**Continuum Description of an Adsorption Process
in a System of Fixed Mass and Fixed Volume**

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I. Problem Formulation

Consider N moles of a fluid with molecular weight m, at initial temperature T_o, in a closed volume, V. Within the volume are N_p spherical particles of diameter D_p. The bulk fluid can be described by the van der Waals equation of state, in which the parameters can be obtained from the critical properties. The fluid adsorbs on the surface of the particles following a Langmuir isotherm, to a maximum surface density, ρ_s. We remove heat from the system at a constant rate, Q, causing the temperature to drop. Describe the time dependence of the system. Specifically, we want the following variables as a function of time: the temperature, T, the bulk pressure, p, the bulk density, the fraction of adsorption sites occupied, θ, the mass fraction of material in the adsorbed phase, w_a.

II. Physical Properties

For the bulk fluid, you must provide
- molecular weight, m
- critical temperature, T_c
- critical pressure, p_c

From these properties, you can obtain the van der Waal's parameters,

$$a = \frac{27R^2T_c^2}{64p_c} \tag{1.a}$$

$$b = \frac{RT_c}{8p_c} \tag{1.b}$$

The van der Waal's thermodynamic properties of interest are thus

- the molar volume, $V_m = \dfrac{m}{\rho}$ $\qquad$ (2.a)

- the pressure, $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2} = \dfrac{RT\rho}{m - b\rho} - \dfrac{a}{m^2}\rho^2$ $\qquad$ (2.b)

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- specific internal energy, $\hat{U} = \dfrac{1}{m}\left[\dfrac{3}{2}RT - \dfrac{a\rho}{m}\right]$ (2.c)

For the solid material that composes the pellets upon which material adsorbs, we provide the following information,
- number of pellets, N_p
- geometry of pellets—spherical
- diameter of pellets, D_p
- density of adsorption sites, ρ_s
- density of pellets, ρ_p—constant
- constant-volume heat capacity of pellets, $C_{v,p}$—constant

Given these parameters, the surface area per particle and the volume per particle are

- surface area per particle, $A_p = \pi D_P^2$

- volume per particle, $V_p = \dfrac{\pi}{6}D_P^3$

- ratio of surface area to volume, $\dfrac{A_p}{V_p} = \dfrac{6}{D_P}$

- number of adsorption sites per particle, $N_s = A_p\rho_s$

- void fraction in the reactor, $\varepsilon = 1 - \dfrac{N_p V_p}{V}$

Adsorption is governed by the Langmuir isotherm

$$\theta = \frac{K\rho_b}{1 + K\rho_b}$$ (3)

where the equilibrium coefficient is given by

$$K = K_o \exp\left(-\frac{\Delta H_{ads}}{RT}\right)$$ (4.a)

and where the internal energy of an adsorbed component is

$$\hat{U}_a = \left[\frac{3}{2}RT + \Delta U_{ads}\right]$$ (4.b)

where we will assume that the parameters, K_o and ΔU_{ads}, are constant.

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III. Mass Balance

In this system, the total mass of material is constant. The distribution between the adsorbed and bulk phases changes. The total mass balance is

$$M_t = M_a + M_b \tag{5}$$

The mass in the bulk phase is given by

$$M_b = \rho_b \varepsilon V \tag{6}$$

The mass in the adsorbed phase is given by

$$M_a = m\theta\rho_s A_p N_p = m\theta\rho_s \pi D_P^2 N_p \tag{7}$$

Thus at equilibrium in a closed system is defined by equations (3) and (5), with substitutions of (6) and (7):

$$\theta = \frac{K\rho_b}{1 + K\rho_b} \tag{3}$$

$$Nm = \rho_b \varepsilon V + m\theta\rho_s \pi D_P^2 N_p \tag{8}$$

Thus we have two equations and two unknowns. Substitution equation (3) into equation (8) and rearranging yields,

$$\left(-K\varepsilon V\right)\rho_b^2 + \left(KNm - \varepsilon V - m\rho_s\pi D_p^2 N_p K\right)\rho_b + \left(Nm\right) = 0 \tag{9.a}$$

This is a quadratic equation with a solution given by

$$\rho_b = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{9.b}$$

where a, b and c are the polynomial coefficients. The positive root of this equation is the physical root of interest.

This is the important equilibrium thermodynamics for this system. There is one degree of freedom, given by the temperature. As the temperature changes, the equilibrium coefficient, K, changes. Consequently the bulk density and the adsorbed fraction also change.

IV. Energy Balance

We require an energy balance. The energy balance monitors the change of energy in the fluid (in either the bulk or adsorbed phase), the change in energy of the solid particle material and the heat that leaves the system.

$$\frac{\partial M_a \hat{U}_a}{\partial t} + \frac{\partial M_b \hat{U}_b}{\partial t} + \frac{\partial M_p \hat{U}_p}{\partial t} = -Q \tag{10}$$

$$m\rho_s \pi D_P^2 N_p \frac{\partial \theta \hat{U}_a}{\partial t} + \varepsilon V \frac{\partial \rho_b \hat{U}_b}{\partial t} + N_P V_P \rho_P \frac{\partial U_P}{\partial t} = -Q \tag{11}$$

We now manipulate the energy balance to get it strictly in terms of temperature derivatives. First we use the product rule,

$$m\rho_s \pi D_P^2 N_p \left(\theta \frac{\partial \hat{U}_a}{\partial t} + \hat{U}_a \frac{\partial \theta}{\partial t} \right) + \varepsilon V \left(\rho_b \frac{\partial \hat{U}_b}{\partial t} + \hat{U}_b \frac{\partial \rho_b}{\partial t} \right) + N_P V_P \rho_P \frac{\partial U_P}{\partial t} = -Q \tag{12.a}$$

Then we use the chain rule,

$$m\rho_s \pi D_P^2 N_p \left(\theta \left(\frac{\partial \hat{U}_a}{\partial \theta} \frac{\partial \theta}{\partial T} + \frac{\partial \hat{U}_a}{\partial T} \right) \frac{\partial T}{\partial t} + \hat{U}_a \frac{\partial \theta}{\partial T} \frac{\partial T}{\partial t} \right)$$
$$+ \varepsilon V \left(\rho_b \left(\frac{\partial \hat{U}_b}{\partial \rho_b} \frac{\partial \rho_b}{\partial T} + \frac{\partial \hat{U}_b}{\partial T} \right) \frac{\partial T}{\partial t} + \hat{U}_b \frac{\partial \rho_b}{\partial T} \frac{\partial T}{\partial t} \right) + N_P V_P \rho_P \frac{\partial \hat{U}_P}{\partial T} \frac{\partial T}{\partial t} = -Q \tag{12.b}$$

Then we collect the derivative and divide by the coefficient of the derivative.

$$\frac{\partial T}{\partial t} = \frac{-Q}{m\rho_s \pi D_P^2 N_p \left(\theta \left(\frac{\partial \hat{U}_a}{\partial \theta} \frac{\partial \theta}{\partial T} + \frac{\partial \hat{U}_a}{\partial T} \right) + \hat{U}_a \frac{\partial \theta}{\partial T} \right) + \varepsilon V \left(\rho_b \left(\frac{\partial \hat{U}_b}{\partial \rho_b} \frac{\partial \rho_b}{\partial T} + \frac{\partial \hat{U}_b}{\partial T} \right) + \hat{U}_b \frac{\partial \rho_b}{\partial T} \right) + N_P V_P \rho_P \frac{\partial \hat{U}_P}{\partial T}} \tag{12.c}$$

Some of the partial derivatives that appear in the denominator on the RHS of equation (12.c) come from the material balances. For example, if we differentiate equations (3) and (8) with respect to temperature, we have

$$\frac{\partial \theta}{\partial T} = \left(\frac{1}{1 + K\rho_b} - \frac{K\rho_b}{(1 + K\rho_b)^2} \right) \left(\rho_b \frac{\partial K}{\partial T} + K \frac{\partial \rho_b}{\partial T} \right) = \frac{1}{(1 + K\rho_b)^2} \left(\rho_b \frac{\partial K}{\partial T} + K \frac{\partial \rho_b}{\partial T} \right) \tag{13.a}$$

$$0 = \varepsilon V \frac{\partial \rho_b}{\partial T} + m\rho_s \pi D_P^2 N_p \frac{\partial \theta}{\partial T} \tag{13.b}$$

Solving equation (13.a) and (13.b) yields

$$\frac{\partial \rho_b}{\partial T} = -\frac{\rho_b \dfrac{\partial K}{\partial T}}{\left[\dfrac{\varepsilon V (1 + K\rho_b)^2}{m \rho_s \pi D_P^2 N_p} + K \right]} \tag{14.a}$$

$$\frac{\partial \theta}{\partial T} = -\frac{\varepsilon V}{m \rho_s \pi D_P^2 N_p} \frac{\partial \rho_b}{\partial T} \tag{14.b}$$

The derivative of the equilibrium coefficient is given by the differentiation of equation (4)

$$\frac{\partial K}{\partial T} = K_o \exp\left(-\frac{\Delta H_{ads}}{RT} \right) \frac{\Delta H_{ads}}{RT^2} \tag{15}$$

The remainder of the partial derivatives in equation (12.c) are thermodynamic derivatives.

$$\frac{\partial \hat{U}_p}{\partial T} = C_{v,p} \tag{16.a}$$

By differentiating equation (2.c) we have

$$\frac{\partial \hat{U}_b}{\partial T} = \frac{\partial}{\partial T} \frac{1}{m} \left[\frac{3}{2} RT - \frac{a\rho_b}{m} \right] = \frac{3}{2} \frac{R}{m} \tag{16.b}$$

$$\frac{\partial \hat{U}_b}{\partial \rho_b} = \frac{\partial}{\partial \rho_b} \frac{1}{m} \left[\frac{3}{2} RT - \frac{a\rho_b}{m} \right] = -\frac{a}{m^2} \tag{16.c}$$

We have not been given an equation of state for the Langmuir isotherm, but we know that there is no loading dependence in the Langmuir isotherm (a basic premise being that particles don't interact)

$$\frac{\partial \hat{U}_a}{\partial \theta} = 0 \tag{16.d}$$

We can assume that the energy well-depth in the Langmuir isotherm is independent of temperature, in which case the temperature dependence of the internal energy in the adsorbed phase is the same as that in the bulk phase.

$$\frac{\partial \hat{U}_a}{\partial T} = \frac{3}{2} \frac{R}{m} \tag{16.e}$$

We can substitute (14.b) and (16.a) through (16.e) into equation (12.c) to obtain

$$\frac{\partial T}{\partial t} = \frac{-Q}{m\rho_s \pi D_P^2 N_p \theta \frac{3}{2}\frac{R}{m} + \varepsilon V \rho_b \frac{3}{2}\frac{R}{m} + N_P V_P \rho_P C_{v,p} + \left(\varepsilon V \hat{U}_b - \hat{U}_a \varepsilon V - \varepsilon V \rho_b \frac{a}{m^2}\right)\frac{\partial \rho_b}{\partial T}} \qquad (17)$$

where the remaining partial on the RHS comes from equation (14.a).

V. Dimensional analysis

We will scale mass by the total fluid mass, Nm. We will scale length by $L = \sqrt[3]{V}$. We will scale temperature by the initial temperature, T_o. We will scale time by t_o. Thus are dimensionless variables are

$$T^\circ = \frac{T}{T_o}, \ t^\circ = \frac{t}{t_o}, \ \text{and} \ \rho_b^\circ = \frac{\rho_b}{\rho_o} \qquad \text{where} \ \rho_o = \frac{Nm}{L^3}$$

Substitution into equation (17) yields

$$\frac{\partial T^\circ}{\partial t^\circ} = \frac{-\dfrac{Qt_o m}{RT_o\rho_o V}}{\left[\dfrac{3}{2}\dfrac{m\rho_s \pi D_P^2 N_p}{\rho_o V}\theta + \dfrac{3}{2}\varepsilon\dfrac{\rho_b}{\rho_o} + \dfrac{N_P V_P}{V}\dfrac{\rho_P}{\rho_o}\dfrac{mC_{v,p}}{R} + \varepsilon\left(\dfrac{m\hat{U}_b}{RT_o} - \dfrac{m\hat{U}_a}{RT_o} - \dfrac{\rho_b}{\rho_o}\dfrac{\rho_o a}{mRT_o}\right)\dfrac{\partial \rho_b/\rho_o}{\partial T/T_o}\right]}$$

$$(18)$$

We identify the following dimensionless constants

$$Q^\circ = \frac{Qt_o m}{RT_o\rho_o V}, \ \text{dimensionless rate of heat removal} \qquad (19.a)$$

$$w_a = \frac{m\rho_s \pi D_P^2 N_p}{\rho_o V}, \ \text{ratio of mass in adsorbed phase to total fluid mass} \qquad (19.b)$$

$$\rho_p^\circ = \frac{\rho_P}{\rho_o}, \ \text{dimensionless particle density} \qquad (19.c)$$

$$C_{v,p}^\circ = \frac{mC_{v,p}}{R}, \ \text{dimensionless particle heat capacity} \qquad (19.d)$$

$$a^\circ = \frac{\rho_o a}{mRT_o}, \ \text{dimensionless van der Waals attraction} \qquad (19.e)$$

$$b^{\circ} = \frac{b\rho}{m}, \text{ dimensionless van der Waals molecular volume} \tag{19.f}$$

$$\Delta U_{ads}^{\circ} = \frac{\Delta U_{ads}}{RT_o}, \text{ dimensionless internal energy of adsorption} \tag{19.g}$$

$$\Delta H_{ads}^{\circ} = \frac{\Delta H_{ads}}{RT_o}, \text{ dimensionless enthalpy of adsorption} \tag{19.h}$$

$$K_o^{\circ} = K_o \rho_o, \text{ dimensionless equilibrium coefficient constant} \tag{19.i}$$

and the dimensionless functions

$$\hat{U}_b^o = \frac{m\hat{U}_b}{RT_o} = \left[\frac{3}{2}T^{\circ} - \rho^{\circ}a^{\circ}\right], \text{ dimensionless intenal energy of bulk} \tag{20.a}$$

$$\hat{U}_a^o = \frac{m\hat{U}_a}{RT_o} = \left[\frac{3}{2}T^{\circ} - \Delta U_{ads}^{\circ}\right], \text{ dimensionless internal energy of adsorbed phase} \tag{20.b}$$

$$K^{\circ} = K_o^{\circ}\exp\left(-\frac{\Delta H_{ads}^{\circ}}{T^{\circ}}\right), \text{ dimensionless equilibrium coefficient} \tag{20.c}$$

$$\frac{\partial K^{\circ}}{\partial T^{\circ}} = K_o^{\circ}\exp\left(-\frac{\Delta H_{ads}^{\circ}}{T^{\circ}}\right)\frac{\Delta H_{ads}^{\circ}}{T^{\circ 2}} \tag{20.d}$$

$$\left(-K^{\circ}\varepsilon\right)\rho^{\circ 2} + \left(K^{\circ} - \varepsilon - w_a K^{\circ}\right)\rho^{\circ} + 1 = 0 \tag{20.e}$$

This is a quadratic equation with a solution given by

$$\rho^{\circ} = \frac{-\left(K^{\circ} - \varepsilon - w_a K^{\circ}\right) \pm \sqrt{\left(K^{\circ} - \varepsilon - w_a K^{\circ}\right)^2 + 4K^{\circ}\varepsilon}}{-2K^{\circ}\varepsilon} \text{ from equation (9)} \tag{20.f}$$

$$\frac{\partial \rho^{\circ}}{\partial T^{\circ}} = -\frac{\rho^{\circ}\dfrac{\partial K^{\circ}}{\partial T^{\circ}}}{\left[\dfrac{\varepsilon\left(1 + K^{\circ}\rho^{\circ}\right)^2}{w_a} + K^{\circ}\right]} \text{ from equation (14)} \tag{20.g}$$

$$\theta = \frac{K^{\circ}\rho^{\circ}}{1 + K^{\circ}\rho^{\circ}} \tag{20.h}$$

$$p^\circ = \frac{pm}{\rho_o RT_o} = \frac{\rho^\circ}{1-b^\circ}T^\circ - a^\circ \rho^{\circ 2} \tag{20.i}$$

Subsitution of equation (19) into equation (18) yields

$$\frac{\partial T^\circ}{\partial t^\circ} = \frac{-Q^\circ}{\left[\frac{3}{2}w_a\theta + \frac{3}{2}\varepsilon\rho^\circ + (1-\varepsilon)\rho_p^\circ C_{v,p}^\circ + \varepsilon\left(\hat{U}_b^\circ - \hat{U}_a^\circ - \rho^\circ a^\circ\right)\frac{\partial \rho^\circ}{\partial T^\circ}\right]} \tag{21}$$

VI. Numerical Example

Initial Temperature

$$T^\circ(t^\circ = 0) = 1,$$

Parameter Values

$Q^\circ = 1$, dimensionless rate of heat removal

$w_a = 0.5$, ratio of mass in adsorbed phase to total fluid mass

$\rho_p^\circ = 10$, dimensionless particle density

$C_{v,p}^\circ = 10$, dimensionless particle heat capacity

$a^\circ = 0.1$, dimensionless van der Waals attraction

$b^\circ = 0.0001$, dimensionless van der Waals molecular volume

$\Delta U_{ads}^\circ = -2$, dimensionless internal energy of adsorption

$\Delta H_{ads}^\circ = -2$, dimensionless enthalpy of adsorption

$K_o^\circ = 1$, dimensionless equilibrium coefficient constant

$\varepsilon = 0.5$, void fraction

I used the Euler method to solve the ODE from 0 to 40 in reduced time units with 1000 time steps. Plots and codes follow.
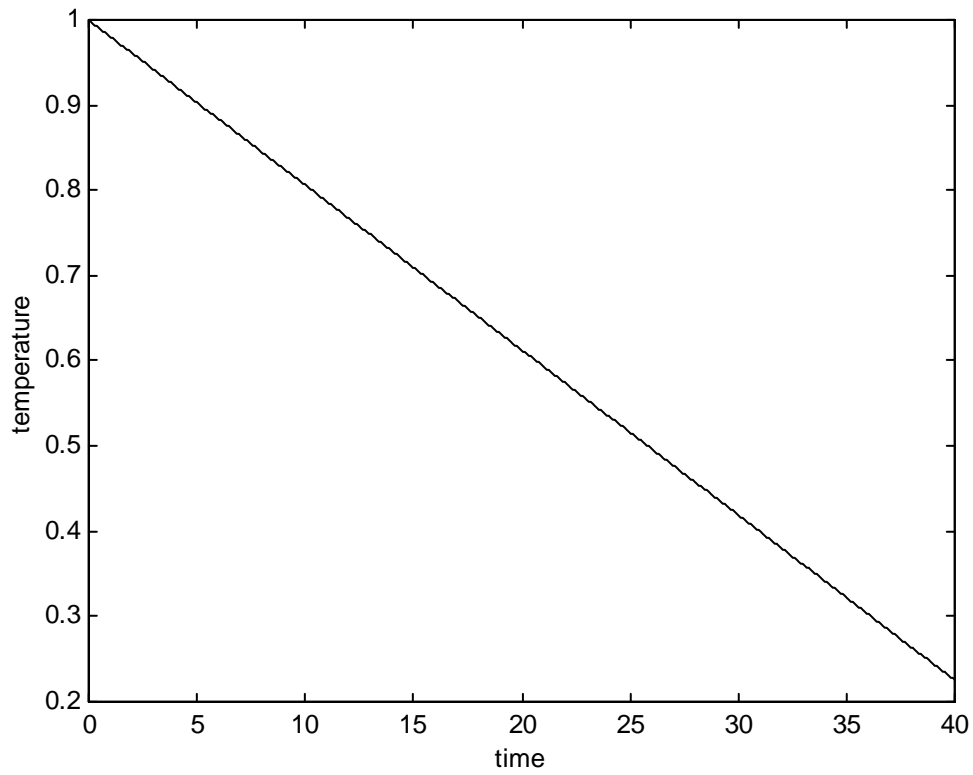
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Figure 1. Temperature as a function of time. The temperature decreases with time because heat is being removed from the system.
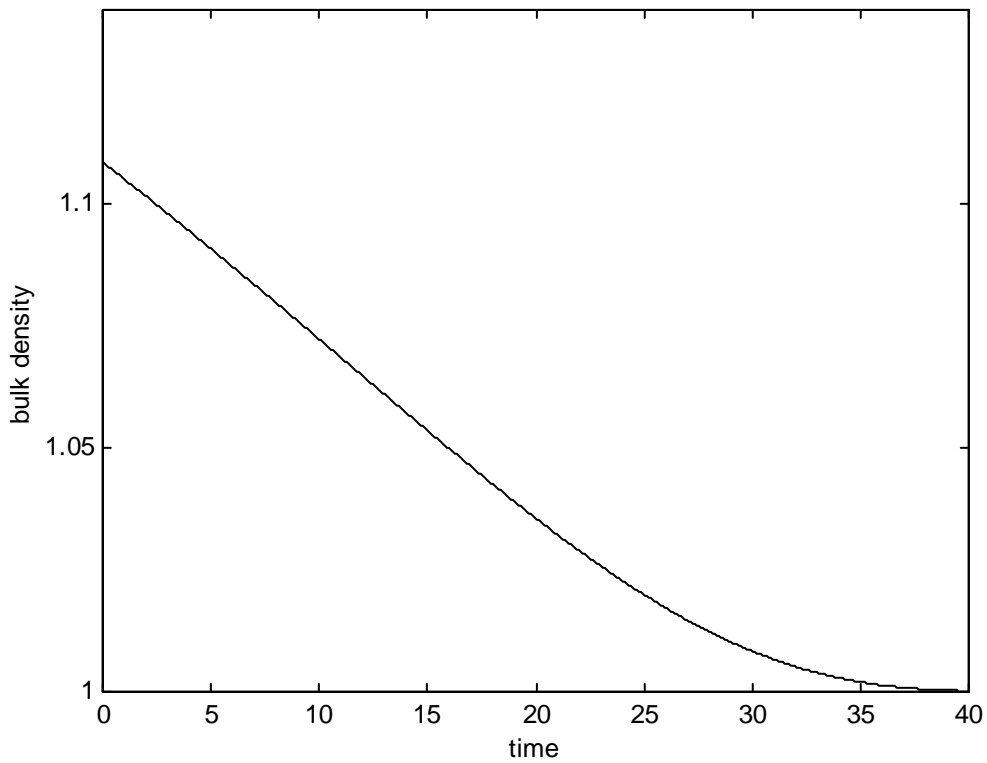
Figure 2. Bulk density as a function of time. The density decreases with time because some material is leaving the bulk phase and adsorbing on the surface of the particles. There is a non-zero asymptote in the bulk density at the point where the surface is completely filled with adsorbates.
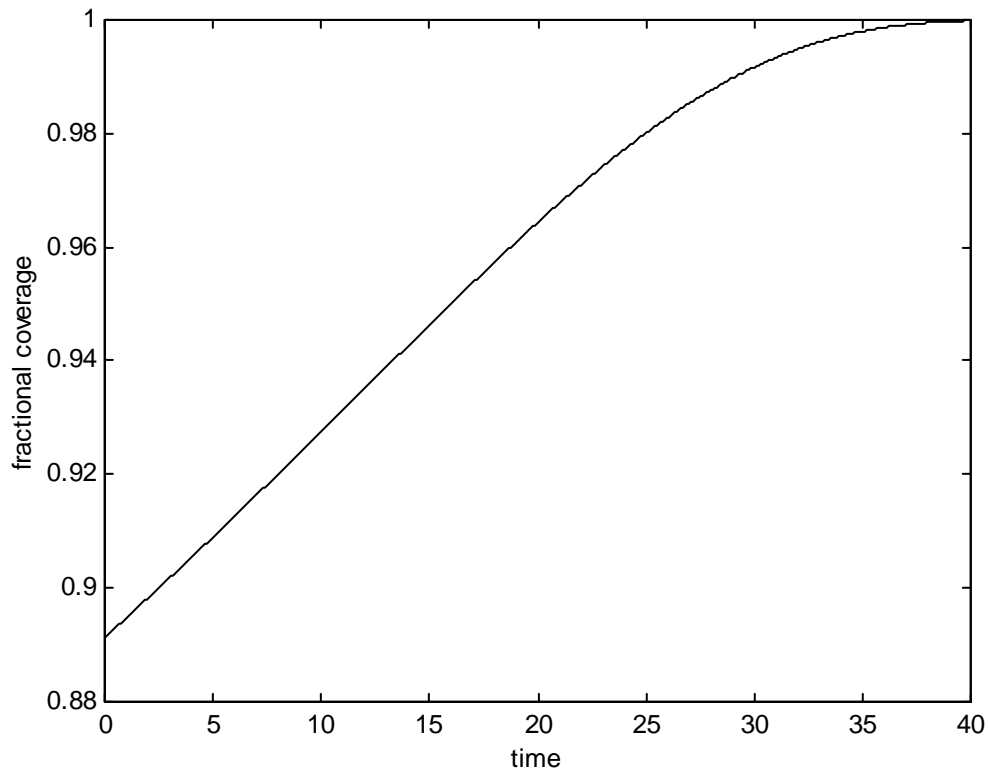
Figure 3. Fractional occupancy of adsorption sites as a function of time. As the temperature decreases the amount of material adsorbed increases until it fills all adsorption sites.
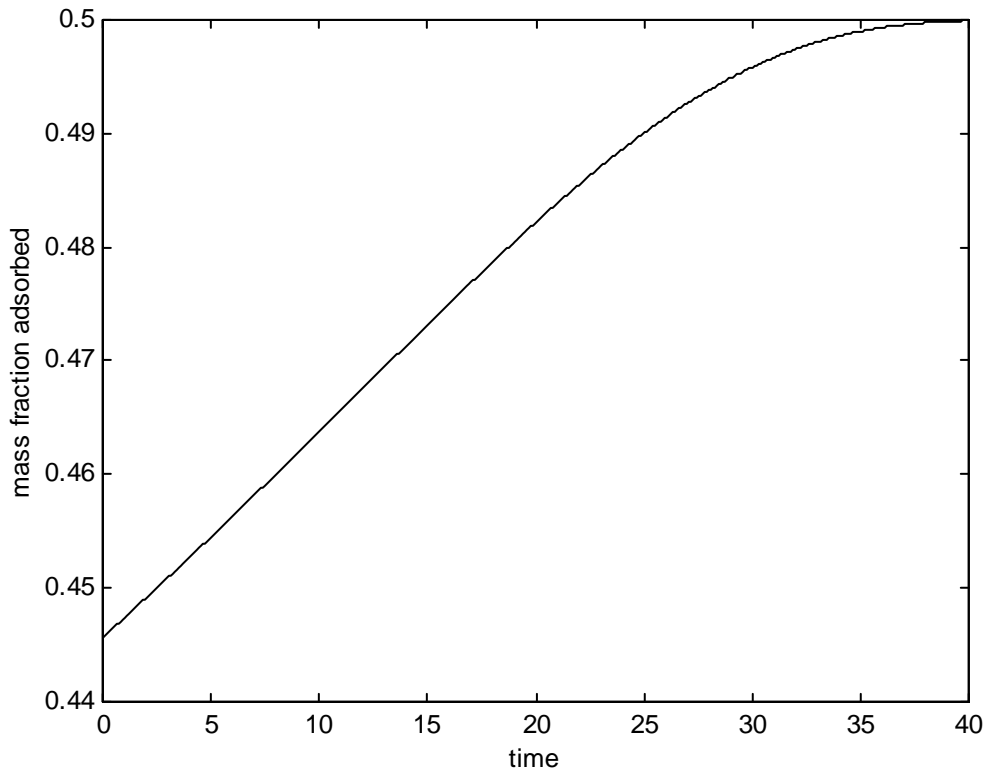
Figure 4. Mass fraction of fluid in the adsorbed phase. The fraction of material in the adsorbed phase increases as the temperature decreases until it reaches a point where all adsorbed sites are filled. This asymptote occurs at 0.5 because that was the value of the dimensionless parameter w_a.
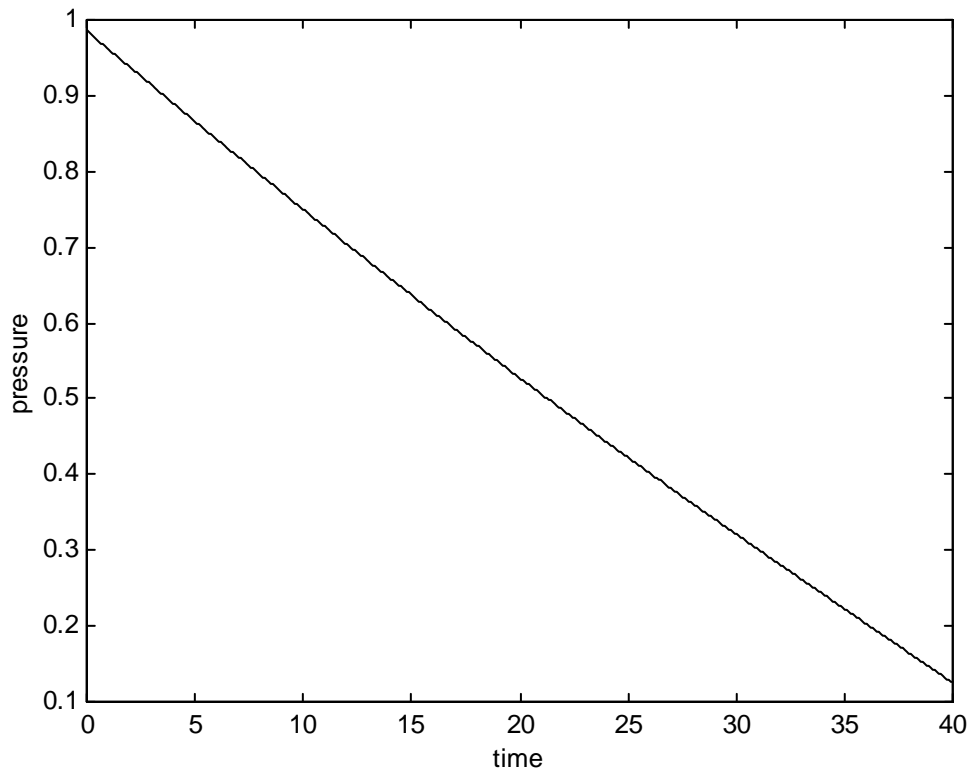
Figure 5. Pressure of the bulk phase as a function of time. The pressure decreases as a function of time because (i) the temperature decreases and (ii) material leaves the bulk phase.

codes

This program requires three codes:
driver.m
sysode.m (not included here as it is not altered from the 505 website)
sysodeninput.m

driver.m

```matlab
%driver.m
clear all;
close all;
format long;
global isave datamat icount
%
method_ODE = 1;
n = 1000;
to = 0;
tf = 40;
To = 1;
isave = 0;
[t,T]=sysode(method_ODE,n,to,tf,To);
% save results
isave = 1;
nT = max(size(T));
% datamat column 1:  bulk density
% datamat column 2:  fractional coverage
% datamat column 3:  mass fraction adsorbed
% datamat column 4:  mass fraction bulk
% datamat column 5:  pressure
datamat = zeros(5,nT);
for icount = 1:1:nT
    f=sysodeinput(t(icount),T(icount));
end
% plot results
figure(1)
plot(t,T,'k-');
xlabel('time');
ylabel('temperature');
%axis([t(1) t(nT) 0 1.1]);
figure(2)
plot(t,datamat(1,:),'k-');
xlabel('time');
ylabel('bulk density');
figure(3)
plot(t,datamat(2,:),'k-');
xlabel('time');
ylabel('fractional coverage');
figure(4)
plot(t,datamat(3,:),'k-');
xlabel('time');
ylabel('mass fraction adsorbed');
figure(5)
plot(t,datamat(4,:),'k-');
xlabel('time');
```

```matlab
ylabel('mass fraction bulk');
figure(6)
plot(t,datamat(5,:),'k-');
xlabel('time');
ylabel('pressure');
```

sysodeinput.m

```matlab
%sysodeinput.m
function dTdt = sysodeinput(t,T,nvec);
global isave datamat icount
%
%  dimensionless parameters
%
Q = 1.0;
wa = 0.5;
rhop = 10.0;
Cvp = 10.0;
a = 0.1;
b = 0.0001;
delUads = -2.0;
delHads = -2.0;
Ko = 1.0;
eps = 0.5;
%
%  dimensionless functions
%
K = Ko*exp(-delHads/T);
dKdT = K*delHads/T^2;
aquad = -K*eps;
bquad = K-eps-wa*K;
cquad = 1;
discrim = sqrt(bquad*bquad-4*aquad*cquad);
rho_plus = (-bquad + discrim)/(2*aquad);
rho_minus = (-bquad - discrim)/(2*aquad);
rho = rho_minus;
theta = K*rho/(1+K*rho);
drhodT = rho*dKdT/(eps*(1+K*rho)^2/wa + K);
Ub = 1.5*T - rho*a;
Ua = 1.5*T + delUads;
%
%  dimensionless energy balance
%
dTdt = -Q/(1.5*wa*theta + 1.5*eps*rho + (1-eps)*rhop*Cvp + …
   eps*(Ub-Ua-rho*a)*drhodT);
%
%  generate properties for plotting
%
if (isave == 1)
   %
   % save extra data
   %
   pressure = rho/(1-b)*T - a*rho^2;
   mb = rho*eps;
   ma = theta*wa;
   datamat(1,icount) = rho;
```

```
   datamat(2,icount) = theta;
   datamat(3,icount) = ma;
   datamat(4,icount) = mb;
   datamat(5,icount) = pressure;
end
```