Reply to the 'Comment on "Pressure enhancement in carbon nanopores: a major confinement effect"' by D. van Dijk, *Phys. Chem. Chem. Phys.*, 2020, 22, DOI: 10.1039/C9CP02890K

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Reply to the 'Comment on "Pressure enhancement in carbon nanopores: a major confinement effect"' by D. van Dijk, *Phys. Chem. Chem. Phys.*, 2020, 22, DOI: 10.1039/C9CP02890K

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Abstract

In their 'Comment' Van Dijk points out that the local pressure at a point **r** in an inhomogeneous thermodynamic system, like other thermodynamic properties, is not uniquely defined; one must make an operational definition that involves deciding how to assign the intermolecular forces between pairs of molecules to the point **r**. This non-uniqueness difficulty is well known, and was discussed in our paper. It was discussed in detail in the 1950 paper of Irving and Kirkwood, and in many books and papers since then. We reply to these comments, and note that an average of the local pressure over a region of space may yield a well-defined pressure. We also discuss other possible ways to quantify the adsorption compression effect near an attractive wall. Van Dijk also suggests that the non-uniqueness difficulty can be avoided by using the pressure of the uniform bulk fluid in equilibrium with the pore. While this pressure is well-defined, it only reflects the intermolecular forces in the bulk phase, and gives no information about the behavior in the pore.

Response

Van Dijk's Comment draws attention to the fact that the local pressure tensor, $\mathbf{P}(\mathbf{r})$, in an equilibrium system that is inhomogeneous is not uniquely defined at the nano-scale, as seen in Eq. (4) of our paper[1], where the configurational term on the right involves an integral along a contour C_{ij} connecting the centres of two molecules, i and j. The choice of this contour is arbitrary, resulting in the non-uniqueness of $\mathbf{P}$. Physically, the non-uniqueness arises because the intermolecular forces are between two molecules located at $\mathbf{r}_i$ and $\mathbf{r}_j$, i.e. they are non-local, whereas we wish to determine the pressure at a local point $\mathbf{r}$, and there is no unique way to assign part of the non-local pair force to the local point $\mathbf{r}$. To pursue the statistical mechanical approach to $\mathbf{P}$ one must first make an operational definition of the contour. All of this is well known in the statistical mechanical community. It is implicit in Kirkwood and Buff's 1949 paper[2], and is discussed at some length in an Appendix of the seminal paper of Irving and Kirkwood (IK)[3]. Irving and Kirkwood[3], writing 70 years ago, stated the situation clearly: "all definitions must have this in common – that the stress[4] definition between a pair of molecules be concentrated near the line of centers. When averaging over a domain large

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compared with the range of the intermolecular forces, these differences are washed out, and the ambiguity remaining in the macroscopic stress tensor is of negligible order." Further discussion of these points were given later by Harasima (H)[5], Schofield and Henderson[6], Rowlinson[7], Hafskjold and Ikeshoji[8], Binder and coworkers[9,10], Hatch and Debenedetti[11] and many others. One choice of contour that has been widely used is a straight line joining the centers of the two molecules. This was the contour used by Irving and Kirkwood (IK) in their 1950 paper3, and follows the line of force between the two molecules. Another quite widely used contour is that of Harasima5, in which the path runs from the position of particle *i,* $\left(x_i, y_i, z_i\right)$, to position $\left(x_j, y_j, z_i\right)$, and then to the position of particle *j*, $\left(x_j, y_j, z_j\right)$. For a planar interface lying in the *xy* plane, there are two independent components to the pressure tensor, $P_N = P_{zz}$ normal to the interface, and $P_T = P_{xx} = P_{yy}$ acting parallel to the interface. It is the tangential pressure, P_T, that is not uniquely defined.

In our paper we were at pains to point out this non-uniqueness of the pressure tensor, as we have in our previous papers on inhomogeneous systems[12,13], and in subsequent papers quoted in the Comment. We say on page 2 "Eqn (4) is formally rigorous, but while the kinetic term is uniquely defined the configurational contribution is not, due to the arbitrary nature of the contour integral…." In a 2013 paper[14] (cited as ref. 4 of the Comment) we compare results for the tangential pressure, P_T, for slit pores using both the IK and H definitions. As expected, the two definitions give different numerical results. However, they have some qualitative similarities. Next to the pore walls the positions of the peaks in P_T coincide with the peaks in the density profile, but the heights and widths of these peaks differ. The integral of P_T over z gives the same average of P_T for both definitions, as it should.6

In studies of adsorbates adsorbed on planar carbon surfaces or in slit-shaped carbon pores, provided the adsorbate wets the walls, as is the case in the paper1 being discussed here, adsorption occurs in well-defined layers parallel to the wall (see Fig. 2 of ref. 1). There is also evidence (described briefly below) of strong compression of the adsorbate molecules close to the walls. The area where there is disagreement, is how best to quantify this compression. One approach might be to try to define a microscopic pressure in the pore phase that results from the intermolecular forces at play, and that would give at least an approximate measure of the compression of the molecules. An alternate approach would be to discuss the compression in terms of the local density of the molecules near the wall.

Van Dijk proposes to use the pressure of the bulk phase in equilibrium with the pore phase, P_{bulk}. This, together with the temperature, determines the chemical potential in both the bulk and pore phases. The configurational part of the bulk pressure provides information about the average intermolecular forces acting on the molecules in the *bulk* phase. However, it provides no information about the local properties of the pore phase, or the intermolecular forces at play there, or how they change with the nature of the adsorbate, adsorbent, pore width and shape, etc., and so does not address the question of interest here. It is these latter intermolecular forces that determine the properties and behaviour of the pore phase.

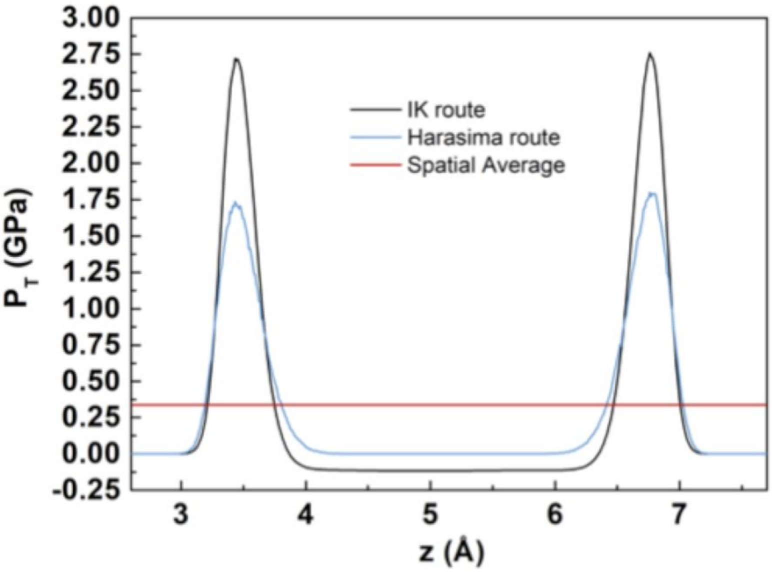

Figure 1. Local tangential pressures using the IK and H definitions, and the spatially averaged tangential pressures (eqn. 2) for four different definitions of C_{ij} (the IK and H definitions, and two alternative contours), for LJ argon in a slit carbon pore of width $H = 3\sigma$ at 87.3K, 1 bar bulk pressure.[15]

Because the local tangential pressure is not uniquely defined, we must exercise caution in attaching physical meaning to the resulting values. However, as shown by Harasima5, and later by Schofield and Henderson6, the integral of $P_T(z)$ over z is unique, so that (for example)

$$\int P_{T,IK}(z)\,dz = \int P_{T,H}(z)dz \tag{1}$$

where IK and H refer to the Irving-Kirkwood and Harasima definitions, respectively. For wetting systems, such as those in ref. 1, we find that it may be sufficient to integrate over a given peak in the local tangential pressure to obtain a well-defined effective tangential pressure for a given adsorbed layer.[16] An example is shown in Figure 1 for a model similar to that used in ref. 1.[15] The effective tangential pressure shown by the horizontal line results from integration of $P_T(z)$ over the width of the adsorbed contact layer, t_c, using four different definitions of the contour C_{ij}; two of these definitions are the IK and H contours, and the other two were chosen randomly. When spatially averaged over the width of the adsorbed layer, these 4 definitions of the contour give pressures that agree within the accuracy of the simulation results. Thus, the spatial average tangential pressure shown in Fig. 1 is given by:

$$P_{T,avg} = \frac{1}{t_c}\int_{z_{\min}}^{H/2} P_T\left(z\right)dz \tag{2}$$

where $H = 3\sigma$ and $t_c = H/2 - z_{\min}$. The size of the dead space near the wall, $z_{\min}$, is the minimum distance of a molecular centre from the surface, $z = 0$, taken to be the value of z where the density profile departs from zero. The tangential pressure averaged in this way is approximately 0.36 GPa. If, instead of averaging over the width of a single peak in P_T, we average P_T over the entire pore width from $z = 0$ to $z = H$, without accounting for the dead space, we again find the 4 definitions give the same averaged tangential pressure, with a value of approximately 0.145 GPa. While these averaged tangential pressures are substantially lower than the peak values of the local pressures, they still show an enhancement over the bulk phase pressure (10^{-4} GPa) of more than 3 orders of magnitude.

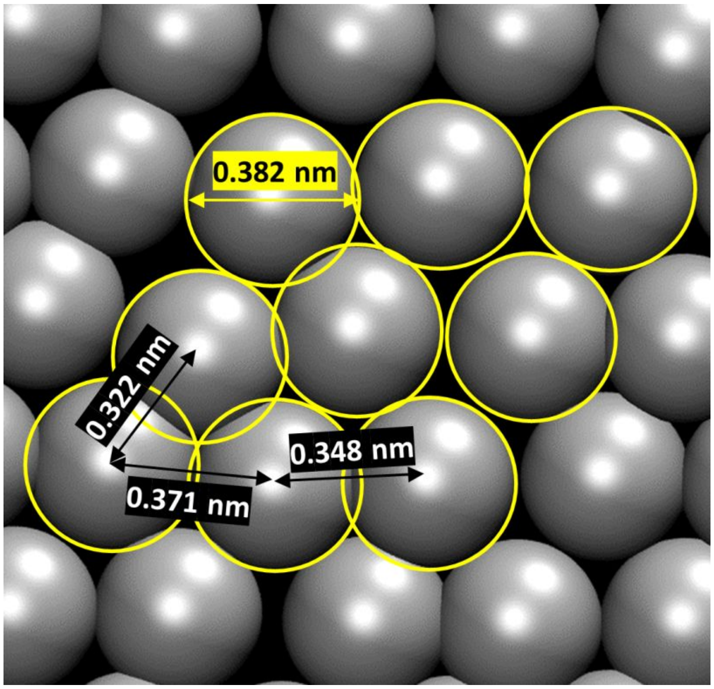

Figure 2. An in-plane view of the contact layer next to the carbon wall for LJ argon in a carbon slit pore of width $H = 3\sigma$ at 87.3 bar, 1 bar bulk pressure, showing separation distances between neighbouring molecules. The open circles show the nearest neighbor separation, 0.382 nm, when there is no compression, i.e the intermolecular force is zero. Overlap of open circles implies strong repulsion between neighbouring pairs (see Figure 4 of ref. 1 and ref. [17])

An alternate approach to quantify the compression is to measure a local density or average area occupied per molecule near the surface of the substrate. The surface area per molecule in a monolayer can be obtained from adsorption experiments, for example, as shown in the early pioneering papers of Brunauer and coworkers.[18,19] Using a local density or area approach does not escape the non-uniqueness difficulty at the nano-scale – we must first define a system volume or area by defining a boundary, as is routinely done in defining a pore width, for example. Thus the partition function, and hence all thermodynamic properties, are not uniquely defined at the nanoscale.[20]

A third approach to measure the compression effect would be to forgo macroscopic measures such as volume and pressure, and use some nano-scale measure such as the average distance separating neighboring molecules in a particular adsorbed layer. This is easy to measure in molecular simulations; an example from the current work is shown in Figure 2 for the contact layer next to the graphite wall. When the intermolecular pair force is zero (no compression) the distance separating the centres of neighbouring molecules is 0.382 nm. However, in the actual contact layer the intermolecular separation between neighbours is smaller; the snapshot of the simulation shown in Figure 2 indicates compression in the *xy* plane for most of the neighbor pairs, as indicated by overlap of the open circles that represent no compression. The result of this compression effect is shown in Figure 4(b) of ref. 1, where the pair force is plotted along with the reduction in average nearest neighbor distance. The average separation distance between nearest neighbours in the contact layer is seen to correspond to a strong repulsive force.

Each of the above approaches has limitations. Defining an average tangential pressure for an adsorbed layer has the merit that the configurational contribution is a direct reflection of the intermolecular forces that lead to the compression. However, although both the IK and H definitions seem to work well for systems that show strong wetting and for which the substrate is planar, they may not work for systems that have different constraints, for example substrates with curved surfaces or weakly wetting systems that do not show strong layering. For example, the H definition is known to give spurious results near the centre for spherical geometry,8 and we observe the same limitation when used for cylindrical geometry. Defining a local density or area per molecule is also not entirely satisfactory, as such definitions are relatively insensitive to the intermolecular forces. The adsorbed films are at high density usually, so that a small decrease in intermolecular separation corresponds to a large increase in the force.

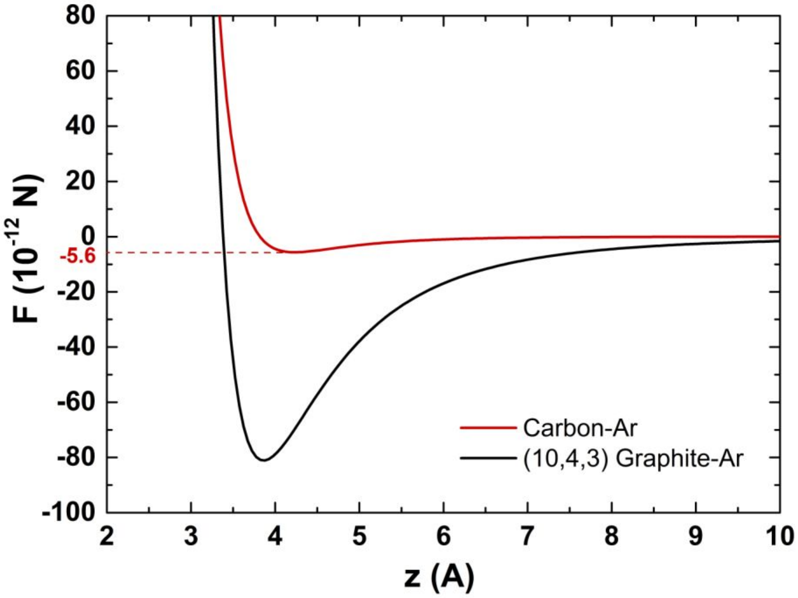

Figure 3. Comparison of the isolated pair force between a carbon atom and an argon molecule with the total force on the Ar from all carbon atoms. The dashed line marks the minimum of the pair force.

Finally, we note that there is strong evidence of adsorption compression for wetting systems on carbons, and this effect can be large in the direction parallel to the surface of the carbon substrate. Starting with the early work of Brunauer and coworkers18,19, experimental studies of monolayers on carbons show that the surface area per molecule is consistently lower than that estimated from bulk liquid densities for simple adsorbates that wet the surface, and that this lowering is significant, ranging from 7-19% for the adsorbates argon, nitrogen, oxygen, carbon monoxide and carbon dioxide. Similar results are obtained from scattering experiments (e.g. ref. 21). The molecular simulation results (e.g. Figure 2) also show reduced surface area per molecule, suggesting that the experimental observations may well result from adsorption-induced compression in the tangential (*xy*) direction. Donahue and coworkers[22,23] have discussed evidence for adsorption compression from both experiment and molecular simulation. In particular, they note that compression can occur in higher adsorbed layers in addition to the contact layer, and that this can lead to oscillations in the isosteric heat as the bulk phase pressure is increased. Gor and coworkers[24,25,26] have studied the elastic properties of confined fluids using both molecular simulation and ultrasonic experiments, and find that the isothermal bulk modulus is enhanced by confinement. Recently, Vasu et al.[27] studied the effect of confinement between two graphene layers of molecules that are susceptible to deformation under pressure in the bulk phase. By comparing Raman spectra for the confined molecules with those for the same molecules in the bulk phase they estimated the effective pressure in the confined phase to be about 12,000 bar, of the same order as the effective tangential pressures obtained in molecular simulations.

The compression effect is most readily observed in molecular simulations, as shown in the above figures and in ref. 1. We note that some authors, e.g. Nijmeijer et al.[28], have reported calculated interfacial tensions, γ, that are positive for weakly wetting walls, but become increasingly negative as adsorbate-wall interaction becomes more attractive (strong wetting). Although Nijmeijer et al. do not report calculated tangential pressures, the interfacial tension from the mechanical route is given by $\gamma = \int \left[P_N - P_T\left(z\right) \right] dz$, where P_N is the component of **P** normal to the wall. P_N is known to be only slightly affected by the strength of wetting, whereas P_T grows rapidly larger as wetting increases (see Fig. 5 of ref. 1). Thus in the strong wetting regime an increasingly negative γ is not unexpected.

The underlying reason for the compression effect in the simulation is the very strong attractive force exerted on the adsorbate molecules by the carbon surface. This is illustrated in Figure 3, which shows the Lennard-Jones force between a LJ argon molecule and a single carbon atom in the planar substrate, and compares that with the total force exerted on the Ar molecule by all of the substrate carbon atoms with which it interacts. Although the pair interaction force is modest, with a minimum of -5.6 piconewtons, the total force at the minimum is -81 piconewtons, about 14 times more attractive. The main reason for this strongly attractive force-field is the high density of carbon atoms in graphite, ~114 nm^{-3}, about 2.6 times higher than for silica (density ~ 44

nm^{-3}). The strong attractive force acting in a direction normal to the surface causes the adsorbate molecules to pack tightly on the surface, resulting in a repulsive force between adsorbate molecules in the tangential direction. This compression mechanism is most readily seen in videos of molecular dynamics simulations for this system.

In summary, that the local pressure in inhomogeneous systems is not well-defined is not in contention; this has been known at least since the early papers of Kirkwood's of the 1940's and 50's. We also agree that the methods used so far to quantify the adsorption compression are not of general application to all inhomogeneous systems, and all have some unsatisfactory features. It is for this reason that we included Figure 4, showing that the compression effect is supported by the results for the radial distribution function and the pair force between neighboring adsorbate molecules. Despite this difficulty in quantification, the combined evidence from experiment, simulation and density functional theory for adsorption compression on systems where the walls are wet is convincing, and the effect can be large. It is worthy of further study and understanding.

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