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Thermodynamic pressure of a fluid confined in a random porous medium

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Up to now, none of the previously derived expressions is usable in simulations for the practical calculation of the thermodynamic pressure of a fluid adsorbed in a random porous medium. A *bona fide* virial expression of this pressure is presented. Contrary to what was believed, we show that this pressure is a measurable quantity and propose an experimental procedure for its measurement.

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Fluid adsorption in porous media has wide applications, e.g., catalysis using porous catalysts, petroleum recovery from porous rocks, and membrane separation processes. The behavior of fluids confined in porous media can undergo drastic modifications compared to that of bulk fluids [1]. A thorough understanding of the thermodynamic and transport properties of confined fluids provides the basis for improving or inventing technologies in the above domains of applications. Many porous solids, e.g., porous glasses and aerogels, can be classified as random porous media which can be characterized by a connected random pore space with a pore size distribution. A very useful and simple model has been proposed by Madden and Glandt [2] for the fluid adsorption in random porous media. Many investigations on both theoretical formalisms and numerical simulations have been devoted to study Madden-Glandt model. The derivation of the statistical-mechanics expression for the pressure of a fluid confined in a random porous medium has not been a straightforward task. Madden has given an expression for the pressure by appealing to the analogy between the quenched-annealed system and a normal fluid mixture [3]. Using a replica technique, Rosinberg, Tarjus, and Stell (RTS) derived a very complicated virial expression for the pressure in a quenched-annealed system and pointed out the expression given by Madden is incorrect [4]. By considering mechanical equilibrium, one of us derived a simple expression for the fluid pressure in a random porous medium [5] which is now called the mechanical pressure (defined as the trace of the pressure tensor satisfying the hydrostatic equation) to distinguish it from that given by RTS (considered as thermodynamic pressure). Kierlik *et al.* (KRTM) found an expression of the thermodynamic pressure without appealing to the replica technique and showed that the thermodynamic pressure is not equal to the mechanical one [6]. Unlike the mechanical pressure, none of the expressions for the thermodynamic pressure (neither RTS nor KRTM expressions) can be used for calculating it from simulations. The origin of this difficulty is that Kierlik *et al.* derived in fact a partial differential equation which should be satisfied by the thermodynamic pressure rather than a virial equation itself. In this work, we show how to derive a *bona fide* virial equation for the thermodynamic pressure truly useful for simulation calculations. Up to now, it is not clear if the thermodynamc pressure in a random porous medium is experimentally measurable. We derived also an exact relation between the fluid pressure inside a porous sample and that in a fluid reservoir outside the sample. This provides, for the first time, the basis of an experimental method for measuring the fluid pressure inside a porous medium.

In all the theoretical works done up to now, the porous sample (denoted also as matrix) and the fluid occupy a single and the same volume. In fact, this restriction is unnecessary for the Madden-Glandt model. In such quenched-annealed systems, a given matrix sample is completely specified by N_0 (number of matrix particles), V_0 (volume of the matrix), and Υ_0 (temperature at which the matrix is prepared) if it is described by a canonical ensemble. The fluid put in a control volume (denoted by V_1) can have a size different from that of V_0 (see Fig. 1). The walls of V_1 are restrictive only to the fluid particles but not to the matrix ones. Choosing a different control volume for the fluid is the key point and allows for a direct calculation of the thermodynamic pressure without resorting to any replica technique. For the system depicted in Fig. 1, it is natural to define the thermodynamic pressure as

$$P = -\left(\frac{\partial F}{\partial V_1}\right)_{T,N_1,N_0,V_0,\Upsilon_0}, \tag{1}$$

where T and N_1 are the temperature and the number of fluid particles. It is to be emphasized that Υ_0 is the temperature at

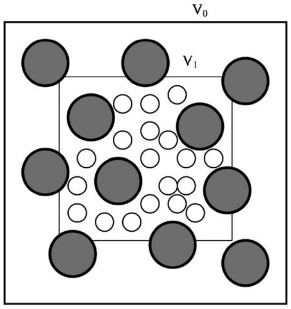

FIG. 1. Sketch of the different control volumes for fluid (V_1) and matrix (V_0). Shaded spheres denote matrix particles and the unshaded ones fluid particles.

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*Corresponding author: Wei.Dong@ens-lyon.fr which the matrix is prepared. Once quenched, the rigid matrix does not have a temperature equal to Υ_0 which becomes just a parameter characterizing the matrix structure. The Helmholtz free energy is given by

$$F = \langle F(\mathbf{q}^{N_0}) \rangle_0, \tag{2}$$

where $F(\mathbf{q}^{N_0})$ is the free energy for a given matrix realization which depends on the configuration of the matrix particles denoted by $\{\mathbf{q}^{N_0}\}$:

$$F(\mathbf{q}^{N_0}) = -kT \ln\left(\frac{Q_1(\mathbf{q}^{N_0})}{\lambda^{3N_1}}\right), \tag{3}$$

where $\lambda = (2\pi\hbar/mkT)^{1/2}$ is the thermal wave length and $Q_1(\mathbf{q}^{N_0})$ is the configurational partition function of the fluid in the external field of a given matrix realization:

$$Q_1(\mathbf{q}^{N_0}) = \frac{1}{N_1!}\int_{V_1} d\mathbf{r}^{N_1} e^{-\beta(U_{11}+U_{10})}, \tag{4}$$

where $\beta = 1/kT$, U_{11} and U_{10} are, respectively, the potential energy of fluid-fluid interaction

$$U_{11} = \sum_{i=1}^{N_1} \sum_{j=2,j>i}^{N_1} u_{11}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{5}$$

and that of fluid-matrix interaction

$$U_{10} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_0} u_{10}(|\mathbf{r}_i - \mathbf{q}_j|). \tag{6}$$

The angle bracket in Eq. (2) denotes the average over matrix configurations and takes the following form in a canonical ensemble:

$$\langle(\cdots)\rangle_0 = \frac{1}{Q_0 N_0!}\int_{V_0} d\mathbf{q}^{N_0} e^{-\beta_0 U_{00}}(\cdots), \tag{7}$$

where $\beta_0 = 1/k\Upsilon_0$, U_{00} is the potential energy of matrix-matrix interaction, and Q_0 the configurational partition function of the matrix. The derivative with respect to V_1 in Eq. (1) can be carried out by using the following change of variables:

$$\mathbf{r}_i = (V_1)^{1/3}\mathbf{a}_i, \tag{8}$$

where $\mathbf{a}_i$ is a vector contained in a unit volume. We obtain the following expression for the pressure:

$$\begin{aligned} P &= \frac{kTN_1}{V_1} - \frac{1}{6V_1}\left[2\int_{V_1} d\mathbf{r}_1 \left\langle \rho_1^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})\sum_{j=1}^{N_0} u'_{10}(|\mathbf{r}_1 - \mathbf{q}_j|)\frac{(\mathbf{r}_1 - \mathbf{q}_j)\cdot\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{q}_j|}\right\rangle_0 + \int_{V_1} d\mathbf{r}_1 \int_{V_1} d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2| u'_{11}(|\mathbf{r}_1 - \mathbf{r}_2|)\langle \rho_{11}^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{q}^{N_0})\rangle_0\right] \\ &= \frac{kTN_1}{V_1} - \frac{1}{6V_1}\left[2\int_{V_1} d\mathbf{r}_1 \int_{V_0} d\mathbf{q}_1 \rho_{10}^{(2)}(\mathbf{r}_1,\mathbf{q}_1) u'_{10}(|\mathbf{r}_1 - \mathbf{q}_1|)\frac{(\mathbf{r}_1 - \mathbf{q}_1)\cdot\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{q}_1|} + \int_{V_1} d\mathbf{r}_1 \int_{V_1} d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2| u'_{11}(|\mathbf{r}_1 - \mathbf{r}_2|)\rho_{11}^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|)\right], \end{aligned} \tag{9}$$

where $\rho_1^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})$ and $\rho_{11}^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{q}^{N_0})$ are, respectively, the one- and two-body distribution functions of the fluid in the field of a given matrix configuration and $\rho_{10}^{(2)}(\mathbf{r},\mathbf{q})$ and $\rho_{11}^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|)$ are the two-body distribution functions after the homogenization procedure over matrix configurations which are defined by

$$\rho_{10}^{(2)}(\mathbf{r},\mathbf{q}) = \left\langle \sum_{j=1}^{N_0} \delta(\mathbf{q} - \mathbf{q}_j)\rho^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})\right\rangle_0 \tag{10}$$

and

$$\rho_{11}^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = \langle \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{q}^{N_0})\rangle_0. \tag{11}$$

Although the above results are based on canonical ensembles for both the fluid and the matrix, other ensembles can be used. For example, the thermodynamic pressure can also be defined by

$$P = -\left(\frac{\partial\langle \Omega_1(\mathbf{q}^{N_0};T,\mu_1,V_1,\Upsilon_0,N_0,V_0)\rangle_0}{\partial V_1}\right)_{T,\mu_1,\Upsilon_0,N_0,V_0}, \tag{12}$$

when the fluid is described by a grand-canonical ensemble and the matrix by a canonical ensemble or by

$$P = -\left(\frac{\partial\langle \Omega_1(\mathbf{q}^{N_0};T,\mu_1,V_1,\Upsilon_0,\mu_0,V_0)\rangle_0}{\partial V_1}\right)_{T,\mu_1,\Upsilon_0,\mu_0,V_0}, \tag{13}$$

when the fluid and the matrix are described both by a grand-canonical ensemble (Ω_1: grand potential). It can be easily checked that either Eq. (12) or (13) leads to the same expression as Eq. (9). It is quite satisfactory to see this independence on the used ensembles. It is to note that the method used by Kierlik *et al.* [6] can be valid only when the matrix is described by a grand-canonical ensemble. Either Eq. (12) or (13) allows us to derive the following generalization of the Gibbs-Duhem equation:

$$\left(\frac{\partial P}{\partial \mu_1}\right)_T = \langle \rho_1^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})\rangle_0. \tag{14}$$

Now, we will discuss in some details the relation of the expression given in Eq. (9) to the ones published previously. First of all, we emphasize that although our result in Eq. (9) looks quite similar at first sight to an expression given previously by Madden [see Eq. (37) in Ref. [3]], it is crucial to note also the difference between them. In the second term on the right-hand side of Eq. (9), the integration of $\mathbf{r}_1$ and that of

$\mathbf{q}_1$ are over different volumes while these integrations are over the same volume in Madden's result. It is highly important to recoganize this difference to be able to understand why Madden's expression [Eq. (39) in Ref. [3]] leads to a wrong result in the case of an ideal gas in a hard sphere matrix. As stated explicitly in Ref. [3], the expression $(\mathbf{r}_1-\mathbf{q}_1)\cdot\mathbf{r}_1/|\mathbf{r}_1-\mathbf{q}_1|$ in the fluid-matrix cross term is replaced by $(\mathbf{r}_1-\mathbf{q}_1)\cdot(\mathbf{r}_1-\mathbf{q}_1)/|\mathbf{r}_1-\mathbf{q}_1|=|\mathbf{r}_1-\mathbf{q}_1|$. This then transforms the fluid-matrix cross term into $\int d\mathbf{r}ru'_{10}(r)\rho^{(2)}_{10}(r)$ [see Eq. (39) in Ref. [3]]. When Eq. (39) in Ref. [3] is applied to an ideal gas in a hard sphere matrix, one obtains the wrong result $P=kT[\rho_1+\pi\rho_1\rho_0\sigma_0^3/6]$ (σ_0: diameter of matrix particle; ρ_1, ρ_0: fluid, matrix densities), while the right result is simply $P=kT\rho_1$ (see Refs. [4] and [5]). In contrast, our result in Eq. (9) leads to the correct result in the following way. In the more general case of $V_1\neq V_0$, the transformation made by Madden is not valid since the fluid-matrix term is no longer symmetric under the permutation of $\mathbf{r}_1$ and $\mathbf{q}_1$. So, we keep $(\mathbf{r}_1-\mathbf{q}_1)\cdot\mathbf{r}_1/|\mathbf{r}_1-\mathbf{q}_1|$ in the cross term of Eq. (9). When $V_1<V_0$, the cross term in Eq. (9) vanishes for an ideal gas in a hard sphere matrix due to the angular integration of $\mathbf{q}_1$. In such a way, Eq. (9) leads to the right result $P=kT\rho_1$. We emphasize also that the cross term does not vanish if the fluid is not an ideal gas. In this case, the angular integration does not vanish because the integrand in the cross term does not have spherical symmetry near the boundary of V_1, i.e., $\rho^{(2)}_{10}(\mathbf{r},\mathbf{q})\neq\rho^{(2)}_{10}(|\mathbf{r}-\mathbf{q}|)$. So, the thermodynamic pressure given by Eq. (9) is not identical to the mechanical pressure obtained by Dong [5] due to the cross term, which is absent in the latter. This confirms the finding of KRTM [6].

Two other expressions for thermodynamic pressure in the literature were derived either from

$$P=-\left(\frac{\partial\langle\Omega_1(\mathbf{q}^{N_0})\rangle_0}{\partial V}\right)_{T,\mu_1,\rho_0}, \tag{15}$$

when the fluid and the matrix are described respectively by a grand-canonical and canonical ensemble [4], or from

$$P=-\left(\frac{\partial\langle\Omega_1(\mathbf{q}^{N_0})\rangle_0}{\partial V}\right)_{T,\mu_1,\mu_0}, \tag{16}$$

when the fluid and the matrix are described both by a grand-canonical ensemble [6]. An immediate question here is whether these expressions are identical to that given in Eq. (9). Since it was claimed that the above two definitions are equivalent [6], we will only focus on the comparison of Eq. (9) with the result of KRTM, which can be written as

$$\begin{aligned}P={}&\frac{kTN_1}{V}-\frac{1}{6V}\left[2\int_V d\mathbf{r}_1\int_V d\mathbf{q}_1|\mathbf{r}_1-\mathbf{q}_1|u'_{10}(|\mathbf{r}_1-\mathbf{q}_1|)\rho^{(2)}_{10}(|\mathbf{r}_1-\mathbf{q}_1|)+\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2|\mathbf{r}_1-\mathbf{r}_2|u'_{11}(|\mathbf{r}_1-\mathbf{r}_2|)\rho^{(2)}_{11}(|\mathbf{r}_1-\mathbf{r}_2|)\right]\\&+\frac{kT}{V}\langle N_0\ln\Xi_1(\mathbf{q}^{N_0})\rangle_0-\frac{1}{6V}\left\langle\ln\Xi_1(\mathbf{q}^{N_0})\sum_{i=1}^{N_0}\sum_{j=2,j>i}^{N_0}u'_{00}(|\mathbf{q}_i-\mathbf{q}_j|)|\mathbf{q}_i-\mathbf{q}_j|\right\rangle_0-P_0\langle\ln\Xi_1(\mathbf{q}^{N_0})\rangle_0,\end{aligned} \tag{17}$$

where $\Xi_1(\mathbf{q}^{N_0})$ is the grand partition function of the fluid for a particular matrix realization

$$\Xi_1(\mathbf{q}^{N_0})=\sum_{N_1=0}^{\infty}\frac{z_1^{N_1}}{N_1!}\int_V d\mathbf{r}^{N_1}e^{-\beta(U_{11}+U_{10})}, \tag{18}$$

[$z_1=\exp(\beta\mu_1)/\lambda^3$: fluid fugacity] and P_0 is the pressure of the matrix (before quenching)

$$P_0=\frac{kTN_0}{V}-\frac{1}{6V}\int_V d\mathbf{q}_1\int_V d\mathbf{q}_2|\mathbf{q}_1-\mathbf{q}_2|u'_{00}(|\mathbf{q}_1-\mathbf{q}_2|)\times\rho^{(2)}_{00}(|\mathbf{q}_1-\mathbf{q}_2|). \tag{19}$$

The first term in Eq. (17) is the contribution of an ideal gas and the second and the third ones are formally identical to the virial terms of a binary mixture which can be readily calculated from simulations. However, the last three terms are not computable from simulations since they all involve $\Xi_1(\mathbf{q}^{N_0})$. This is why Eq. (17) is not an useful expression for calculating the pressure from simulations. In contrast, the expression given in Eq. (9) can be rewritten as

$$\begin{aligned}P={}&\frac{kTN_1}{V_1}-\frac{1}{3V_1}\left\langle\left\langle\sum_{i=1}^{N_1}\sum_{j=1}^{N_0}u'_{10}(|\mathbf{r}_i-\mathbf{q}_j|)\frac{(\mathbf{r}_i-\mathbf{q}_j)\cdot\mathbf{r}_i}{|\mathbf{r}_i-\mathbf{q}_j|}\right\rangle_1\right\rangle_0\\&-\frac{1}{6V_1}\left\langle\left\langle\sum_{i=1}^{N_1}\sum_{j=2,j>i}^{N_1}u'_{11}(|\mathbf{r}_i-\mathbf{r}_j|)|\mathbf{r}_i-\mathbf{r}_j|\right\rangle_1\right\rangle_0,\end{aligned} \tag{20}$$

where $\langle(\cdots)\rangle_1$ denotes the average over fluid configurations for a particular matrix realization. All the terms in Eq. (20) can be readily calculated from simulations.

It can be shown that the term containing $\langle N_0\ln\Xi_1(\mathbf{q}^{N_0})\rangle_0$ in Eq. (17) is related to $(\partial P/\partial z_0)_{T,z_1}$, where z_0 is the fugacity of the matrix. So, Eq. (17) is, in fact, not a *bona fide* expression of the thermodynamic pressure, but a partial differential equation it should satisfy. Deriving a *bona fide* expression by the direct integration of this equation seems to be a formidable task. One question we can ask here is whether Eq. (9) is consistent with Eq. (17), i.e., Eq. (9) is a solution of Eq. (17). After some algebraic manipulations, Eq. (9) can be rewritten as

$$P=\frac{kTN_1}{V_1}-\frac{1}{6V_1}\left[2\int_{V_0}d\mathbf{q}_1\int_{V_1}d\mathbf{r}_1|\mathbf{r}_1-\mathbf{q}_1|u'_{10}(|\mathbf{r}_1-\mathbf{q}_1|)\rho^{(2)}_{10}(|\mathbf{r}_1-\mathbf{q}_1|)+\int_{V_1}d\mathbf{r}_1\int_{V_1}d\mathbf{r}_2|\mathbf{r}_1-\mathbf{r}_2|u'_{11}(|\mathbf{r}_1-\mathbf{r}_2|)\rho^{(2)}_{11}(|\mathbf{r}_1-\mathbf{r}_2|)\right]$$
$$+\frac{kT}{V_1}\langle N_0\ln\Xi_1(\mathbf{q}^{N_0})\rangle_0-\frac{1}{6V_1}\left\langle\ln\Xi_1(\mathbf{q}^{N_0})\sum_{i=1}^{N_0}\sum_{j=2,j>i}^{N_0}u'_{00}(|\mathbf{q}_i-\mathbf{q}_j|)|\mathbf{q}_i-\mathbf{q}_j|\right\rangle_0-\frac{kT}{3V_1\Xi_0}\sum_{N_0=0}^{\infty}\frac{N_0z_0^{N_0}}{N_0!}\oint_{\Sigma_0}d\mathbf{s}_1\cdot\mathbf{q}_1\int_{V_0}d\mathbf{q}^{N_0-1}e^{-\beta_0U_{00}}\ln\Xi_1(\mathbf{q}^{N_0}), \tag{21}$$

where the surface integral is to be performed on Σ_0 (boundary of V_0). In the thermodynamic limit

$$\lim_{V_0>V_1,V_0\to\infty,V_1\to\infty}\frac{V_0}{V_1}=1, \tag{22}$$

all the terms in Eq. (21) become identical to those in Eq. (17) except the last one. The limit in Eq. (22) indicates clearly that we consider the cases that the distance l between the boundary surfaces of V_0 and V_1 can be large but *finite*. Mathematically, this means that $\Delta V=V_0-V_1$ tends to ∞ as $V_1^{2/3}$ so that $\Delta V/V_1\to 0$ in the above thermodynamic limit. Thus, the proof to be given below is valid for systems without long range interactions. Now, it remains to see if one can prove the equivalence between the last terms in Eqs. (17) and (21). When l is larger than the range of fluid-matrix interaction $\Xi_1(\mathbf{q}^{N_0})$ becomes independent of $\mathbf{q}_1$ since it is located on Σ_0 while all the fluid particles are inside V_1 far from Σ_0. Thus, the last term of Eq. (21) becomes

$$I=\frac{kT}{3V_1\Xi_0}\sum_{N_0=0}^{\infty}\frac{N_0z_0^{N_0}}{N_0!}\int_{V_0}d\mathbf{q}_2\cdots\int_{V_0}d\mathbf{q}_{N_0}$$
$$\times\ln\Xi_1(\mathbf{q}_2,\ldots,\mathbf{q}_{N_0})\oint_{\Sigma_0}d\mathbf{s}_1\cdot\mathbf{q}_1e^{-\beta_0U_{00}}. \tag{23}$$

In the case of $U_{00}=0$, it is straightforward to show

$$I=P_0\langle\ln\Xi_1(\mathbf{q}^{N_0})\rangle_0, \tag{24}$$

where $P_0=kTz_0$. Until now, we have not succeeded in establishing Eq. (24) in the most general case. However, note that Eq. (24) holds for arbitrary U_{11} and U_{10}. This covers already a large class of models. Our expression for the thermodynamic pressure is equivalent to that of KRTM for any fluid in an overlapping matrix.

Until now, it has been believed that neither the mechanical nor the thermodynamic pressures of a fluid confined in a porous medium are experimentally measurable. Now, we will show that it is in fact possible to devise an experimental method. Consider a porous sample connected to a fluid reservoir. The fluid pressure inside the sample P_{in} satisfies Eq. (14) and that of the reservoir satisfies

$$\left(\frac{\partial P_{\text{bulk}}}{\partial\mu_1}\right)_T=\rho_{\text{bulk}}, \tag{25}$$

where ρ_{bulk} is the bulk fluid density in the reservoir. Combining Eqs. (14) and (25), we obtain

$$\left(\frac{\partial P_{\text{in}}}{\partial P_{\text{bulk}}}\right)_T=\frac{\langle\rho_1^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})\rangle_0}{\rho_{\text{bulk}}}. \tag{26}$$

The right-hand side (RHS) of Eq. (26) is the so-called partition coefficient. A sum rule has been derived for it by Dong *et al.* [7]. We see here that the derivative of P_{in} with respect to P_{bulk} at constant temperature satisfies the same sum rule. Equation (25) can be rewritten as

$$P_{\text{in}}=\int_0^{P_{\text{bulk}}}dP\frac{N_1^{\text{in}}(\mu(P),T)}{N_1^{\text{bulk}}(\mu(P),T)}, \tag{27}$$

where $N_1^{\text{in}}(\mu(P),T)$ is the number of fluid particles adsorbed in the porous sample and $N_1^{\text{bulk}}(\mu(P),T)$ the number of the bulk fluid particles in the reservoir contained in a volume with the same size as the porous sample. To emphasize that N_1^{in} and N_1^{bulk} are measured at the same temperature and the chemical potential, we have written explicitly their dependence on T and μ in Eq. (27). All the quantities on the RHS of Eq. (27) can be measured experimentally. So, P_{in} is an experimentally measurable quantity and can be obtained from the properties of the reservoir and the adsorption isotherms which provide the data for N_1^{in}.

In summary, we derived an expression which can be readily used for calculating, from simulations, the thermodynamic pressure of fluids adsorbed in random porous media. While the proof of the complete equivalence is still wanting, we proved the equivalence of our expression with that obtained by Kierlik *et al.* [6] in a number of cases [8]. Moreover, a procedure is proposed for measuring experimentally the the thermodynamics pressure.

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[8] In addition, it has just been proved that Eq. (9) gives the same result as KRTM expression for a HS fluid in a HS matrix in the lattice gas version. The details will be presented in a forthcoming paper by W. Dong and V. Krokoviack.