent and they also estimated the correction to the isosteric heat of adsorption for the non-inertness of the adsorbent to be 10–15%, when the strain was not more than 0.1%. In case of CO_2 and H_2S sequestration, even though the strain is small it has been reported that large stresses developed due to adsorption may significantly affect the geomechanical and permeability characteristics, thereby implicating sorption estimates (Cui et al., 2007; Day et al., 2008; Viete and Ranjith, 2006). Also in the case of chemisorption, it has been shown that not only the properties of the adsorbent but also the adsorbate properties are modified in a strained adsorbent (Packard and Webb, 1988; Gsell et al., 1998). Wu and Metiu (2000) also showed using atomistic level modeling of CO adsorption on Pd that the parameters controlling the thermodynamics of chemisorption, like binding energy and vibrational frequencies, were altered when the adsorbent was strained.

Recognizing the non-inertness of an adsorbent and realizing the significance of the effect of adsorption-induced strain and stress on: (i) the adsorption characteristics, (ii) the adsorbent, and (iii) the adsorbate, theoretical studies have also been performed in this field. Dergunov et al. (2005) developed a model which took into account the adsorption deformation to calculate the potential energy of adsorption. They showed that the maximum contraction in the adsorbent corresponds to the minimum stress. Recently Pan and Connell (2007) combined Myers' solution thermodynamics approach for adsorption in micropores (Myers, 2002) and Scherer's strain model (Scherer, 1986) to calculate gas adsorption-induced swelling in coal. Serpinskii and Yakubov (1981) had developed an analytical expression between the strain and the amount of gas adsorbed using vacancy solution theory and Hooke's law, but their expression required the bulk modulus to be a function of the amount of gas adsorbed, if compression and dilation in the adsorbent were to be observed. A similar approach was also taken by Jakubov and Mainwaring (2002), where they expressed the strain as a function of the amount of gas adsorbed and the difference between the chemical potentials of the gas, adsorbed on a strained and on an unstrained adsorbent. However, prior information of strain was required to calculate the chemical potential of the adsorbate that would have been adsorbed if the solid was prevented from strain. Ravikovitch and Neimark (2006) developed a non-local density functional theory-based model to calculate the adsorption-induced strain for Kr and Xe adsorption on zeolite. They were successfully able to reproduce the experimentally observed contraction and expansion of the adsorbent. When adsorption is treated as a 2-D surface phenomenon, Ibach (2004) showed that a Maxwell type relation exists between the dependence of chemical potential of an adsorbate on surface strain and the dependence of surface stress on coverage. Weissmüller and Kramer (2005) studied the metal–electrolyte system, using a continuum description of a solid adsorbent, where they identified experimentally measurable state variables in the system and established a relation between the state variables of the surface and those of an adsorbate. Lemier and Weissmüller (2007) also calculated hydrogen adsorption-induced strain in nanocrystalline Pd using the theory of thermochemical equilibrium in solids, developed by Larche and Cahn (1973), and by expressing the adsorption-induced strain as a function of state variables, pressure and chemical potential of the adsorbate. Müller and Saúl (2004) reviewed some key theoretical contributions in adsorption-induced stress on a plane surface, including some of the well recognized work of Ibach (1997).

In summary, the significant facts in the adsorption-induced stress and strain literature lead to the following observations: (i) experimental investigations clearly show the existence and implications of adsorption-induced strain and stress (Meehan, 1927; Haines and McIntosh, 1947; Wiig and Juhola, 1949; Levine, 1996; Kharitonov et al., 2001; Yakovlev et al., 2003, 2005; Viete and Ranjith, 2006; Cui et al., 2007; Day et al., 2008), (ii) theoretical studies are needed to better understand the phenomenon, (iii) some fundamentally significant research, using thermodynamic and atomistic approaches, has been done to study the effects of stress and strain on the physics of surface adsorption (Ibach, 1997, 2004; Wu and Metiu, 2000; Weissmüller and Kramer, 2005; Lemier and Weissmüller, 2007), and (iv) a better understanding of the adsorption-induced strain, particularly in microporous adsorbents like activated carbon and zeolites, where an adsorbent first undergoes contraction followed by an expansion, needs further research in this area. Hence, this paper focuses on the adsorption-induced strain in microporous adsorbents. Two previous significant and very valuable contributions in this problem are: (i) the recent work of Ravikovitch and Neimark (2006) using non-local density functional theory approach; however, in this work a simple relation between the adsorption-induced strain and an equilibrium adsorption property was not established and the strain was assumed to be entirely due to the deformation of pore space, thereby neglecting the change in the volume of the solid matrix (a solid adsorbent is composed of pore space and solid matrix, c.f. Fig. 2). (ii) Jakubov and Mainwaring (2002) developed a relation between the adsorption-induced strain and the difference in the chemical potentials of an adsorbate, when adsorbed on a strained and on an unstrained adsorbent and they make a similar assumption of strain in pore space only. However, when they calculate the difference in the chemical potentials using the difference in adsorption isotherms, on a strained and on an unstrained adsorbent, the magnitude of the difference in the isotherms appears to be too large (up to 50%) for the observed strain ($\leqslant$ 0.05%).

In the present paper: (i) we develop a simple relationship between the adsorption-induced strain and an equilibrium adsorption property by (ii) taking into account the strain in the solid matrix and in the pore space and (iii) we show that this relationship can be used to predict the adsorption-induced strain in microporous adsorbents, and (iv) can provide a molecular level explanation for the adsorption-induced strain which to the best of our knowledge has not been previously done. A novel feature of this model is the integration of adsorbent mechanics with statistical thermodynamics.

The organization of this paper is as follows. Section 2.1 presents the key equations of the mechanics and thermodynamics of porous adsorbents (Coussy, 2004) and the method to calculate the difference between the chemical potentials of the gas, adsorbed on a strained and on an unstrained adsorbent. The statistical mechanical model for the chemical potential difference is described in Sections 2.2 and 2.3 describes a method to predict the adsorption-induced strain by combining the approaches in Sections 2.1 and 2.2. Section 3 discusses and validates the results with previously presented experimental data (Yakovlev et al., 2005). Section 4 presents the conclusions.

2. Model development

Microporous adsorbents like activated carbon and zeolites exhibit a typical deformation behavior where the adsorbent undergoes contraction in the initial stage of adsorption and later it expands. An illustration of this behavior is shown in Fig. 1, where the adsorption-induced strain is plotted as a function of amount of gas adsorbed. As mentioned above, the model is based on the integration of the