Chapter 1

Analogues of Effective Slip

We have found the effective slip length for Stokes flow over a periodic mixed-slip surface. However, on a purely mathematical level we have shown that if Laplace's equation holds on a domain, and a particular boundary condition holds on a boundary:

$$\nabla^2 u = f \tag{1.1}$$

$$u = b(x,y)\frac{\partial u}{\partial z} \tag{1.2}$$

where b is some periodic function on the boundary with units of length and period L, then there exists an effective boundary parameter b_{eff} that is a good approximation in the appropriate limits:

$$b_{\text{eff}} = \left\langle \frac{1}{b} \right\rangle^{-1} \text{ if } L \ll b, \qquad \text{and} \qquad b_{\text{eff}} = \langle b \rangle \text{ if } b \ll L \tag{1.3}$$

This models our slip problem. It is also interesting to ask what other physical systems these results might apply to. If we can find appropriate systems, then we automatically have an effective boundary parameter — some analogue of effective slip length.

We shall investigate two such physical systems forthwith: a thermal insulation problem and a heterogeneous catalyst problem.

1.1   Thermal Insulation

Consider an atypical New Zealand house: one with insulation in the roof. A standard house has an angled roof situated above a flat ceiling, with a fairly large crawlspace in between. The ceiling panels are attached to the underside of wooden beams known as rafters, which are spaced 600 mm apart. It is traditional to devote several entire weekends to laying insulating material on top of the ceiling panels, in the gaps between the rafters. Thus, above the warm living space of a house, is a heterogeneous insulator, comprising wood (the rafters), highly insulating material, and those air gaps that are left over because you couldn't be bothered cutting scatchy, unwieldy fibreglass batts to exactly the right size. A schematic is presented in Figure (1.1).
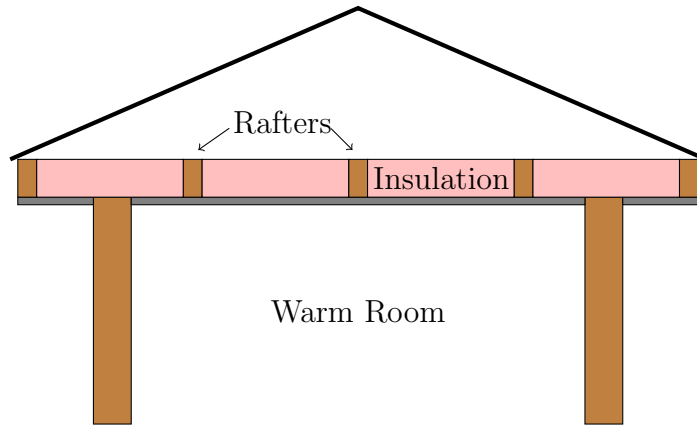
Figure 1.1: Schematic of ceiling insulation in a house.

1.1.1   Mathematical Model

We are interested in the 'net' insulating properties of the heterogeneous insulator comprising wood, insulating material and possibly air gaps. To that end, we model the heterogeneous insulator as a bulk material with: a warm room at the lower boundary, and convection-dominated heat loss on the top boundary. For consistency with our slip model, we shall invert the vertical dimension, and let $z = 0$ denote the top of the bulk and $z = P$ the bottom

of the bulk. The temperature field is $T(x, y, z)$, with boundary conditions at $T(x, y, 0)$ and $T(x, y, P)$, denoted $T(0)$ and $T(P)$. See Figure (1.2).
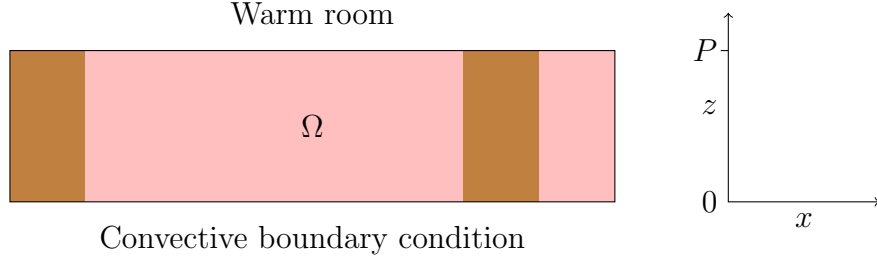
Warm room

Ω

Convective boundary condition

Figure 1.2: The domain Ω is the wooden rafters plus any insulating material. For consistency with the slip model, the domain is 'upside down'.

Dirichlet Condition

The warm room can be considered to be held at a constant temperature, due to the interventions of its human occupants. Therefore, on the $z = P$ boundary is the Dirichlet condition

$$T(P) = T_{\text{room}} = \text{constant} \tag{1.4}$$

Bulk Condition

The distribution of temperature T in a material is governed by the heat equation:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \nabla^2 T \tag{1.5}$$

where k is the thermal conductivity, and C_p is the specific heat capacity.

We shall assume that the system is steady-state, so that the time dependent term vanishes. Hence, the solid material – wooden rafters and insulating material – is governed simply by Laplace's equation:

$$\nabla^2 T = 0 \tag{1.6}$$

Conductive Heat Current

Consider a bar of test material of cross-sectional area A clamped between a hot reservoir and a cold reservoir, as shown in Figure (1.3).
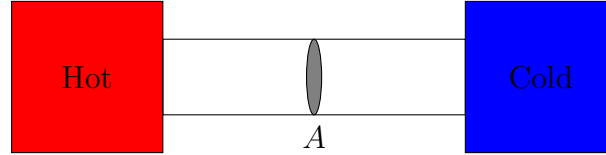

Figure 1.3: Bar of material of cross-section A between hot and cold reservoirs.

The heat current in the bar (Joules per second) depends on the temperature gradient, the thermal conductivity k and the area A:

$$\frac{dQ}{dt} = kA\frac{\partial T}{\partial x} \tag{1.7}$$

Convective Heat Current

Convection is harder to quantify than conduction. A plate at temperature T convecting into an infinite reservoir of gas at temperature T_0 shows a heat flux approximately proportional to $(T - T_0)^{5/4}$. However, consider the experimental setup in the diagram of Figure (1.4): a body of convecting air between a hot body and a cold body.

$$\frac{dQ}{dt} = hA(T - T_0)$$

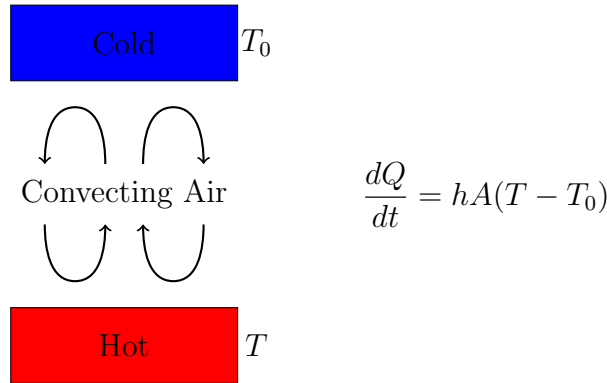Figure 1.4: Convection between hot and cold reservoirs of surface area A.

For such a system, the heat flux is usually considered to have a simple

linear relationship to temperature difference:

$$\frac{dQ}{dt} = hA(T - T_0) \tag{1.8}$$

This is known as Newton's law of cooling. h is the *heat transfer coefficient* of the system, and depends on the fluid and the physical situation.

Convective Boundary Condition

The highly-conductive steel roof of a house can be presumed to be at the same low temperature T_0 as the outside air. We assume that radiative heat transfer is negligible, and that the only heat transfer is due to convection occurring between the bulk heterogeneous insulator and the cold roof.

The heat flux *leaving* the boundary is given approximately by Newton's law of cooling. Furthermore, heat flux will arrive *at* the boundary in accordance with the heat conduction equation. See Figure (1.5).

Flux from boundary: $\dfrac{dQ}{dt} = hA(T - T_0)$

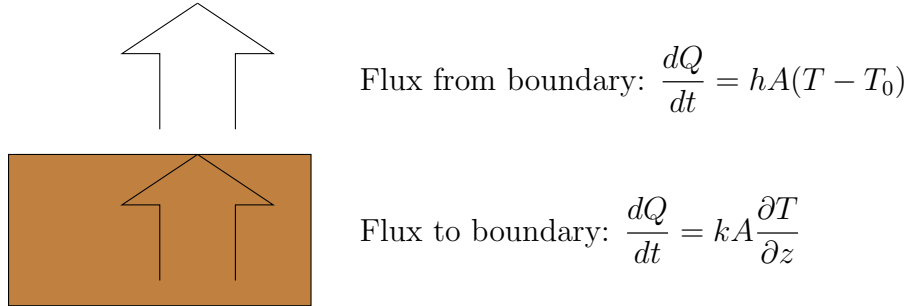Flux to boundary: $\dfrac{dQ}{dt} = kA\dfrac{\partial T}{\partial z}$

Figure 1.5: Heat fluxes conducted *to* boundary and convected *from* boundary.

Since the boundary is a virtual plane with no heat capacity, the fluxes are always equal:

$$hA(T - T_0) = kA\frac{\partial T}{\partial z} \tag{1.9}$$

For convenience, define a new variable $\tau = T - T_0$. Then the convective boundary condition is:

$$\tau = \frac{k}{h}\frac{\partial \tau}{\partial z} \tag{1.10}$$

The heat transfer coefficient h is constant for a given system. But the thermal conductivity k varies spatiallly because the insulation layer is heterogenous. Define:

$$b(x, y) = \frac{k}{h} \tag{1.11}$$

Then $b(x, y)$ is periodic function on the boundary and has dimensions of length.

We now have a system of equations similar to those describing Stokes flow with Navier slip:

$$\nabla^2 \tau = 0 \tag{1.12}$$

$$\tau = b\frac{\partial \tau}{\partial z} \tag{1.13}$$

Note that while the boundary condition is heterogeneous – $b(x, y)$ is a function of position on the boundary plane – this is due to the fact that *bulk* is heterogeneous. The coupling occurs because the heat fluxes match at the boundary.

The function $b(x, y)$ has units of length, and we can now solve to find an effective 'insulation length' for the heterogeneous insulation. We assume that all heat in the room is ultimately lost by convection above the insulator. Since the convective heat flux depends on the temperature on the convective boundary, to minimize heat loss for a given room temperature, we want the lowest temperature on the convective boundary. This in turn demands the lowest effective insulation length. See Figure (1.6).
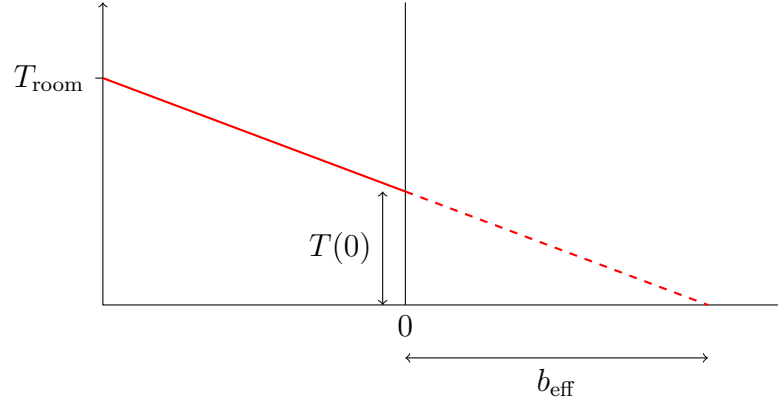
Figure 1.6: Minimizing heat loss requires minimal $T(0)$, which implies minimal 'insulation length' b_{eff}.

1.1.2 Ready-Made Solution

To apply one of the two formulae we have already found, we need to know which regime the system is in. We first use empirical data on typical insulating materials to estimate a range for b.

The heat transfer coefficient for air is experimentally determined to be in the range 10 - 100 $\text{Wm}^{-2}\text{K}^{-1}$. The thermal conductivity for wood depends on the moisture content: from 0.04 - 0-.12 $\text{Wm}^{-1}\text{K}^{-1}$ for oven-dry wood, and up to 0.4 $\text{Wm}^{-1}\text{K}^{-1}$ for wood with more than 12% water content. Typical highly-insulating materials might be polystyrene foam or polyurethane foam, with $k = 0.03\ \text{Wm}^{-1}\text{K}^{-1}$, or mineral wool, sheep's wool, or fibreglass wool, at $k = 0.04\ \text{Wm}^{-1}\text{K}^{-1}$. Air itself – if sufficiently constrained to avoid convection – has a very low thermal conductivity of $k = 0.024\ \text{Wm}^{-1}\text{K}^{-1}$.

Thus values of $b = k/h$ are in the range 0.0003 to 0.012 meters, i.e. at most about one centimeter.

This analysis of effective insulation parameter was motivated by the familiar example of ceiling insulation in a house, with domain height P being the 10 - 15 centimeter thickness of ceiling insulation, and period L being the rafter-to-rafter spacing of 60 centimeters. Then b is clearly much less than

the other length scales. However, in this example, we do not have $L \ll P$, so strictly speaking, none of our results can be assumed to be good approximations. But, for general macroscale insulation layers made up of materials like those mentioned above, if they are constructed such that $L \ll P$, then we would be in the regime $b \ll L \ll P$, and the effective insulation length would be reasonably approximated by the area-weighted average:

$$b_{\text{eff}} = \langle b \rangle \tag{1.14}$$

For 'deep' insulation layers with $L \ll P$, Equation (1.14) has serious implications. An insulator may be constructed with steel components, which has a thermal conductivity of around 40 $\text{Wm}^{-1}\text{K}^{-1}$. An air gap in the insulator may form a closed convective cell with a heat transfer coefficient of 10 - 100 $\text{Wm}^{-2}\text{K}^{-1}$; for convenience say 40 $\text{Wm}^{-2}\text{K}^{-1}$. Then a one meter tall convection cell would have the same heat current per unit area as solid steel. Thus, it is possible to have regions with a thermal conductivity 3 or more orders of magnitude higher than the best regions. If the worst regions occupy 1% of the surface area, the effective insulating length is 10 times worse than if the insulator were constructed purely of a good insulator like polystyrene. For a deep insulating layer, then, it is critical to eliminate any air gaps that are big enough to allow convection.

An interesting historical note: The first expression for effective slip is the one by J.R. Philip from 1972. His method 'generalizes a device of Karush and Young'. The 1952 paper by Karush and Young dealt with the effect of a periodic array of perfectly insulating stripes or circles, that partially block the loss of heat from a lump of radioactive material.

1.2 Catalysis

One particularly widespread application of catalysts is in the catalytic converters fitted to the exhaust systems of motorcars. Efforts are underway to improve these catalysts by the use of nanostructured material. The improvement is partly from the increased surface area, and partly from a geometric effect: the sharp corners of a catalyst nanoparticle seem to be more active than flat surfaces of the same catalyst.

Thus, it is possible that a nanostructured catalyst has a catalytic activity that varies across a nominal surface – the catalyst is heterogeneous, and may be a candidate for modelling as a homogenization problem. We shall attempt this here.

Figure (1.7) is a schematic diagram of a catalyst in action. We shall consider the simplest case of a single gas species – say N_2O_4, that diffuses to the surface of the catalyst, where a catalysed reaction breaks the molecule down into separate N_2 and O_2 molecules. The catalyst surface has some 'sharp bits' that have greater catalytic activity than the flat regions.
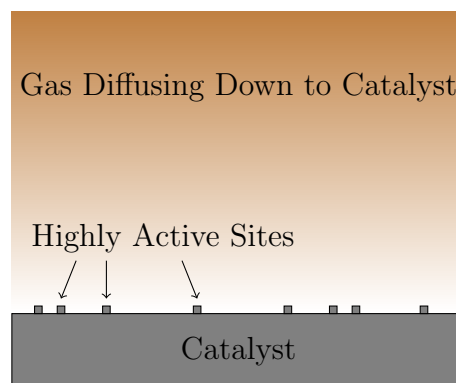
Figure 1.7: Schematic of a catalyst with surface structure.

1.2.1   Model

The concentration of the gas species (eg. N_2O_4) is C. The presence of the reaction products is presumed to not influence the behaviour of the gas species, so they are ignored.

The system is a flat (ish) plane of catalytic material, with gas flowing past parallel to the surface. The velocity of the gas is not important; the gas species of interest *diffuse* down to the surface. At some height P above the surface, the gas concentration can be considered static, constantly being replenished by uncatalysed exhaust gas. Thus the system is 'driven' by a fixed concentration C_P at the top of the domain. The size of P depends on how the catalyst is engineered; for example the catalyst could consist of hundreds of parallel pipes, each with a diameter of several millimeters. Then P would be the radius of a pipe, with a magnitude of several millimeters.

Bulk Condition: Laplace

Oxides of nitrogen comprise less than 1% of exhaust gas, so our gas species is very dilute, and so its concentration is governed by the diffusion equation. Furthermore, we shall assume steady-state conditions, so the time-dependent term vanishes, and the bulk gas obeys Laplace's equation:

$$\nabla^2 C = 0 \tag{1.15}$$

Boundary Layer

For convenience, we shall define the layer of gas adjacent to the surface as the **boundary layer.** All atoms that rain down onto the surface come from the boundary layer. There are four fluxes of molecules associated with the boundary layer: the flux of particles *into* the boundary layer from the bulk gas; the flux of particles that adsorb to the surface; the flux of particles that desorb from the surface before being catalysed; and the virtual flux of

molecules destroyed by the catalyst, that leave the boundary layer by ceasing to exist. These fluxes are illustrated in the schematic of Figure (1.8).
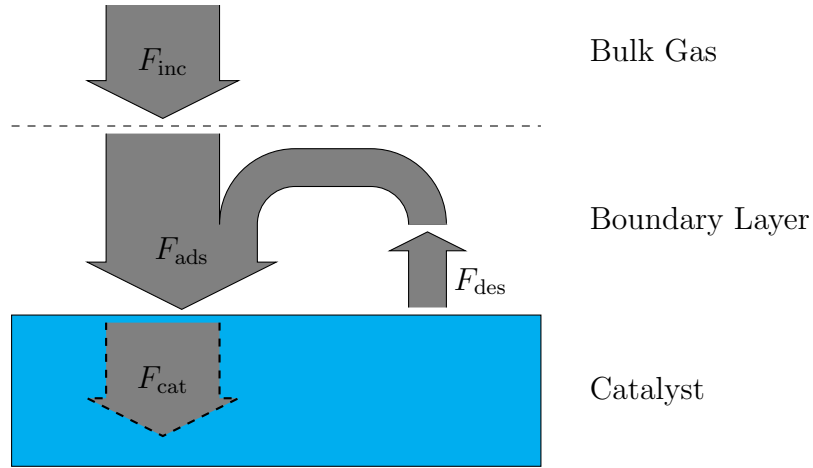

Figure 1.8: Balance of gas fluxes. In the steady-state, the net molecular flux into the boundary layer must equal the (virtual) flux of catalysed molecules leaving the boundary layer.

Mass Balance

There is a *net* flux F_{inc} of molecules per second entering the boundary layer. There is a flux F_{cat} of molecules per second permanently leaving the boundary layer by adsorbing to the surface and being catalysed out of existence. Eg. if we are concerned with the concentration C of N_2O_4, the catalysed reaction $N_2O_4 \rightarrow 2O_2 + N_2$ causes the N_2O_4 molecule to cease to exist (the N_2 and O_2 detach from the catalyst and diffuse away from the surface).

In the steady state, the concentration C in the boundary layer is constant, so by conservation of mass, the incoming flux must equal the outgoing flux:

$$F_{\text{inc}} = F_{\text{cat}} \tag{1.16}$$

As an aside, there may also be an auxiliary flux cycle: In order to be catalysed, a molecule must first adsorb to the catalyst. However, in principle,

an adsorbed molecule may *desorb* before being catalysed. Thus:

$$F_{\text{ads}} = F_{\text{cat}} + F_{\text{des}} \tag{1.17}$$

A desorbed molecule may adsorb again, or it may diffuse out of the boundary layer. Since F_{inc} is defined as a *net* incoming flux, we may not need to worry about this. In any case, for the sake of simplicity, we shall assume that desorption can be neglected.

Incoming Flux

The flux of molecules entering the boundary layer – moles per second per square meter – is given by Fick's first law of diffusion:

$$F_{\text{inc}} = D\frac{\partial C}{\partial z} \tag{1.18}$$

For an ideal gas, the diffusion coefficient D is given by $\frac{1}{3}\lambda\bar{u}$, where λ is the mean free path in the gas and $\bar{u}$ is the mean speed of gas particles. We will use this as an approximation to the diffusion coefficient of our gas. So:

$$F_{\text{inc}} = \frac{1}{3}\lambda\bar{u}\frac{\partial C}{\partial z} \tag{1.19}$$

Catalyzed Flux

One can imagine how the behaviour of a catalyst could be studied experimentally. Keeping a well-mixed body of gas in contact with a catalyst at a constant temperature and pressure, for a given concentration of gas, the experimentalist will observe a certain number of moles catalysed per second (per square meter). If the concentration is not too high, then we would expect the catalyzed flux to be proportional to concentration. That is, if we double the concentration, we double the number of molecules hitting the surface, thus double the number of opportunities for a molecule to be catalysed. (At higher concentrations, the catalyst will saturate.)

$$F_{\text{cat}} \propto C \tag{1.20}$$

We are assuming that if a molecule strikes the surface, it has an opportunity to be catalysed, and the *probability* that it *is* catalysed does not change with C. Define k_{cat} as the probability that a particle striking the surface is subsequently catalysed (rather than bouncing off or desorbing before being catalysed).

(It is possible break k_{cat} down into a probability k_{ads} that an incident particle adsorbs, and a conditional probability (per unit time) $k_{\text{ads}\rightarrow\text{cat}}$ that an already-adsorbed particle is catalysed. Essentially, we are assuming that $k_{\text{ads}\rightarrow\text{cat}}$ is large enough that the dwell time $1/k_{\text{ads}\rightarrow\text{cat}}$ is shorter than the mean time between impacts at a catalyst site. In the fuller treatment, one accounts for a pool of adsorbed particles that may build up if $k_{\text{ads}\rightarrow\text{cat}}$ is low. At some level of coverage, there is a non-negligible chance that an incident particle will bounce off an adsorbed particle, rather than striking the catalyst. In these saturated conditions, k_{cat} stops being a constant and becomes a function of C. This treatment leads to the Langmuir equation. However, the simplified treatment we give here is compatible with our effective boundary parameter expressions.)

We can apply some gas kinetics. In Appendix A, we show that the flux incident on a surface in a gas of concentration C is:

$$F = \frac{1}{4}\bar{u}C \tag{1.21}$$

Since k_{cat} is the probability that an incident particle is subsequently catalysed, the flux of particles hitting the surface and being catalysed out of existence is:

$$F_{\text{cat}} = \frac{1}{4}k_{\text{cat}}\bar{u}C \tag{1.22}$$

Catalyst Boundary Condition

As noted, in the steady-state, by mass balance, $F_{\text{inc}} = F_{\text{cat}}$. Therefore:

$$\frac{1}{3}\lambda\bar{u}\frac{\partial C}{\partial z} = \frac{1}{4}k_{\text{cat}}\bar{u}C \tag{1.23}$$

Let us introduce the catalytic parameter:

$$b = \frac{4}{3}\frac{\lambda}{k_{\text{cat}}} \tag{1.24}$$

Then the catalyst boundary condition is:

$$C = b\frac{\partial C}{\partial z} \tag{1.25}$$

which once again resembles the Navier slip condition. Furthermore, b again has units of length, since it is a multiple of the mean free path.

If the catalyst is heterogeneous, perhaps due to nanostructure, then the catalytic parameter $b(x, y)$ is a function on the surface of the catalyst.

1.2.2   Solution

We can provide a ready-made solution to

$$\nabla^2 C = 0 \qquad \text{in the bulk} \tag{1.26}$$

$$C = b\frac{\partial C}{\partial z} \qquad \text{on the boundary} \tag{1.27}$$

provided that we know $b(x, y)$ as a function of position on the catalyst surface. The homogenization technique may be applied, and an effective parameter for catalytic activity b_{eff} can be calculated.

Since k_{cat} is a probability between 0 and 1, b is in the range $\frac{4}{3}\lambda$ to ∞. The mean free path of air at standard temperature and pressure is $\lambda = 68$nm. However temperatures and pressures in automotive catalytic converters are much higher: they need a temperature of at least 250°C to work properly, and actual operating temperatures vary from 300°C at idle up to 1000°C if driven by bogans. Now,

$$\lambda = \frac{k_{\text{B}}T}{\sqrt{2}\pi d^2 p} \tag{1.28}$$

(where k_{B} is Boltzmann's constant, T is temperature, p is pressure and d is the diameter of the gas particle). So, if typical T is double or triple room

temperature, and p is somewhat higher than ambient, then we would expect $\lambda \sim 100$nm, and similarly:

$$b \geq 100 \text{ nanometers} \tag{1.29}$$

The height of the domain P depends on how the catalytic converter is engineered, but is at least millimeters. If the catalyst is truly 'nanostructured', with a period L of at most tens of nanometers, then obviously $L \ll P$, and the harmonic mean formula for rough surfaces should give a good approximation for the effective catalytic parameter of the surface. If the catalyst surface is described by the periodic function $h(x, y)$, then we have:

$$b_{\text{eff}} = \left\langle \frac{\sqrt{1 + |\nabla h|^2}}{b} \right\rangle^{-1} \tag{1.30}$$

Conversely, if the effective catalytic activity of a nanostuctured catalyst is measured, and compared with the standard flat plane morphology, then the activity of the most active regions of the catalyst may be estimated using the homogenized harmonic mean (or mean) formula.

In the dilute limit, the mean free path λ is approximately constant. Therefore, since $b = \frac{4}{3}\frac{\lambda}{k_{\text{cat}}}$, we have

$$b_{\text{eff}} = \frac{4\lambda}{3\left\langle k_{\text{cat}}\sqrt{1 + |\nabla h|^2} \right\rangle} \tag{1.31}$$

Solving $b = \frac{4}{3}\frac{\lambda}{k_{\text{cat}}}$ for k_{cat} we may define an effective catalytic activity:

$$k_{\text{cat(eff)}} = \frac{4\lambda}{3b_{\text{eff}}} \tag{1.32}$$

which gives:

$$k_{\text{cat(eff)}} = \left\langle k_{\text{cat}}\sqrt{1 + |\nabla h|^2} \right\rangle \tag{1.33}$$

Therefore, the effective catalytic activity of a nanostructured catalyst with a short dwell time and negligible desorption, is simply the average activity of its various regions, weighted by the area of contact between solid and gas.