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Martin Schoen, Gerrit Günther. Capillary condensation in deformable mesopores: Wetting versus nanomechanics.. Molecular Physics, 2010, pp.1. 10.1080/00268976.2010.513346 . hal-00627930

HAL Id: hal-00627930

<https://hal.science/hal-00627930>

Submitted on 30 Sep 2011

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Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2010-0296
Manuscript Type:	Special Issue Paper -EIGHTH LIBLICE CONFERENCE on the Statistical Mechanics of Liquids
Date Submitted by the Author:	19-Jul-2010
Complete List of Authors:	Schoen, Martin; Technische Universität Berlin, Stranski-Lab. f. Physikalische und Theoretische Chemie Günther, Gerrit; Stranski-Lab. f. Phys. und Theor. Chemie
Keywords:	Phase transition, Capillary condensation, Sorption strain, Monte Carlo simulation
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
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Capillary condensation in deformable mesopores: Wetting versus nanomechanics.

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(Dated: July 19, 2010)

Abstract

We employ grand canonical ensemble Monte Carlo simulations to investigate the strain experienced by a nanoscopic slit pore when this pore fills with fluid material. Both solid substrates of our model system consist of a single layer of solid atoms bound to their equilibrium lattice sites by a harmonic potential such that these atoms are thermally coupled to molecules of a fluid phase confined between them. Parameters are tuned such that they represent an experimental situation in which pentane is adsorbed by mesoporous silica. Our focus is on strain isotherms, that is the net deformation of the solid as fluid material is imbibed by the pore. At low pressures prior to pore filling strain isotherms are dominated by wetting characteristics of the fluid-solid interface whereas nanomechanical properties of the pore may be deduced quantitatively from high-pressure portions of the strain isotherm after the pore is completely filled with fluid. To that end we introduce a thermodynamic analysis of the high-pressure portion of the sorption isotherm that permits us to determine the elasticity of the confining solid material in terms of a so-called pore-load modulus that is accessible experimentally.

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I. INTRODUCTION

Nanoconfined fluids have been under intense investigation for quite some time because of their unique and fascinating properties [1–4]. These properties are caused by a competition between several length scales such as the range of the intermolecular interaction potentials, the characteristic dimensions of the nanoscopic container to which the fluid is confined, or any chemical or geometrical patterns with which the inner surfaces of these containers may be endowed.

A particularly interesting realization of nanoconfined soft-matter phases are fluids adsorbed to mesoscopic porous solids. These systems have received a lot of attention because they play a key role in many important applications or processes such as nanoreactors in catalysis [5], filtering processes [6], or the purification of tiny amounts of multi-component mixtures [7]. Most of these applications are possible only because of the large internal surface of mesoporous materials. The broad variety of practical applications has spurred the development of many different mesoporous materials such as glasses and ceramics [8] or various carbon materials [9]. Very recently, even metallic systems have been synthesized [10]. A broad variety of adsorbates ranging from classical polar and nonpolar fluids [11, 12] to quantum fluids [13] have been investigated. Particularly prominent examples both from an experimental and from a theoretical perspective are mesoporous silicas such as MCM-41 [14] or SBA-15 [15]. This is because these mesoporous solids consist of regular hexagonal arrays of parallel, unconnected cylindrical pores with typical pore widths in the range of 2–10 nm. These materials are particularly fascinating because the pore-size distribution is narrow and because individual pores are accurate to shape.

Compared with a single solid surface, confinement to spaces of nanoscopic dimensions has important ramifications for adsorption and desorption phenomena (which we shall subsequently subsume under the term “sorption”) and therefore for the phase behavior of such nanoconfined fluids [1–4]. From a broad spectrum of theoretical approaches ranging from density functional theory over integral-equation techniques to computer simulations a rather detailed picture of phase transitions in nanoconfinement has emerged over the years [1–4]. Traditionally, in almost all these studies the confining solid material has been perceived as a representation of a *temporally* static external field that may only vary *spatially*. An example of this kind of a situation is a fluid confined by nonplanar or chemically patterned substrates

[3] where neither the geometry nor the shape of the chemical pattern varies with time. In other words, the underlying assumption in the overwhelming number of previous works has been that the mesoporous solid does not “respond” to whatever changes may occur in the thermophysical properties of the confined fluid phase. However, it has recently been demonstrated by us that deformability of the mesoporous matrix may have important consequences for the phase behavior of the confined fluid [16]. Consequently, we deviate from most earlier work by allowing the external field to vary during the course of the simulation (i.e., with time). This permits us to consider confining substrates that may to a certain extent deform in response to changes in the thermodynamic state of the confined fluid.

Our approach is motivated by the experimental observation that mesoporous materials can by no means be considered to be completely rigid. Mechanical deformation has been observed, for example in mesoporous silicon, where the lattice constant is changed in comparison to bulk silicon upon fluid sorption and condensation [17]. Other examples are mesoporous glasses that were found to deform elastically during capillary condensation [12, 18]. Moreover, mechanical deformation of the solid support has been observed in mesoporous metals as a consequence of surface charging or fluid wetting and condensation [19, 20]. This shows that the enormous amount of surface per unit volume makes a significant contribution to the total energy of the system in mesoporous materials. By using a single-pore model it could be demonstrated by Günther *et al.* that pore deformation has a marked impact on the location of phase boundaries between coexisting gas- and liquid-like phases of the confined fluid [18]. Prass *et al.* recently showed that elastic properties of the mesoporous solid may be determined quantitatively from *in-situ* small-angle X-ray diffraction experiments during the sorption process [12].

One of the interesting consequences of this condensation-induced deformation is that it constitutes a *macroscopic* signature of a *microscopic* effect related to the nature of the fluid phase in the mesopores. In this sense, macroscopic deformation of the solid support may be used to sense fluid condensation or, conversely, the support can be seen as being actuated by changes in the pores at the molecular level. Recently, nanoporous metals have been discussed as actuators driven by various signals on the internal surface, such as charge or fluid condensation [19, 20]. Here, we discuss similar effects in glassy silica, which, compared to metals, have the advantage of comparatively low reactivity, as well as higher stiffness and lack of plastic deformation. Our focus will be on strain isotherms, that is the strain

“experienced” by the solid matrix as the pore fills with fluid. At low pressures, at which only a thin fluid film is adsorbed onto the solid surfaces, strain isotherms depend on wetting characteristics of the solid material. However, once the pore is completely filled with fluid material strain isotherms reflect the elasticity of the confining solid.

Our paper is organized as follows. In Sec. II we give a brief account of relevant experimental techniques and results. In Sec. III we introduce our model system. Relevant methodological and theoretical aspects of the Monte Carlo simulations, on which this work is based, are summarized in Sec. IV. Section V is given to a presentation of the results obtained which are discussed and put into perspective in the concluding Sec. VI.

II. EXPERIMENTAL BACKGROUND

To make contact with a specific experimental situation we focus on sorption experiments [21] employing ordered mesoporous silica of the type MCM-41 [14]. These materials consist of grains of roughly $1\text{ }\mu\text{m}$ size, containing cylindrical nanopores on a well ordered two-dimensional hexagonal pore lattice with pore diameter of the order of 3–4 nm and narrow size distributions. Typical lattice parameters, pore sizes, as well as the pore volume fractions of these materials are listed in Table 2.1 of Ref. 21. For the sake of concreteness we focus only on experiments using pentane as the adsorbate. During the sorption process *in-situ* X-ray diffraction measurements are performed using synchrotron radiation [22]. The experimental setup is described elsewhere [11, 23] and consists essentially of a thermostatted sample chamber with X-ray transparent windows, which is connected to a fluid reservoir via a gas dosing system. The gas pressure in the sample chamber is changed slowly but continuously while the X-ray powder patterns are recorded. This provides datasets of the diffracted intensity as a function of the relative gas pressure P/P_0 and the magnitude of the scattering vector q . Upon filling the contrast between the solid matrix and the interior of the pores changes. Therefore, a decrease in diffracted intensity with increasing P/P_0 can be attributed to enhanced adsorption of fluid material by the mesoporous matrix.

The region of capillary condensation is easily recognized as a sharp drop in intensity from the diffraction data due to the contrast change upon pore filling [see Fig. 2.1(a)]. The Bragg peaks from the ordered pore lattice show characteristic shifts with gas pressure [see

FIG. 2.1: (a) Characteristic X-ray diffraction patterns measured isothermally as functions of gas pressure from $P = 0$ to the bulk vapor pressure at coexistence P_0 . Part (a) shows the azimuthally averaged diffraction profiles as a function of P/P_0 and the magnitude of the scattering vector $q = (4\pi/\lambda) \sin \theta$ where 2θ is the scattering angle and λ is the X-ray wavelength. The sharp drop in intensity at $P/P_0 \simeq 0.35$ indicates capillary condensation. The shift of the 11 peak in this region is clearly seen in part (b) of the figure. From Ref. 21 - reproduced by permission from the PCCP owner societies.

Fig. 2.1(b)]. From data such as the ones shown in Fig. 2.1 one may calculate a lattice strain

$$\varepsilon \equiv \frac{a(P) - a_0}{a_0} = \frac{q_{hk}(0) - q_{hk}(P)}{q_{hk}(P)} \quad (2.1)$$

as a quantitative measure of substrate deformation during the sorption process. In Eq. (2.1), $a(P)$ and a_0 are the lattice constants of the hexagonal array of cylindrical pores filled with fluid at pressure P and of the empty mesoporous matrix, respectively. Similarly, $q_{hk}(P)$ and $q_{hk}(0)$ are the magnitudes of the scattering vector of the respective Bragg peak hk at bulk pressure P and of the empty mesoporous matrix. The far right side of Eq. (2.1) obtains because $q_{hk} \propto 1/a$. As the relative shifts were identical for all reflection orders hk , it has been concluded that the associated lattice strain ε is isotropic within the plane perpendicular to the pore axis [12]. This implies that during the sorption process the radius of each pore changes isotropically such that its cylindrical shape remains unaffected as well as its length. Hence, the deformation of the sample may be discussed appropriately in terms of the scalar quantity ε defined in Eq. (2.1). This experimental result is important to validate the parallel theoretical model to be introduced in Sec. III. Strain isotherms $\varepsilon(P)$ are reversible and show

also the characteristic hysteresis between condensation and evaporation in the regime where capillary condensation occurs.

The parallel theoretical analysis is based upon a couple of assumptions. First, we assume the filling of these pores to be essentially controlled by the (slightly different) widths of individual pores. Pores of different widths are distributed randomly across the macroscopic grains of which the mesoporous solid consists. If the pressure P in a bulk reservoir is larger than that pressure at which capillary condensation occurs in an *individual* pore of a certain width *all* pores up to the same pore diameter would completely and spontaneously be filled with a liquid-like phase. Like the empty pores of the pristine sample these now liquid-filled pores are also distributed at random across the mesoporous grains.

It has been suggested recently [24–26] that upon filling with liquid the subsequent deformation of an individual pore might have an impact on neighboring pores as well and this would cause a transmission of sorption-induced strain over a certain distance in the mesoporous solid. This, in turn, could affect the pore size distribution such that pores of certain sizes are no longer randomly distributed across the sample. Instead, a sorption-strain driven spatial correlation of pore sizes could exist which then would lead to some sort of clustering of liquid-filled pores in specific regions of the mesoporous solid. This notion prompted Grosman and Ortega [25] to propose a long-range interaction between individual pores through which local elastic strains are transmitted through the mesoporous solid. These authors base their proposition on detailed analyses of sorption isotherms where the surmised correlation effects can be ascertained only rather *indirectly*. However, very recent neutron scattering experiments on SBA-15 silica contradict the clustering phenomenon [27]. The neutron scattering data are fully consistent with the assumption that the spatial distribution of pores of different sizes remains random despite the sorption-induced deformation of individual pores in the sample. This observation permits us to theoretically describe the sorption process essentially in terms of a *single* isolated pore.

Moreover, as long as very narrow pores of typical widths of only a few nanometers are concerned, the precise geometry of the pore is subdominant. For example, capillary condensation, which constitutes a gas-to-liquid phase transition in nanoporous materials, occurs in slit-pores and in cylindrical pores irrespective of pore geometry. To establish contact between theory and experiment in this manuscript we estimate both the diameter σ of a hypothetical pentane molecule in a dense liquid phase and a realistic distance s_{z0} of the

substrates of our empty model slit-pore as described in detail in Ref. 21.

Introducing next the concept of a *degree of confinement* [28] permits us to match the cylindrical pores of the experimental systems to a model slit-pore in the Monte Carlo simulations where both have the same ratio of pore volume to surface area. Applying this concept we obtain a pore width of $s'_{z0} = 4.8\sigma$ for the empty model slit-pore based upon experimental data for MCM-41(16) (see Table 2.1 of Ref. 21) which we adopt for sake of concreteness and to enable a direct comparison between experimental and theoretical data discussed in this work. Finally, noticing that both wall atoms and fluid molecules are assumed to be of the same size and on account of repulsive forces between them there is a distance of about σ at each of the solid substrates that is inaccessible to fluid molecules. Thus, the correct width of our slit pores (in units of σ) is given by $s_{z0} = s'_{z0} + 2 = 6.8$ which is the value used in all our Monte Carlo simulations throughout this work. In a similar spirit we wish to abstract from details of the chemical structure of the adsorbate to keep the complexity of any model system to the absolute minimum. For a study of gas-liquid phase transition the only necessary ingredient are attractive van der Waals forces between the molecular constituents. This is reflected by the fact that even a simple mean-field type of approach is capable of capturing key aspects of the effect of nanoconfinement on gas-liquid phase transitions in both pure fluids and binary mixtures [2].

III. MODEL SYSTEM

We base the theoretical work of the present study on a model consisting of spherically-symmetric particles (i.e., wall atoms *and* confined-fluid molecules) which we assume to interact with each other in a pairwise additive fashion. In view of the experimental situation summarized in Sec. II we base our numerical analysis on a model of maximum simplicity retaining, however, key features of the experimental situation. Specifically, we express the fluid-fluid contribution to the total configurational energy as

$$U_{\text{ff}}(\mathbf{R}) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1 \neq i}^N u(r_{ij}) \quad (3.1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between molecules i and j located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ represents the configuration of fluid molecules,

$$u(r) = \begin{cases} u_{\text{sh}}(r), & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (3.2)$$

where

$$u_{\text{sh}}(r) = u_{\text{LJ}}(r) - u_{\text{LJ}}(r_c) - \left. \frac{du_{\text{LJ}}(r)}{dr} \right|_{r=r_c} (r - r_c) \quad (3.3)$$

is a so-called shifted-force potential. Unlike the full Lennard-Jones (LJ) potential

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.4)$$

$u_{\text{sh}}(r)$ vanishes continuously together with its first derivative (i.e., the intermolecular force) at the radius r_c of a cutoff sphere centered on $\mathbf{r}_i$. Throughout this work we use $r_c = 3.5\sigma$ for *all* interactions. Because of its definition and unlike $u_{\text{LJ}}(r)$, $u_{\text{sh}}(r)$ is explicitly short-range which is advantageous in the Monte Carlo simulations on which this work is based [2, 29]. In Eq. (3.4), σ is the “diameter” of a fluid molecule and ϵ determines the strength of intermolecular interactions in the usual manner where we henceforth identify σ with the diameter of a hypothetical spherical pentane molecule.

As in our previous work [16, 18, 21, 30] fluid molecules are confined by two planar solid substrates. The substrates consist of individual solid atoms whose equilibrium positions are distributed according to the (100) plane of the face-centred cubic (fcc) lattice where $\ell/\sigma = \sqrt[3]{4}$ is the lattice constant. Hence, the substrates are characterized by an areal density $\rho_s = 2/\ell^2$. Equilibrium positions of substrate atoms are so arranged that they are distributed across an area A_0 in the x - y plane. In this case the distance between each pair in upper and lower substrate is s_{z0} . Because the substrates are atomically structured there is a fluid-solid (fs) contribution to the total configurational energy. It can be cast as

$$U_{\text{fs}}(\mathbf{R}, \mathbf{R}_s) = \alpha \sum_{k=1}^2 \sum_{i=1}^N \sum_{j=1}^{N_s} u(|\mathbf{r}_i - \mathbf{r}_j^{[k]}|) \quad (3.5)$$

where $N_s = 2n^2$ is the total number of substrate atoms located in wall k and n is an integer specifying the number of unit cells of the fcc (100) plane. In Eq. (3.5), $\mathbf{R}_s = (\mathbf{r}_1^{[1]}, \dots, \mathbf{r}_{N_s}^{[1]}, \mathbf{r}_1^{[2]}, \dots, \mathbf{r}_{N_s}^{[2]})$ represents the configuration of substrate atoms in both substrates identified through the superscripts. The potential u in Eq. (3.5) is given in Eq. (3.2). The

(dimensionless) parameter α is introduced in Eq. (3.5) to vary the strength of the fluid-substrate interaction relative to that of the fluid-fluid interaction.

Because we are concerned with sorption-induced deformations of the substrates and the impact of these deformations on the sorption process the substrates themselves need to be thermally coupled to the confined fluid phase. This way they can respond to whatever change in the thermodynamic state of the confined fluid may occur. Thermal coupling requires the substrate atoms to be able to depart from their equilibrium lattice sites $\{\mathbf{r}_{i0}^{[k]}\}$ to a certain extent under the action of both neighboring solid atoms and fluid molecules. Thermal coupling causes a deformation of the solid substrates such that a solid-solid contribution to the total configurational energy arises. It may be cast here as

$$U_{ss} = \sum_{k=1}^2 \left[\alpha^2 \sum_{i=1}^{N_s-1} \sum_{j=i+1}^{N_s} u(|\mathbf{r}_i^{[k]} - \mathbf{r}_j^{[k]}|) + \kappa \sum_{i=1}^{N_s} |\mathbf{r}_i^{[k]} - \mathbf{r}_{i0}^{[k]}|^2 \right] \quad (3.6)$$

In this expression u is again given by Eq. (3.2). The first term on the right side of Eq. (3.6) is necessary because substrate atoms must not approach each other arbitrarily (and therefore unrealistically) close. To prevent the substrates from “melting” we bind each solid atom to its equilibrium lattice site by introducing a harmonic potential [see second term in brackets in Eq. (3.6)] where $\kappa > 0$ determines the binding strength (i.e., the “stiffness” of a harmonic spring). In other words, κ is a measure of rigidity of the substrates. For values of κ used below we utilized a modified Lindemann criterion to ensure that over the temperature ranges studied the solid substrates do in fact not melt [30]. Hence, in the system of interest the total configurational energy may be expressed as [see Eqs. (3.1), (3.5), and (3.6)]

$$U(\mathbf{R}, \mathbf{R}_s; \kappa) = U_{ff}(\mathbf{R}) + U_{fs}(\mathbf{R}, \mathbf{R}_s) + U_{ss}(\mathbf{R}_s; \kappa) \quad (3.7)$$

and depends on $\mathbf{R}$, $\mathbf{R}_s$, and κ as a parameter. Setting $\kappa \geq 30$ and $s_z = 6.8\sigma$ guarantees that pairs of solid atoms bound to different substrate planes do not interact with one another.

IV. THEORETICAL AND NUMERICAL ASPECTS

As we pointed out in Sec. II experimentally the adsorbate is in contact with a bulk reservoir of the same fluid. Ideally the two are in thermodynamic equilibrium during the sorption process. Assuming the reservoir to be sufficiently large such that its density does not change appreciably during the sorption process, which is guaranteed by the experimental setup,

suggests the grand potential Ω as the natural thermodynamic potential for the subsequent analysis of strain isotherms. As we already demonstrated elsewhere [21] the exact differential of Ω may be cast as

$$d\Omega(T, \mu, A, s_z) = -\mathcal{S}dT - Nd\mu - P_{\parallel}s_{z0}dA - P_{zz}A_0ds_z \quad (4.1)$$

where T is temperature, $\mathcal{S}$ is entropy, N is the number of molecules of which the adsorbate consists, and μ is its chemical potential. The last two terms in Eq. (4.1) represent the mechanical work associated with components $P_{\parallel}$ and P_{zz} of the pressure tensor $\mathbf{P}$ acting in directions parallel and perpendicular to the plane of the solid substrates, respectively. Because no shear forces are acting on the confined fluid, $\mathbf{P}$ is diagonal. Notice also that on account of nanoconfinement $P_{\parallel} \neq P_{zz}$ in general whereas

$$\lim_{s_z \rightarrow \infty} P_{\parallel} = \lim_{s_z \rightarrow \infty} P_{zz} = P \quad (4.2)$$

Because of thermal coupling between adsorbate and adsorptive both the fluid-solid interfacial area A and the substrate distance s_z may in principle deviate from the equilibrium values A_0 and s_{z0} [21].

To link the above phenomenological treatment to a molecular level of description we employ conventional concepts of statistical thermodynamics. To that end

$$\Omega = -k_B T \ln \Xi \quad (4.3)$$

is the key expression where k_B is Boltzmann's constant,

$$\Xi = \sum_{N=0}^{\infty} \exp(\beta\mu N) \mathcal{Q} \quad (4.4)$$

is the grand canonical partition function, and $\beta \equiv 1/k_B T$. In the classical limit [2], with which we are exclusively concerned in this work, the canonical-ensemble partition function may be cast as

$$\mathcal{Q} = \frac{\mathcal{Z}}{\Lambda^{3(N+2N_s)} N!} \quad (4.5)$$

where

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (4.6)$$

is the thermal de Broglie wavelength, h is Planck's constant, and m is the mass of a fluid molecule. We note that all thermodynamic quantities of interest can be expressed as partial

derivatives of $\ln \Xi$ with respect to T , μ , A , or s_z [31]. Therefore, the value of m does not matter as one can verify from Eqs. (4.1)–(4.6) and as one would have anticipated for an equilibrium situation all along. The specific form of Eq. (4.5) results from an integration over momentum subspace formed by the N fluid molecules and $2N_s$ substrate atoms each of which possess three translational degrees of freedom. Substrate atoms, which are bound to their individual equilibrium lattice sites [see Eq. (3.6)], are distinguishable such that only the factor $1/N!$ arises for the (indistinguishable) fluid molecules in the denominator of Eq. (4.5). Finally, for our system of interest the configuration integral in Eq. (4.5) is then given by

$$\mathcal{Z}(T, N, N_s, A, s_z) = \int d\mathbf{R} \int d\mathbf{R}_s \exp[-\beta U(\mathbf{R}, \mathbf{R}_s; \kappa)] \quad (4.7)$$

where the dependence on A and s_z is buried in the limits of integration with respect to fluid-particle coordinates [see, for example, Eq. (3.10) of Ref. 31].

The integration over substrate-atom configurations reflects the thermal coupling between the substrate and the confined fluid which causes the deformability of the former. In other words, for finite κ the substrates cannot be treated as a *static* external field over the course of the simulation but are part of the system in the same spirit in which the specific configuration of a porous matrix enters the statistical physical analysis of quenched-annealed models of disordered mesoporous materials (see, for example, Chap. 7.2 of Ref. 2). The reader should also note that through the introduction of the harmonic binding potential in Eq. (3.6) we are *effectively* dealing with a macroscopically thick solid substrate where more remote lattice planes (beyond the one in immediate contact with the confined fluid phase) are taken into account in a continuum type of fashion through the stiffness parameter κ .

In the actual Monte Carlo simulations we place N fluid molecules in a rectangular simulation cell of volume $V = A_0 s_z$. For a typical (non-critical) liquid-like state $N \approx 700$ depending on the choice of T and μ . In a standard simulation the walls comprise $2N_s = 256$ solid atoms such that each solid surface consists of $n = 8$ unit cells in both (x - and y -) directions corresponding to sidelengths $s_0 = s_{x0} = s_{y0} \simeq 12.7$ of the simulation box. We refer to a “Monte Carlo cycle” as a sequence of $N + 2N_s$ attempted sequential displacements of all particles followed by N attempted creations or destructions of fluid molecules where N denotes the actual number of molecules present in the system at the beginning of the cycle. Typical simulations comprise between 5×10^5 and 10^6 such cycles and are therefore rather long. The generation of a Markov chain in configuration space proceeds in a stan-

dard fashion [2, 31]. Because all interaction potentials are short-ranged we employ periodic boundary conditions at the planes $x = \pm s_0/2$ and $y = \pm s_0/2$. To save computer time a Verlet neighborlist is combined with a link-cell list [32].

V. RESULTS

A. Strain isotherms

As we have argued in Sec. II the specific experimental conditions permit us to describe the sorption process essentially in terms of a single pore. However, this poses an immediate problem to a direct comparison with the experimental results which were obtained for a regular array of disconnected individual pores. On account of its regularity the mechanical state of the latter may be characterized by a sorption-induced lattice strain ε defined in Eq. (2.1). Obviously, for the theoretical model a meaningful definition of ε is impossible because we are dealing with a *single* pore rather than with an ordered *array* of pores. However, a change of a in the experimental system suggests that upon sorption of fluid material each individual pore of the entire matrix changes its width so that ε will be proportional to that change. However, the experimental observation of in-plane isotropy of the lattice strain permits us to discuss substrate deformation in terms of a single scalar parameter, too (see Sec II). To that end we define an *effective* pore width

$$s_z^{\text{eff}} \equiv \langle z^{[2]} \rangle - \langle z^{[1]} \rangle \quad (5.1)$$

where

$$\langle z^{[k]} \rangle \equiv \frac{1}{N_s} \left\langle \sum_{i=1}^{N_s} z_i^{[k]} \right\rangle \quad (5.2)$$

and $\langle \dots \rangle$ denotes an average in the grand canonical ensemble. With these definitions we introduce the pore strain

$$\xi = \frac{s_z^{\text{eff}} - s_{z0}}{s_{z0}} \quad (5.3)$$

as a quantitative measure of deformation of the slit-pore. The above considerations immediately suggest that $\varepsilon \propto \xi$ thereby enabling a qualitative comparison between experiment and simulation (see also Sec. VI).

Figure 5.1 confirms this expectation. For a subcritical isotherm $T = 1.00$ both experimental and theoretical data are plotted as functions of the *reduced* pressure P/P_0^+ of the

FIG. 5.1: Lattice strain ε (experiment) ($\bullet$) and substrate strain ξ (theory) ($\circ$) as functions of P/P_0^+ where the factor 10^4 applies to both quantities (see text, left ordinate). The full line is intended to guide the eye. Theoretical data are obtained for $s_z = 6.8$, $\kappa = 50$, $\alpha = 1.2$ [see Eq. (3.5)], and $T = 1.00$; experimental data are presented for n-pentane in MCM-41(16) as a mesoporous matrix (see Table 2.1 of Ref. 21 and Sec. II). Also shown is the sorption isotherm ρ ($\triangle$) (right ordinate) which changes discontinuously at $P/P_0^+ = 1$. From Ref. 21 - reproduced by permission from the PCCP owner societies.

bulk reservoir with which the confined fluid phase is in equilibrium where P_0^+ is the (bulk) pressure at which capillary condensation occurs. The overall agreement between theoretical and experimental data is very gratifying especially in view of the relative crudeness of the theoretical model. The reader should note, however, that on account of this crudeness of the theoretical model P_0^+ will differ between the experimental and theoretical data sets. However, apart from this restriction the plots in Fig. 5.1 reveal a remarkable, semi-quantitative agreement of the two sets of data. We therefore conclude that with proper calibration the theoretical model is sufficiently realistic to reveal molecular details about the relation between substrate deformation and the sorption process in mesoporous materials. That the discontinuity at $P/P_0^+ = 1.00$ reflects capillary condensation is inferred from a discontinuous change in the sorption isotherm also plotted in Fig. 5.1. In our Monte Carlo simulations we have direct access to the pressure (or chemical potential) at phase coexistence and the associated mean densities of the fluid in the pore through the procedure described in Ref. 16. Note also that the sorption isotherm plotted in Fig. 5.1 does not exhibit hysteresis unlike its

experimental counterpart would. Hysteresis is due to the existence of metastable thermodynamic states of considerable lifetime. However, within the framework of an equilibrium simulation method such as Monte Carlo metastability must be regarded an artifact with no real physical meaning as was pointed out quite some time ago by Schoen *et al.* [33].

That both lattice strain ε and pore strain ξ drop to negative values at capillary condensation can be understood if one keeps in mind that condensation of fluid phases depends crucially on *attractive* intermolecular interactions. Hence, at capillary condensation the solid atoms in our slit-pore model are subject to an attractive field exerted by the condensed liquid-like confined fluid which consequently pulls them inward. This causes $s_z^{\text{eff}} < s_z$ because of our definition of the effective pore width given in Eq. (5.1). Therefore, at capillary condensation $\xi < 0$ as one can easily verify from Eq. (5.3). Another macroscopically motivated argument for the drop of the lattice strain to negative values was used in Ref. 12. It is based on the Laplace pressure between the liquid- and the gas phase separated by a meniscus. As this pressure is negative, a compressive deformation of the pore walls is expected at capillary condensation.

Data plotted in Fig. 5.1 are obtained for $\alpha = 1.20$ [see Eq. (3.5)], that is for pore walls that are wet by the adsorbate. To investigate the impact of different wetting scenarios on the shape of the strain isotherm in more detail we plot in Fig. 5.2 data for different strengths of the fluid-substrate interaction by varying α in Eq. (3.5). Focusing on low-pressure portions of the isotherms first we see from Fig. 5.2(a) that ξ increases slightly with P up to that pressure at which capillary condensation occurs ($P/P_0 \simeq 0.70$). Over a comparable range of pressures the plot in Fig. 5.2(b) indicates that $\xi \approx \text{const.}$ if one enhances the wettability of the substrate from $\alpha = 1.0$ to 1.5. For substrates that are even better wet by the fluid phase the plot in Fig. 5.2(c) reveals that even at low bulk pressures the slope of the sorption strain is negative indicating that in this case the fluid-substrate attraction is strong enough to slightly pull the solid atoms inward even before the pore begins to imbibe fluid material appreciably.

These phenomena can be correlated with variations of P_{zz} . There exist two different ways of deriving molecular expressions for P_{zz} . Traditionally, we refer to those as the “force” and “virial” routes (for details of the derivation, see Appendix E. 3 of Ref. 2). As these terms indicate the former simply expresses the normal component of the pressure tensor as the

FIG. 5.2: Sorption strain ξ ($\bullet$) (left ordinate) as a function of pressure P/P_0 in the bulk reservoir where the full line is a fit to the discrete data points. Also shown are data for P_{zz}^{id} ($-\cdot-$), P_{zz}^{pot} ($\cdots$), and P_{zz} ($---$) (right ordinate); (a) $\alpha = 1.0$, (b) $\alpha = 1.5$, (c) $\alpha = 2.0$ [see Eq. (3.5)].

TABLE 5.1: Comparison of virial and force expressions for P_{zz} . Also listed is the associated pore strain ξ computed from Eq. (5.3).

s_z	Eq. (5.6)		Eq. (5.4)		$\sigma_{zz} \times 10^4$
	$P_{zz}^{\text{id}} + P_{zz}^{\text{ff}}$	P_{zz}^{fs}	P_{zz}	P_{zz}	
1.5	0.502	3.235	3.737	3.739	1076.4
1.6	0.481	2.061	2.542	2.544	683.8
1.7	0.455	1.011	1.466	1.467	371.8
1.8	0.432	0.128	0.560	0.561	139.1
1.9	0.411	-0.555	-0.144	-0.142	-24.4
2.0	0.396	-1.047	-0.651	-0.649	-131.3
2.1	0.390	-1.357	-0.967	-0.965	-186.0
2.2	0.400	-1.476	-1.076	-1.072	-204.7
2.3	0.441	-1.421	-0.980	-0.975	-177.9
2.4	0.542	-1.171	-0.629	-0.622	-105.0
2.5	0.721	-0.769	-0.048	-0.038	-1.3
3.0	0.580	-0.695	-0.115	-0.109	-6.6
3.5	0.615	-0.638	-0.023	-0.017	6.8
4.0	0.421	-0.616	-0.195	-0.196	-12.5
5.0	0.351	-0.469	-0.118	-0.135	-5.0

mean force exerted by the fluid on the substrate. It may be cast as [37]

$$P_{zz} = \frac{\text{sgn}(\langle F_z^{[1]} \rangle)}{2A_0} \sum_{k=1}^2 |\langle F_z^{[k]} \rangle| \quad (5.4)$$

where [see Eq. (3.5), Ref. 31]

$$F_z^{[k]} = - \sum_{i=1}^N \sum_{j=1}^{N_s} \frac{\partial}{\partial z_{ij}^{[k]}} u(r_{ij}^{[k]}) \quad (5.5)$$

$r_{ij}^{[k]} = |\mathbf{r}_i - \mathbf{r}_j^{[k]}|$, and $\text{sgn } x = \pm 1$ if $x \gtrless 0$, respectively. In a similar fashion the “virial”

route leads to

$$P_{zz} = P_{zz}^{\text{id}} + P_{zz}^{\text{pot}} \quad (5.6)$$

where

$$P_{zz}^{\text{id}} = \frac{\langle N \rangle k_B T}{A_0 s_z} \quad (5.7a)$$

$$P_{zz}^{\text{pot}} = P_{zz}^{\text{ff}} + P_{zz}^{\text{fs}} = -\frac{1}{2} \frac{1}{A_0 s_z} \sum_{i=1}^N \sum_{j=1}^N \langle u'(r_{ij}) r_{ij} (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{e}}_z)^2 \rangle$$

$$- \frac{1}{A_0 s_z} \sum_{k=1}^2 \sum_{i=1}^N \sum_{j=1}^{N_s} \left\langle u'(r_{ij}^{[k]}) r_{ij}^{[k]} \left[(\hat{\mathbf{r}}_{ij}^{[k]} \cdot \hat{\mathbf{e}}_z) (\hat{\mathbf{r}}_{ij}^{[k]} + \delta \hat{\mathbf{r}}_{ij}^{[k]}) \cdot \hat{\mathbf{e}}_z \right] \right\rangle \quad (5.7b)$$

where notation “ $\hat{\cdot}$ ” is used to refer to unit vectors. In particular $\hat{\mathbf{e}}_z$ is a unit vector pointing along the z -axis of the Cartesian coordinate system. In Eq. (5.7b)

$$\delta \hat{\mathbf{r}}_{ij}^{[k]} \equiv (\mathbf{r}_i^{[k]} - \mathbf{r}_{i0}^{[k]}) - (\mathbf{r}_j^{[k]} - \mathbf{r}_{j0}^{[k]}) \quad (5.8)$$

accounts for the departure of both solid atoms i and j from their respective equilibrium lattice sites. For reasons explained in Ref. 31 there is no contribution to P_{zz} from solid-solid interactions. Because of the different functional forms of Eqs. (5.4) and (5.5) on one hand and (5.6) and (5.7) on the other hand, “force” and “virial” routes provide an internal consistency check on reliability of Monte Carlo simulations. Notice also that mechanical stability requires $\langle F_z^{[1]} \rangle + \langle F_z^{[2]} \rangle = 0$. Entries in Table 5.1 illustrate the agreement between “force” and “virial” routes.

Plots in Fig. 5.2 illustrate the correlation between P_{zz} and ξ . In particular, the marked drop of ξ at pore filling is accompanied by a substantial decrease of P_{zz} . Once the pore is filled with a liquid-like phase further increase of the bulk pressure causes both P_{zz} and ξ to increase, too. Even at bulk pressures below pore filling the initial slope of ξ seems correlated with the variation of P_{zz} even though this correlation is more difficult to see on account of the small values of P_{zz} in this regime. Nevertheless, the dependence of ξ on α in Fig. 5.2 prior to pore filling indicates that in the low-pressure regime the pore strain depends on wetting characteristics of the substrate. To see this we analyze the local density

$$\rho(z) \equiv \left\langle \sum_{i=1}^N \delta(z - z_i) \right\rangle = \frac{\langle N(z) \rangle}{A_0 \delta_z} \quad (5.9)$$

where $\delta(z - z_i)$ denotes the Dirac δ -function and $\delta_z = 0.01$ is the width of a histogram entry to which we bin the local number of fluid molecules $N(z)$. Plots in Fig. 5.3 show

that $\rho(z) = 0$ in the immediate vicinity of the substrate surfaces on account of repulsive fluid-substrate interactions. As one moves away from the substrate surfaces both curves exhibit a maximum representing a wetting layer of fluid. As one may have anticipated the maximum is much more pronounced for $\alpha = 2.0$ compared with $\alpha = 1.0$ reflecting stronger fluid-substrate attraction in the former case. That the fluid wets the substrate much better for $\alpha = 2.0$ is also indicated by the formation of a secondary layer of fluid molecules located at larger distances from either substrate. In turn, the curve for $\alpha = 1.0$ does not exhibit a similar secondary peak. To illustrate the difference in wetting characteristics we have selected thermodynamic states characterized by the same density $\rho(z) \simeq 0.028$ in the bulk-like region of the adsorbate centered on $z = 0$. Because of the different strengths of the fluid-substrate interaction this approach requires to choose different chemical potentials for the confined fluid such that its thermodynamic state is different for different α .

FIG. 5.3: Local density $\rho(z)$ as a function of position z between lower ($z/s_{z0} = -0.5$) and upper substrate ($z/s_{z0} = +0.5$); (—) $\alpha = 1.0$ $\mu = -12.15$, (---) $\alpha = 2.0$, $\mu = -13.00$ where $\kappa = 30$ and $T = 1.0$ in both cases.

However, once the pore is filled with a liquid-like phase variations of the wetting characteristics of the substrate do not matter as one might have anticipated intuitively. This is illustrated in Fig. 5.4 where the pore strain is plotted as a function of the bulk pressure for various values of α . As one can see from the plot all data sets collapse onto a straight line irrespective of α . The reader should appreciate that in Fig. 5.4 data are presented over a

range from moderately drying ($\alpha = 0.75$) to strongly wetting ($\alpha = 1.50$) substrates. This observation is in line with experimental results where for the same mesoporous solid ε turns out to be independent of the chemical nature of the confined fluid [12].

FIG. 5.4: Pore strain ξ as a function of bulk pressure P on a logarithmic scale. Data are presented for various strengths of the fluid-substrate interaction α indicated in the figure [see Eq. 3.5]. Solid line is a linear fit to guide the eye.

If, on the other hand, the deformability of the substrates is altered the pore strain changes markedly. This can be seen from Fig. 5.5 where ξ still depends linearly on $\ln(P/P_0)$ similar to the plot in Fig. 5.4 but the slope of the straight lines increases with decreasing stiffness of the harmonic binding potential in Eq. (3.6). Similar effects have been seen experimentally for various MCM materials (see Fig. 9 of Ref. 21). Depending on conditions of the synthesis of the mesoporous solids materials with different pore widths D and lattice parameters a_0 can be realized. If a_0 varies the thickness of the solid matrix between neighboring pores changes, too. Therefore, materials with larger a_0 are expected to be stiffer. Plots in Fig. 9 of Ref. 21 reveal that the slope of lattice strain ε versus $\ln(P/P_0)$ decreases with increasing a_0 similar to the variation of pore strain ξ with κ in the theoretical model (see Fig. 5.5). Once again this observation supports our earlier notion that $\varepsilon \propto \xi$ and provides additional support for the validity of our single-pore model.

FIG. 5.5: As Fig. 5.4, but for various values of κ [see Eq. (3.6)]; ($\circ$) $\kappa = 30$, ($\square$) $\kappa = 40$, ($\triangle$) $\kappa = 50$, ($\diamond$) $\kappa = 100$. Perfectly rigid substrates ($\kappa = \infty$) would be represented by a horizontal line $\xi = 0$.

B. Thermomechanical analysis and quasi-Kelvin equation

To rationalize the logarithmic dependence of ξ on P we start from Eq. (4.1). For the subsequent discussion it will prove useful to introduce the Gibbsian potential $\mathcal{G} \equiv \Omega + A_0 s_z P_{zz}$ as the relevant thermodynamic potential through a Legendre transformation of Ω such that

$$d\mathcal{G} = -SdT - Nd\mu - P_{\parallel}s_{z0}dA + A_0s_zdP_{zz} \quad (5.10)$$

follows. Under conditions of fixed T , μ , and P_{zz} , $\mathcal{G}$ is *approximately* a homogeneous function of degree one in A as we explained elsewhere [21]. Hence, we may apply Euler's theorem which gives (see, for instance, Appendix A.3 of Ref. 2)

$$\mathcal{G} \approx -As_{z0}P_{\parallel} \quad (5.11)$$

Taking the exact differential of this expression ($s_{z0} = \text{const}$) and combining it with Eq. (5.10) the Gibbs-Duhem equation

$$0 = -SdT - Nd\mu + As_{z0}dP_{\parallel} + A_0s_zdP_{zz} \quad (5.12)$$

obtains without much ado. Equation (5.12) expresses the fact that an equation of state of the form $P_{zz} = P_{zz}(T, \mu, P_{\parallel})$ exists *in principle* even though we do not know its functional form.

To proceed we perform a *gedankenexperiment* in which we decompose the entire confined fluid into a lamella of thickness s_z and finite extent A in the x - y plane. Henceforth, the lamella is perceived as “the system” in a thermodynamic sense. Consequently, the remainder of the confined fluid plus the bulk are taken as “the environment”. The planes $x = \pm s_x/2$ and $y = \pm s_y/2$ separating the system from the environment may be viewed as imaginary and immaterial pistons through which the system can exchange mechanical work with its environment. It is then conceivable that upon varying the bulk pressure P one could readjust the pistons such that $P_{\parallel}$ is held constant. The mechanical work done on the system would then be completely transformed into a change of the lamella’s thickness s_z . Therefore, under the conditions of the *gedankenexperiment* we may drop the term $As_{z0}dP_{\parallel}$ in Eq. (5.12). Notice also that the *gedankenexperiment* is fully consistent with the experimental observation of in-plane isotropy of the lattice strain which prevents pores from changing their length as the pressure of the bulk reservoir varies.

Hence, under conditions of fixed T and $P_{\parallel}$ we may rearrange terms and integrate Eq. (5.12) to obtain

$$\mu^l [P_{zz}(P_0), T] = \mu^l [P_{zz}(P), T] + \frac{1}{\rho^l} [P_{zz}(P_0) - P_{zz}(P)] \quad (5.13)$$

where superscript “l” is used to emphasize that we focus solely on liquid-like thermodynamic states of the confined fluid, that is a situation in which the pore is completely filled with fluid material. We take this fluid to be incompressible such that its density $\rho^l \equiv N^l/A_0s_z \simeq \text{const.}$ Notation $P_{zz}(P_0)$ refers to the normal component of $\mathbf{P}$ at *bulk* saturation, that is at the bulk pressure P_0 at which the sorption experiment naturally ceases at a any given T . Obviously, this notation already takes notice of the fact that experimentally the confined fluid is in thermodynamic equilibrium with a bulk-gas reservoir maintained at some pressure P and temperature T . Note that for Eq. (5.13) to make sense, $P \leq P_0$ must hold, too.

Under conditions of both experiment and simulation the confined liquid-like fluid is in thermodynamic equilibrium with bulk gas. Therefore, we may write

$$\mu^l [P_{zz}(P_0), T] = \mu_b^g(P_0, T) = \mu_0 + k_B T \ln P_0 \quad (5.14a)$$

$$\mu^l [P_{zz}(P), T] = \mu_b^g(P, T) = \mu_0 + k_B T \ln P \quad (5.14b)$$

where μ_b^g is the chemical potential of a gaseous bulk phase at the same P and T . The far right side of Eqs. (5.14) obtains if we assume this bulk gas to be ideal with μ_0 being the standard-state chemical potential. Inserting now Eqs. (5.14) into Eq. (5.13) gives a

FIG. 5.6: Plot of m versus $1/\kappa$ (●) [see Eq. (5.18)] using the Monte Carlo data presented in Fig. 5.5. Also shown is the dependence of m on α (○) using data presented in Fig. 5.3 where each point represents the slope of a best (linear) fit to an individual data set characterized by a specific value of α . Lines (---) and (—) are fits intended to guide the eye.

quasi-Kelvin equation, namely

$$P_{zz}(P) = \rho^l k_B T \ln \frac{P}{P_0} + P_{zz}(P_0) \quad (5.15)$$

Finally, to rationalize the plots in Fig. 5.5 we notice that under realistic conditions and for the present class of materials the substrate deformation is rather minute and typically of the order of 10^{-4} . For such small deformations it seems reasonable to assume that the substrate responds to the confined fluid as a Hookean solid for which we may write

$$P_{zz}(P) = M\xi(P) \quad (5.16)$$

where we call M the “pore-load modulus”. Because of its definition, M is a quantitative measure of nanomechanical properties of the mesoporous solid. Combining Eqs. (5.15) and (5.16) permits us to write

$$\xi(P) \propto \frac{\rho^l k_B T}{M} \ln \frac{P}{P_0} \quad (5.17)$$

which gives the linear dependence of ξ on $\ln(P/P_0)$ already suggested by the plots in Figs. 5.4 and 5.5. Realizing in addition that M is a measure of deformability of the solid substrates and because the confined liquid-like phase was assumed incompressible from the outset [i.e.,

$\rho^l \approx \text{const}$, see Eq. (5.13)] one anticipates

$$m \equiv \frac{\rho^l k_B T}{M} \propto \frac{1}{\kappa} \quad (5.18)$$

under isothermal conditions. The plot in Fig. 5.6 confirms the linear dependence of m on $1/\kappa$ quite nicely. In retrospect, this indicates that concepts borrowed from phenomenological thermodynamics of macroscopic systems in combination with Hooke's Law for elastic solids provide an understanding of nanomechanical properties of mesoporous solids. The apparent applicability of these concepts demonstrated above provides a novel route for an experimental determination of nanomechanical properties of mesoporous solids from the response of the porous matrix to a liquid-like adsorbate.

VI. SUMMARY AND CONCLUSIONS

In this paper we discuss pore-strain isotherms computed in grand canonical ensemble Monte Carlo simulations of a “simple” Lennard-Jones fluid confined to a nanoscopic slit-pore. In the simulations we employ a *single* slit-pore model. The walls of this slit-pore are composed of one (explicitly treated) layer of solid atoms bound to their equilibrium lattice sites through a harmonic binding potential of variable stiffness. The binding potential serves as a means to prevent the layer of solid atoms from melting and also mimics in a continuum sense the remainder of the solid matrix behind the first layer of atoms forming its surface. Hence, solid atoms may depart from their equilibrium lattice sites because of their own kinetic energy, their interaction with neighboring solid atoms, and under the influence of their interaction with adsorbate molecules. Because solid atoms may move slightly during the course of the simulation a pore strain ξ may be calculated from an ensemble average of positions of the solid atoms. By tuning parameters of the model a semi-quantitative agreement between the measured lattice strain ε and ξ over the entire pressure range is obtained. This indicates that the somewhat simplistic model employed in the Monte Carlo simulations is sufficiently realistic to capture the essential physics governing the experimental results.

We focus primarily on branches of the strain isotherm *before* and *after* pore filling. Prior to pore filling the initial slope of the strain isotherm depends on the strength of the fluid-solid attraction. If this interaction is sufficiently weak the pore initially expands whereas

contraction is observed if the fluid-substrate interaction strength exceeds a certain threshold. These observations suggest that initially (i.e., at low bulk pressure) strain isotherms are dominated by wetting phenomena. This interpretation is further corroborated by plots of the local density showing that in the pressure regime considered the confined fluid consists of a thin film that is more strongly adsorbed by the solid material if the fluid-solid interaction is stronger.

A qualitatively different dependence of the strain isotherms is observed once the pore is completely filled with a liquid-like phase. In this regime the pore strain always increases with bulk pressure and exhibits a linear dependence on $\ln(P/P_0)$. We rationalize this linear relationship through a simple thermodynamic analysis which leads to an equation that permits one to deduce elastic properties of the porous solid (namely, the pore-load modulus). Experimentally, it is observed that the pore-load modulus varies as the pore volume fraction of the mesoporous solid is changed. However, the pore-load modulus turns out to be independent of the chemical nature of the confined fluid phase [12]. Similar observations are made in this work where we demonstrate that the high-pressure part of the strain isotherms is independent of the strength of the fluid-substrate interaction. In the theoretical model a change of the stiffness of the harmonic binding potential accounts for a change of the mesoporous material similar to that in the corresponding experimental system. In agreement with the experimental findings [21] it is observed in the Monte Carlo simulations that the linear relationship between ξ and $\ln(P/P_0)$ is preserved whereas the slope changes with varying stiffness of the confining solid material.

However, regardless of whether thermodynamic states prior or after pore filling are concerned the form of the strain isotherm appears to be correlated with variations of the normal component P_{zz} of the pressure tensor $\mathbf{P}$. Intuitively, one would expect such a correlation which indicates that variations of P_{zz} with increasing bulk pressure P are the cause of pore deformation. The dependence of P_{zz} on the bulk pressure P is equivalent to the dependence of the Laplace pressure Π of a liquid droplet (or a gas bubble) on P as predicted by the celebrated Kelvin equation [34]. However, the Kelvin equation is usually derived by considering the coexistence of gas and liquid phases along an (arbitrarily) curved interface of some mean curvature. This thermodynamic analysis is combined with force-balance considerations at the gas-liquid-solid interface of a drop sitting on a substrate and in equilibrium with surrounding gas.

The reader should note that the above derivation of a quasi-Kelvin expression given in Eq. (5.15) does not invoke assumptions about the specific geometrical properties of or forces acting on an interface between coexisting phases. The isomorphism between Kelvin's equation and Eq. (5.15) is merely a consequence of the assumption of thermodynamic equilibrium between a liquid and a gas phase as stated in Eqs. (5.14) where the latter is perceived as ideal. In textbook derivations of Kelvin's equation [34] the interpretation of P and P_0 would be that of the gas pressure at saturation at a *curved* and at a *planar* interface, respectively. Thus, the reader should appreciate the different physical situations depicted by Eq. (5.15) as opposed to that to which Kelvin's equation applies. Nonetheless, because Eq. (5.15) is identical in form with the classical Kelvin equation [except for the additive term $P_{zz}(P_0)$], the use of such a thermodynamic expression together with a simple mechanical picture is useful to understand nanomechanical properties upon fluid condensation, as was shown in Ref. 12. The simple Kelvin equation approach was used to derive a pore-load modulus for materials with pore diameters as small as 3nm. For such small pores, the pore filling mechanism should not proceed via liquid-bridge formation (i.e., formation of menisci), but rather via an axial filling mode [35]. However, because Eq. (5.15) is functionally equivalent to the classical Kelvin equation, but is not restricted to a specific filling mode via formation of a meniscus, the use of this phenomenological approach should not break down even for very small pores and should therefore remain extremely useful to understand and quantify nanomechanical properties upon fluid condensation.

However, very recently it has been suggested that for nanoporous metals surface-stress effects may outweigh the (Laplace-) pressure related phenomena discussed within the scope of the present model [36]. However, it remains to be demonstrated beyond doubt that for the present class of mesoporous solids, which are much more rigid than the metallic systems considered in Ref. 36, the scenario discussed by these latter authors is also applicable. In fact, assuming lattice strains to be caused by the pressure in the confined fluid alone, Prass *et al.* were able to extract realistic values of the nanomechanical properties of the mesoporous matrix [12]. This experimental observation sheds some doubt on whether or not the more sophisticated analysis put forth in Ref. 36 is required for mesoporous silica materials. In turn, the experimental results obtained in Ref. 12 validate the present numerical analysis.

Acknowledgments

We thank Oskar Paris (Montanuniversität Leoben) and Peter Fratzl (Max-Planck-Institut für Kolloid- und Grenzflächenforschung) for many fruitful discussions and for providing the experimental data presented in Fig. 2.1. Financial support from the Deutsche Forschungsgemeinschaft (Collaborative Research Area 448 “Mesoscopically structured composites”) is gratefully acknowledged.

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