$1/t$ Pressure and Fermion behaviour of Water in Two Dimensions

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Abstract. A variety of metal vacuum systems displays the celebrated $1/t$ pressure, namely, power-law dependence on time t, with the exponent close to unity, as to the origin of which there has been long-standing controversy. Here we propose a chemisorption model for water adsorbates, based on the argument for fermion behaviour of water vapour adsorbed on a stainless-steel surface, and obtain analytically the power-law behaviour of pressure, with an exponent unity. Further, the model predicts that the pressure should depend on the temperature T according to $T^{3/2}$, which is indeed confirmed by our experiment. Our results should help elucidate the unique characteristics of the adsorbed water.

Water is a natural wonder; this makes its unusual behaviour of great interest, let alone the structure of the water molecule that helps to explain this behaviour [1]. Unlike other common liquids, not only does water expand and become less dense as it cools from $4\,^\circ$C to $0\,^\circ$C, it becomes even less dense as it freezes to ice [2]. Although the uniqueness of water inheres largely in its liquid phase, such uniqueness can also be found in its adsorbed phase. Water adsorption has been observed to produce $1/t$ pressure (i.e., pressure p with a power-law dependence on time t: $p \sim t^{-\alpha}$ with α close to unity) in a tremendous variety of metal vacuum systems [3, 4]. As simple as the function may seem, scientists have long been baffled about why the pressure obeys such a power-law [5, 6, 7, 8, 9]. Despite 60 years of intense effort, however, the nature of their solution remains obscure. In this communication, we argue that water vapour, when adsorbed on a stainless-steel surface, behaves as fermions in two dimensions and, on this basis, propose a chemisorption model for water adsorbates. Remarkably, there follows analytically the power-law behaviour of the pressure, with an exponent $\alpha = 1$. Further, the model predicts that the pressure should depend on the temperature T according to $T^{3/2}$. Indeed, this prediction is borne out by our experimental measurements.

The most direct examination of the adsorption behaviour of water is to measure the pump-down characteristics of a system. The experimental work has been performed on an extreme high vacuum (XHV) chamber shown in figure 1, a stainless-steel vessel with a thin, dense Cr_2O_3 film at the inner surface. This film has very few surface singularities and a very low specific surface area [10]. Prior to each experimental run the chamber is heated to about $100\,°C$ for about $6\,h$ and then cooled. At a pressure below 10^{-8} Torr, deionized water is admitted through a UHV leak valve to the chamber. As the adsorption proceeds, the pressure in the chamber decreases quite slowly after the rapid initial increase, then levels off after about $24\,h$, when it approaches its "terminal value." Since the chemical potential and hence the initial number of adsorbates must be the same for each run, further adjustments are made to the terminal pressure. During the run, the temperature of the vacuum system is regulated to $\pm 0.2\,K$. Figure 2 shows a typical pump-down curve for the XHV system with adsorbed water. Immediately after pump-down starts, most of the gas which goes into the pumping system is the volume gas. Though not shown here, the pressure p in the system falls exponentially with time t. Subsequently, as surface desorption takes over as the predominant source of the gas load, the fall becomes less marked and the pressure follows the power-law $p \sim t^{-1}$, as indicated in figure 2. It is this power-law that makes adsorbed water deserve special attention. The emerging power-law indicates that the system of adsorption, being far from random, organizes itself to criticality. At this stage the pressure still decreases, but only slowly, and the system is said to be in the quasi-steady state [8].

The mathematical description of the desorption process begins with the pumping equation. We suppose that the pump evacuates a vacuum vessel of volume V, which has long been exposed to water, with the effective pumping speed S. At any instant the system pressure p is governed by the competition between the rate of gas supply due to desorption and the rate of depletion due to adsorption on the walls of the vessel as well as through pumping by the pump. Particle conservation thus yields

$$V\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\mathrm{d}N}{\mathrm{d}t}kT - sA\Gamma kT - Sp = -kT\frac{\mathrm{d}N}{\mathrm{d}t} - (R+S)p \tag{1}$$

at temperature T (with k being the Boltzmann constant), where N denotes the total number of adsorbed molecules, s the sticking probability, and A the inner surface area of the vacuum chamber. According to the kinetic gas theory, the rate Γ at which particles, each of mass m, impinge on a surface (per unit area and time) is given by $\Gamma = p/\sqrt{2\pi mkT}$, thus the re-adsorption rate (per unit density) is given by $R \equiv sA\sqrt{kT/2\pi m}$. Under the quasi-steady state conditions, where the change in pressure is very slow, the pressure p and the sticking probability s may be regarded as effectively constant during the variation of N. Equation (1) then reduces to

$$p = -\frac{kT}{R+S}\frac{\mathrm{d}N}{\mathrm{d}t}. \tag{2}$$

Thus, studying the desorption rate directly yields interesting information about the pressure and vice versa.

We need to assess the desorption rate. For simplicity, no gas is assumed to diffuse out of the bulk of the system walls and adsorbates are considered confined to the (two-dimensional) surface of the wall. Unfortunately, the details as to how water molecules are adsorbed on a stainless-steel surface are not known: Whereas according to the traditional view, a few, say, ν water molecules form a cluster via hydrogen bonding, it is not clear whether some of the ν molecules should dissociate into hydrogen atoms (H) and hydroxyl groups (OH) so that local bonding could occur with individual fragments [11, 12, 13]. In any case, some oxygen atoms are expected to bind to the surface atoms through hybridization. It then appears reasonable to assume that only one particle (i.e., fragment of a few water molecules and possibly hydroxyl groups) can occupy each location of the surface, binding through hybridization. The binding energy for an additional particle is expected to be substantially smaller, which means that rather higher energy is involved for additional occupancy; disregarding this results in the single-occupancy condition, which forbids multi-layer adsorption and may be taken effectively into account by introducing a hard core to each particle. Accordingly, upon adsorption, each (fragment) particle, in general consisting of an even number of fermions (regardless of the presence/absence of dissociation), may be regarded as a boson with a de facto hard core taking care of the single occupancy condition. The total number of those bosons is given by $\tilde{N} = N/\nu$; hereafter the tilde sign will be omitted for simplicity.

Note that in two dimensions such a boson with a hard core is equivalent to a fermion in an appropriate gauge field, as follows [14, 15, 16]: In the second quantized representation the system is described by the boson operators $b_i^\dagger$ and b_i creating and annihilating a boson at (surface) site i, respectively. The single occupancy condition reads $n_i \equiv b_i^\dagger b_i = 0, 1$ or $(b_i^\dagger)^2 = b_i^2 = 0$. The Jordan-Wigner transformation then maps such a boson system into a fermion system in the gauge field corresponding to the flux per plaquette given by $\Phi = (\alpha/\gamma_c) \sum_i n_i$ in units of the flux quantum (i.e., $\Phi_0 \equiv 1$), where α is an odd integer, γ_c denotes the coordination number, and the summation is over γ_c sites around the plaquette. The interactions between adsorbate (fragment) particles, which are neutral, are expected to be weak and negligible compared with the interactions with the surface. Neglecting the latter as well gives two-dimensional (2D) free fermions. Conversely, in the limit of strong interactions with the surface, the system reduces to 2D tight-binding fermions. Since the two opposite limiting cases give mostly the same results, we may take the system to be just free fermions for simplicity.‡ We are thus left with 2D free fermions in a gauge field, which are known to form Landau levels. The mean occupation number is then given by the Fermi function $f(\varepsilon_n) = g[e^{\beta(\varepsilon_n - \mu)} + 1]^{-1}$ with $\beta \equiv 1/kT$, where g denotes the degeneracy factor of each level, $\varepsilon_n = (2n+1)\varepsilon_0$ the energy at the nth Landau level, and μ the "effective" chemical potential of an adsorbate

‡ To be precise, the interplay of the surface potential and the gauge field leads the system to be described by Harper's equation in both the two limits, with the frustration parameters reciprocal to each other. As a result, some of the degeneracy of each level is lifted, if the flux Φ is not an integer, yielding sublevels. This, however, does not alter the subsequent analysis based on the continuum approach.

particle with the binding energy ε_b included. (Thus the "bare" chemical potential is given by $\mu_b = \mu - \varepsilon_b$.)

According to equation (2), the pressure depends on the desorption rate. As the vessel is evacuated by pumping, some adsorbate particles tend to desorb, escaping dominantly via thermal activation at room temperature. For a given energy, the number of adsorbate particles reduces with time, proportionally to $e^{-t/\tau}$ with the characteristic time τ measuring the average lifetime on the surface. It depends on the energy of the particle: In the case of thermal activation, the activation probability is proportional to the Boltzmann factor $e^{-\beta \Delta U}$, where ΔU is the energy barrier. For a particle with energy ε_n, it is given by $\Delta U = \varepsilon_b - \varepsilon_n$. Accordingly, the average lifetime on the surface, which is inversely proportional to the activation probability, takes the form $\tau(\varepsilon_n) = \tau_0 e^{\beta \Delta U} = \tau_0 e^{\beta(\varepsilon_b - \varepsilon_n)}$, where τ_0 is a characteristic "attempt time", usually of the order of an inverse phonon frequency for many activated processes in solids.

The total number of adsorbate particles at time t is then given by

$$N = \sum_{n=0}^{\infty} e^{-t/\tau(\varepsilon_n)} f(\varepsilon_n) = g \sum_{n=0}^{\infty} \frac{e^{-t/\tau(\varepsilon_n)}}{e^{\beta(\varepsilon_n - \mu)} + 1}, \tag{3a}$$

which, via the Euler-Maclaurin formula, is expanded as

$$N = D \int_0^{\infty} d\varepsilon \frac{e^{-t/\tau(\varepsilon)}}{e^{\beta(\varepsilon - \mu)} + 1} - \frac{\beta \varepsilon_0^2 D}{6} \frac{e^{-t/\tau(0)}}{1 + e^{-\beta \mu}} \left(\frac{t}{\tau_0} e^{-\beta \varepsilon_b} + \frac{1}{e^{\beta \mu} + 1} + \cdots \right). \tag{3b}$$

Note that the ground-state energy ε_0 and the degeneracy factor g are related via $g = 2\varepsilon_0 D$, where $D = \nu m A/2\pi\hbar^2$ is the (constant) density of states in two dimensions. Taking the derivative with respect to time gives the desorption rate

$$-\frac{dN}{dt} = D \int_0^{\infty} \frac{d\varepsilon}{\tau(\varepsilon)} \frac{e^{-t/\tau(\varepsilon)}}{e^{\beta(\varepsilon - \mu)} + 1} - \frac{\beta \varepsilon_0^2 D}{6\tau_0} \frac{e^{-\beta \varepsilon_b - t/\tau(0)}}{1 + e^{-\beta \mu}} \left(\frac{t}{\tau_0} e^{-\beta \varepsilon_b} - \frac{1}{1 + e^{-\beta \mu}} + \cdots \right). \tag{4}$$

Since the binding energy is of the order of $1\,\text{eV}$, the (effective) chemical potential is much larger than the thermal energy kT at room temperature, i.e., $\beta \mu \gg 1$. Then the Fermi function in the right-hand side of equation (4) reduces to the step function: $f(\varepsilon) = g[e^{\beta(\varepsilon - \mu)} + 1]^{-1} \approx g\theta(\mu - \varepsilon)$. On the other hand, since the factor $e^{-\beta \varepsilon_b} \ll 1$, the second term in the right-hand side of equation (4) is negligible compared with the first term. Thus equation (4) becomes

$$-\frac{dN}{dt} \approx D \int_0^{\mu} \frac{d\varepsilon}{\tau(\varepsilon)} e^{-t/\tau(\varepsilon)} = DkT \int_{\tau(\mu)}^{\tau(0)} \frac{d\tau}{\tau^2} e^{-t/\tau}. \tag{5}$$

Typically, we have $\tau_0 \sim 10^{-13}\,\text{s}$; thus $\tau(\mu) \equiv \tau_0 e^{-\beta(\mu - \varepsilon_b)}$ and $\tau(0) \equiv \tau_0 e^{\beta \varepsilon_b}$ are sufficiently smaller and larger than the observation time in figure 2, respectively. The lower and upper limits of the integral in equation (5) can then be replaced by 0 and ∞ with negligible error, leading to the desorption rate

$$-\frac{dN}{dt} = \frac{DkT}{t}. \tag{6}$$

Substituting equation (6) into equation (2), we obtain

$$p = -\frac{\nu kT}{R + S} \frac{dN}{dt} = \frac{\nu D k^2 T^2}{(R + S)t} \equiv \gamma t^{-1}, \tag{7}$$

which is the desired $1/t$ pressure.

We now make a quantitative test of our assumptions by probing the temperature dependence of the proportionality coefficient γ. This temperature dependence has been measured for the pump-down of adsorbed water. At different temperatures, equation (7) gives a group of parallel straight lines on the log-log plot, as shown in figure 3. The conductance and hence the pumping speed for molecular flow of an orifice is proportional to the mean speed of gas molecules. Namely, S as well as R is proportional to $\sqrt{T}$, thus γ takes the form

$$\gamma = \frac{\nu D k^2 T^2}{R + S} = C T^{3/2} \tag{8}$$

with constant C or

$$\log \gamma = \log C + \frac{3}{2} \log T, \tag{9}$$

which indicates a linear dependence of $\log \gamma$ on $\log T$ with slope $3/2$. Figure 4 indeed reveals a linear relation between the two, with the slope estimated as 1.515 ± 0.198. Such excellent agreement with experiment strongly supports the validity of our analytical approach, particularly the argument for effective fermion behaviour.

As a further check of equation (7), the adsorption isotherm is computed and compared with the empirical isotherm in the existing literature. Integrating equation (6) and using equation (7) to eliminate t, we obtain N as a function of p and T:

$$N = DkT \ln \left(\frac{R + S}{\nu D k^2 T^2} p \right) \tag{10}$$

up to an additive constant. At a set temperature equation (10) essentially describes the Temkin isotherm between the number of adsorbate particles and the pressure, which is known to adequately reproduce the experimental $1/t$ behaviour over restricted pressure ranges [8, 9, 17, 18, 19]. Further, a close look at the proportionality constant shows that the Temkin isotherm also predicts the $T^{3/2}$ dependence. Note, however, that the Temkin isotherm is obtained by assuming without substantiation a constant density of sites over a wide range of energy [9]. It is remarkable that such a constant distribution in fact corresponds to the Fermi function here. In this respect, our analytical approach also provides a theoretical basis for the empirically-obtained isotherm.

The power-law behaviour of the $1/t$ pressure indicates that a characteristic time scale does not exist. This can be seen by examining the distribution $g(\tau)$ of the average surface lifetime τ, which depends on the energy ε. It is related with the energy distribution, which is just the Fermi function $f(\varepsilon)$, via $g(\tau) = f(\varepsilon)|\mathrm{d}\tau/\mathrm{d}\varepsilon|^{-1}$. This yields

$$g(\tau) \propto \tau^{-1} \tag{11}$$

in the rather wide range $\tau(\mu) \lesssim \tau \lesssim \tau(0)$. Thus the lifetime distribution in adsorption is scale free, following a power-law with exponent unity: The number of adsorbates with given surface lifetime is inversely proportional to the lifetime. Such absence of a characteristic lifetime in turn gives rise to the power-law behaviour of the pressure.

In this article, we have probed both experimentally and theoretically the $1/t$ pressure, observed frequently in systems with adsorbed water. Theoretical focus on a strongly bonded surface monolayer allows us to regard adsorbates as bosons with de facto hard cores, which transform into fermions in two dimensions. The $1/t$ pressure as well as the power-law distribution of surface lifetimes has then been obtained analytically, as a consequence of the fermion behaviour of adsorbed water. Accurate measurements have been carried out with the XHV system to confirm the validity of this theoretical analysis. In particular, the $T^{3/2}$ dependence observed in the measurement has been shown to be fully consistent with the prediction of the theoretical analysis. While the structure of water adsorbed on a well-defined metal surface remains as a subject of debate [11, 12, 13], our results suggest that water, upon adsorption on a stainless-steel surface, exhibits fermion behaviour. This gives rise to criticality without a characteristic time scale, which provides an explanation of the power-law behaviour with exponent unity. Thus, like liquid and solid water, adsorbed water also exhibits unique characteristics. Based on the theoretical analysis, we expect similar adsorption characteristics of other molecular systems as well: a few molecules form a small network and only one of the resulting "particles" can occupy a site, binding rather strongly, e.g., through hybridization. The adsorption system controlled by the vapour of appropriate molecules should be prepared carefully in XHV, with water vapour removed thoroughly. It would be of interest to build such a system and examine adsorption and corresponding pressure behaviours.

Acknowledgments

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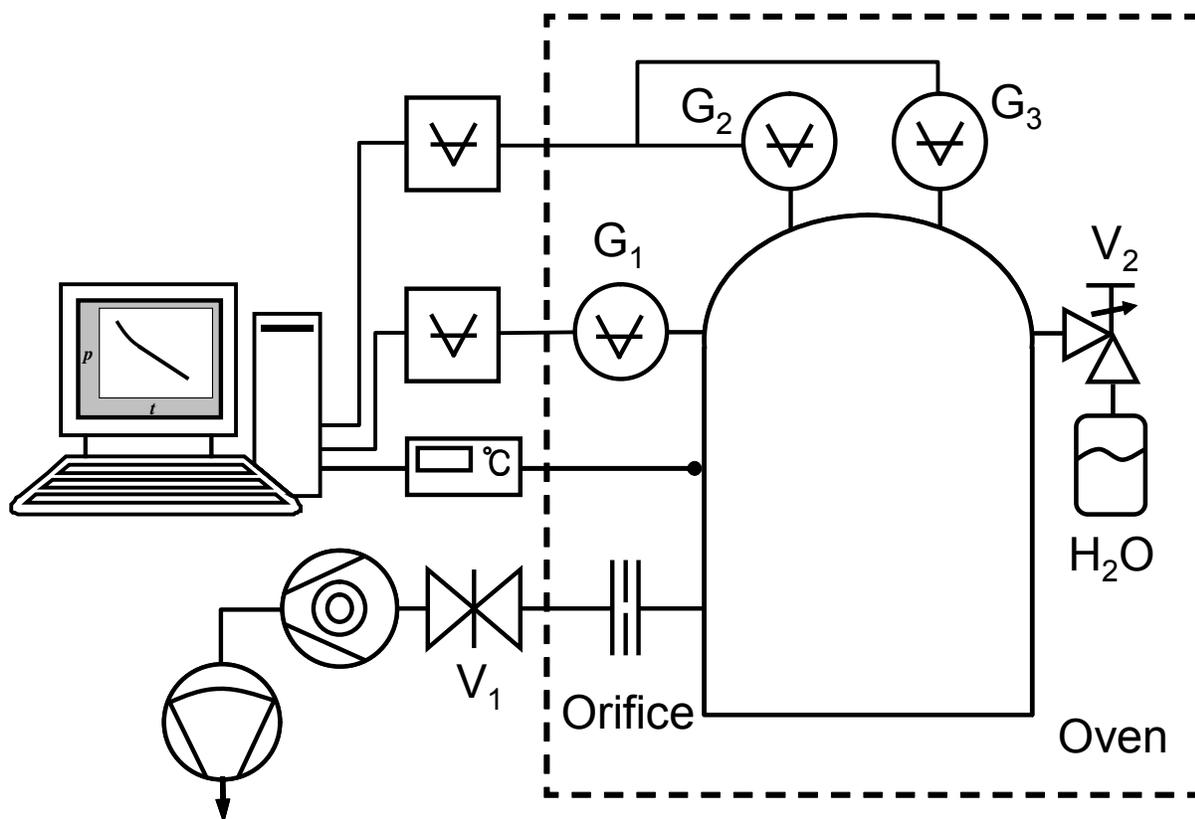
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Figure 1.   Schematic of the metal (stainless-steel) vacuum system used in this experiment. The test chamber has a volume of about $42\,\mathrm{L}$ and an internal surface of about $10\,600\,\mathrm{cm}^2$ whereas the diameter of the pumping orifice placed at the end of a short high-vacuum line, $8\,\mathrm{cm}$ long of $15\,\mathrm{cm}$ diameter, is $0.8\,\mathrm{cm}$. Pressure, which is nitrogen equivalent, is measured with the extractor gauge (G_1). Measurements are also performed with two capacitance manometer gauges (G_2 and G_3); in particular, G_3 is used as a transfer standard from $0.05\,\mathrm{Torr}$ to $10^{-5}\,\mathrm{Torr}$.
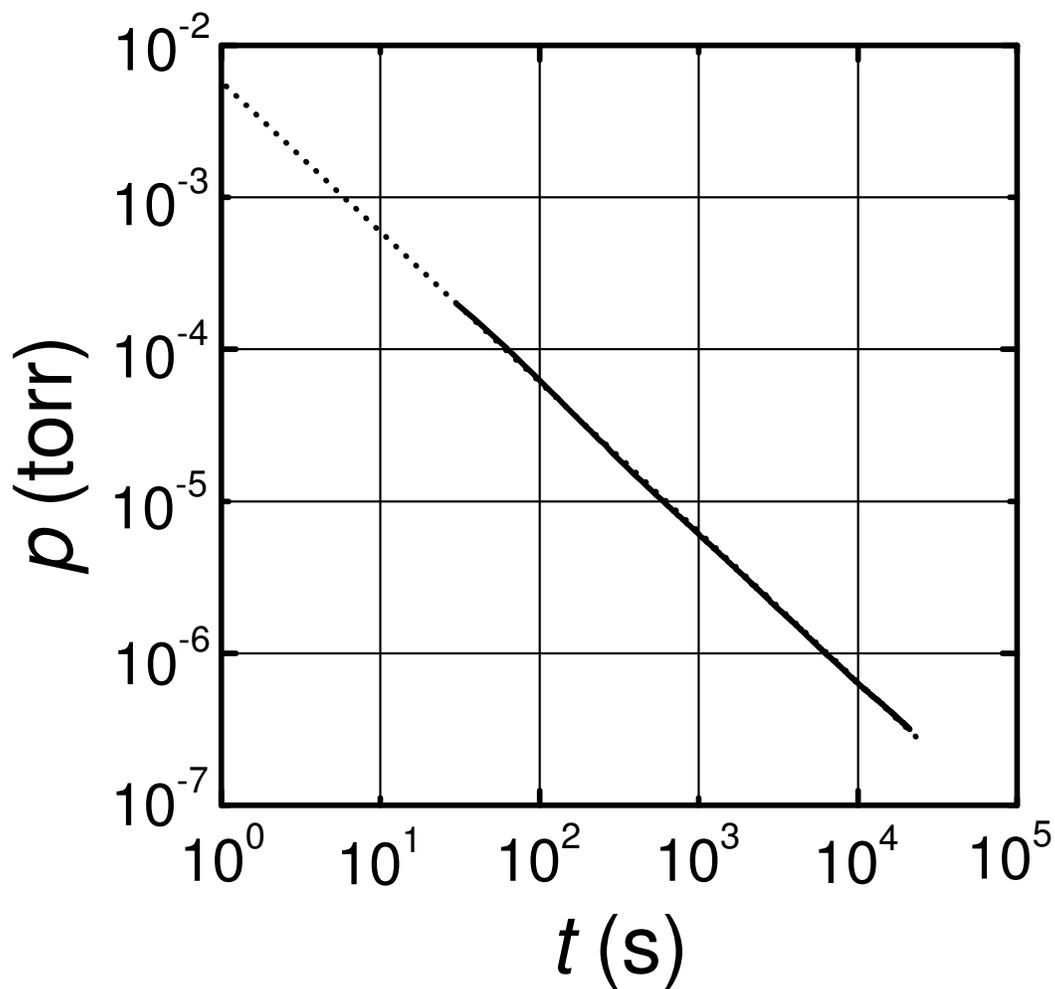
Figure 2. Sample set of pump-down curves, displaying the time evolution of the system pressure on a logarithmic scale. The pressure follows $p(t) \sim t^{-\alpha}$ with $\alpha = 1$. The dashed line represents the extrapolation to estimate the intercept on the p-axis.
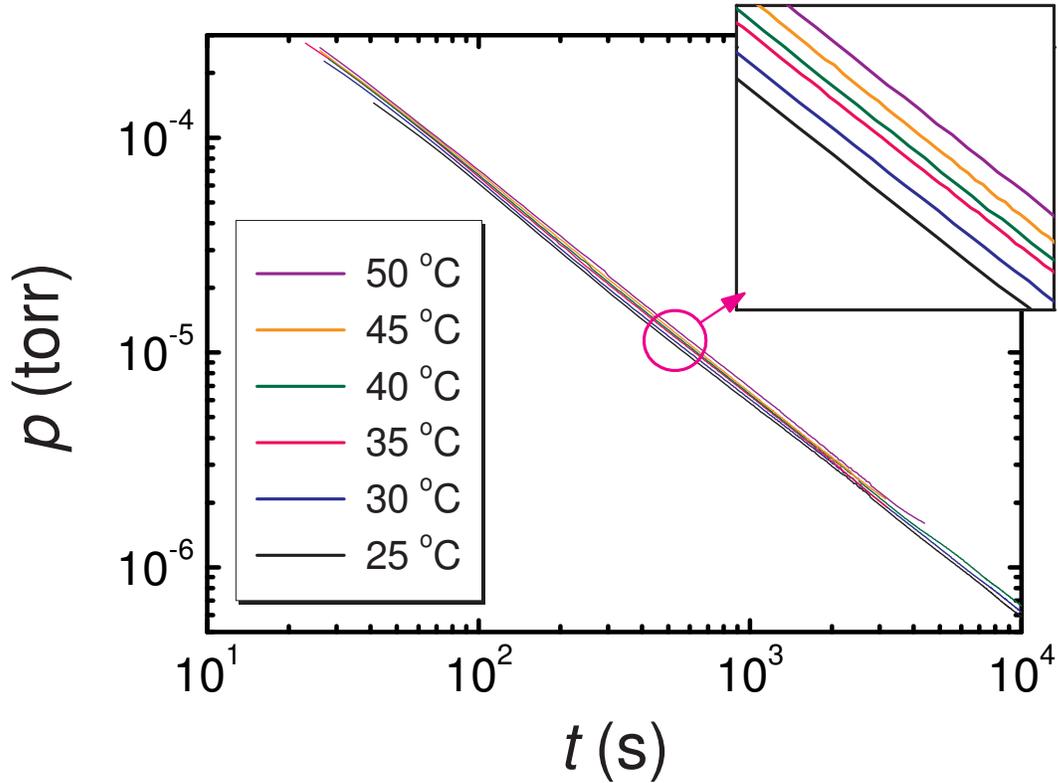
Figure 3. Pump-down curves at various temperatures. The initial number of adsorbates and hence the chemical potential [related by equation $(3a)$ at $t = 0$] should be the same for each experimental run. We choose the numeric value of the (bare) chemical potential $\mu_{\mathrm{b}} = -0.677\,\mathrm{eV}$ and determine the initial pressure according to: $p = (mkT/2\pi\hbar^2)^{3/2}kT\mathrm{e}^{\mu_{\mathrm{b}}/kT}$. Note that pumping performance tends to degrade with temperature, as all thermally activated processes are accelerated. The inset reveals that this shows up as a shift to the right of the pump-down curves.
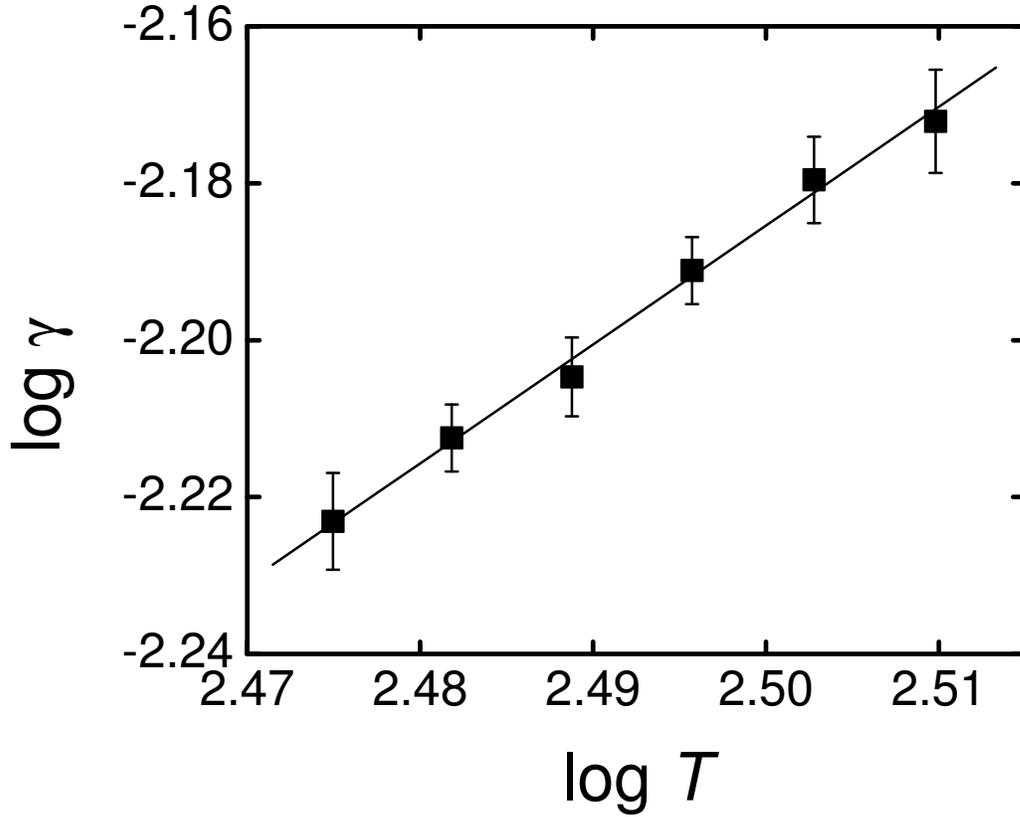
Figure 4. Proportionality coefficient γ in equation (8) versus temperature T, presented in the logarithmic scale. To estimate γ, we have extrapolated the pump-down curve, as shown by the dashed line in figure 2. Each data point consists of five independent measurements and error bar indicate standard deviation. The solid line represents the least-squares fit of the data, with the slope 1.515.