

Solutions to exercises

Exercise 1.1

The standard barrel of crude oil is 42 US gallons, that is, 42×3.785 litres = 0.159 m^3 . The $100\,000 \text{ m}^3$ of crude oil pumped through the Trans-Alaska Pipeline per day given in Section 1.1 hence correspond to 630 000 barrels. With a current price of some 50 US dollars per barrel (mid 2016), the value of the crude oil transported through the Trans-Alaska Pipeline in a day is given by the impressive number of 31 000 000 US dollars.

Exercise 2.1

Straightforward differentiations of the probability density $p_{\alpha_t \Theta_t}(x)$ defined in (2.16) give the following results:

$$\frac{\partial}{\partial t} p_{\alpha_t \Theta_t}(x) = \left[\frac{\dot{\Theta}_t}{2\Theta_t^2} (x - \alpha_t)^2 + \frac{\dot{\alpha}_t}{\Theta_t} (x - \alpha_t) - \frac{\dot{\Theta}_t}{2\Theta_t} \right] p_{\alpha_t \Theta_t}(x),$$

$$-\frac{\partial}{\partial x} [A_0(t) + A_1(t)x] p_{\alpha_t \Theta_t}(x) = \left[\frac{A_1(t)}{\Theta_t} (x - \alpha_t)^2 + \frac{A_1(t)\alpha_t + A_0(t)}{\Theta_t} (x - \alpha_t) - A_1(t) \right] p_{\alpha_t \Theta_t}(x),$$

and

$$\frac{1}{2} \frac{\partial^2}{\partial x^2} D_0(t) p_{\alpha_t \Theta_t}(x) = \frac{D_0(t)}{2\Theta_t^2} [(x - \alpha_t)^2 - \Theta_t] p_{\alpha_t \Theta_t}(x).$$

By comparing the prefactors of $(x - \alpha_t)^2$, $x - \alpha_t$, and 1, we recover the evolution equations (2.9) and (2.10).

Exercise 2.2

According to the superposition principle, we have

$$\begin{aligned} p(t, x) &= \int_{-1/2}^{1/2} p_{y,t}(x) dy = \int_{-1/2}^{1/2} p_{0,t}(x-y) dy = \int_{(x-1/2)/\sqrt{2t}}^{(x+1/2)/\sqrt{2t}} p_{0,1/2}(z) dz \\ &= \frac{1}{2} \left[\operatorname{erf} \left(\frac{x+1/2}{\sqrt{2t}} \right) - \operatorname{erf} \left(\frac{x-1/2}{\sqrt{2t}} \right) \right]. \end{aligned}$$

Exercise 2.3

In Mathematica:

```
convol[x_, sig_]=
  Integrate[(1-t)*PDF[NormalDistribution[t, sig], x], {t, 0, 1}] +
  Integrate[(1+t)*PDF[NormalDistribution[t, sig], x], {t, -1, 0}]
Plot[{Piecewise[{{1+x, -1<x<=0}, {1-x, 0<x<1}}, 0],
  convol[x, Sqrt[.03]], convol[x, Sqrt[.3]]}, {x, -2, 2},
  PlotRange->{0, 1}, AxesLabel->{Text[Style[x, FontSize->20]],
  Text[Style[p[t, x], FontSize->20]]}]
```

Notice that Mathematica $\text{\textcircled{R}}$ actually gives an analytical result for the integral implied by the superposition principle in terms of error functions. The resulting curves are shown in Figure C.9.

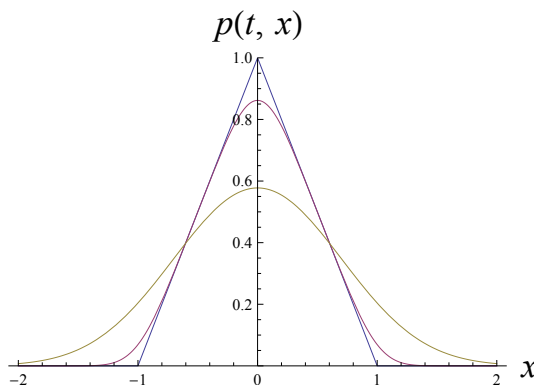


Figure C.9 Mathematica $\text{\textcircled{R}}$ output for the diffusion problem of Exercise 2.3.

Exercise 2.4

$$\frac{d}{dt} \left[- \int p \ln(p/p_{\text{eq}}) dx \right] = - \int \left[\frac{\partial p}{\partial t} \ln(p/p_{\text{eq}}) + \frac{\partial p}{\partial t} \right] dx$$

$$= \int \ln(p/p_{\text{eq}}) \frac{\partial J}{\partial x} dx = - \int J \frac{\partial}{\partial x} \ln(p/p_{\text{eq}}) dx,$$

where the normalization of p and the diffusion equation have been used. By inserting the expression for J given in (2.25) we obtain the desired result.

Exercise 2.5

The eigenvalue problem for pure diffusion with $D = 1$ is given by

$$-\lambda p(x) = \frac{1}{2} \frac{d^2 p(x)}{dx^2},$$

which has the solutions

$$p(x) = C_1 \sin(\sqrt{2\lambda} x + C_2).$$

The boundary condition $p(0) = 0$ suggest $C_2 = 0$ and the boundary condition $p(1) = 0$ then selects discrete values of λ ,

$$\sqrt{2\lambda_n} = n\pi, \quad \lambda_n = \frac{n^2 \pi^2}{2}.$$

We can now write the solution as the Fourier series

$$p(t, x) = \sum_{n=1}^{\infty} c_n \sin(n\pi x) e^{-\lambda_n t},$$

where the coefficients c_n are determined by the initial condition at $t = 0$. By multiplying with $\sin(m\pi x)$ and integrating, we find

$$\int_0^1 \sin(m\pi x) dx = \sum_{n=1}^{\infty} c_n \int_0^1 \sin(m\pi x) \sin(n\pi x) dx,$$

leading to the explicit expressions

$$\frac{1}{m\pi} [1 - (-1)^m] = \frac{c_m}{2}.$$

Note that all the coefficients c_n with even n vanish. The fraction of the substance released as a function of time is given by

$$1 - \int_0^1 p(t, x) dx = 1 - \sum_{n=\text{odd}} \frac{8}{n^2 \pi^2} e^{-\lambda_n t}.$$

Exercise 2.6

According to the respective definitions, we have

$$\mathcal{T} - \exp\{\mathbf{M}(t_1) + \mathbf{M}(t_2)\} = \mathbf{1} + \mathbf{M}(t_1) + \mathbf{M}(t_2)$$

$$\begin{aligned}
& + \frac{1}{2} [\mathbf{M}(t_1)^2 + \mathbf{M}(t_2)^2] + \mathbf{M}(t_2) \cdot \mathbf{M}(t_1) \\
& + \frac{1}{6} [\mathbf{M}(t_1)^3 + \mathbf{M}(t_2)^3] + \frac{1}{2} [\mathbf{M}(t_2) \cdot \mathbf{M}(t_1)^2 + \mathbf{M}(t_2)^2 \cdot \mathbf{M}(t_1)] + \dots,
\end{aligned}$$

and

$$\begin{aligned}
\exp\{\mathbf{M}(t_1) + \mathbf{M}(t_2)\} &= \mathbf{1} + \mathbf{M}(t_1) + \mathbf{M}(t_2) \\
& + \frac{1}{2} [\mathbf{M}(t_1) + \mathbf{M}(t_2)]^2 + \frac{1}{6} [\mathbf{M}(t_1) + \mathbf{M}(t_2)]^3 + \dots.
\end{aligned}$$

In terms of the commutator $\mathbf{C} = \mathbf{M}(t_2) \cdot \mathbf{M}(t_1) - \mathbf{M}(t_1) \cdot \mathbf{M}(t_2)$, the difference can be written as

$$\begin{aligned}
\mathcal{T} - \exp\{\mathbf{M}(t_1) + \mathbf{M}(t_2)\} - \exp\{\mathbf{M}(t_1) + \mathbf{M}(t_2)\} &= \frac{1}{2} \mathbf{C} \\
& + \frac{1}{6} [\mathbf{C} \cdot \mathbf{M}(t_1) + \mathbf{M}(t_2) \cdot \mathbf{C} + \mathbf{M}(t_2) \cdot \mathbf{M}(t_1)^2 - \mathbf{M}(t_1)^2 \cdot \mathbf{M}(t_2) \\
& + \mathbf{M}(t_2)^2 \cdot \mathbf{M}(t_1) - \mathbf{M}(t_1) \cdot \mathbf{M}(t_2)^2] + \dots.
\end{aligned}$$

Exercise 2.7

Straightforward differentiations of the probability density $p_{\alpha_t \Theta_t}(\mathbf{x})$ defined in (2.39) give the following results:

$$\begin{aligned}
\frac{\partial}{\partial t} p_{\alpha_t \Theta_t}(\mathbf{x}) &= \left[\frac{1}{2} (\mathbf{x} - \alpha_t) \cdot \Theta_t^{-1} \cdot \dot{\Theta}_t \cdot \Theta_t^{-1} \cdot (\mathbf{x} - \alpha_t) \right. \\
& \left. + (\mathbf{x} - \alpha_t) \cdot \Theta_t^{-1} \cdot \dot{\alpha}_t - \frac{1}{2} \text{tr} \left(\dot{\Theta}_t \cdot \Theta_t^{-1} \right) \right] p_{\alpha_t \Theta_t}(\mathbf{x}),
\end{aligned}$$

$$\begin{aligned}
-\frac{\partial}{\partial \mathbf{x}} \cdot [\mathbf{A}_0(t) + \mathbf{A}_1(t) \cdot \mathbf{x}] p_{\alpha_t \Theta_t}(\mathbf{x}) &= \\
& \left[\frac{1}{2} (\mathbf{x} - \alpha_t) \cdot (\Theta_t^{-1} \mathbf{A}_1(t) + \mathbf{A}_1^T(t) \cdot \Theta_t^{-1}) \cdot (\mathbf{x} - \alpha_t) \right. \\
& \left. + (\mathbf{x} - \alpha_t) \cdot \Theta_t^{-1} \cdot (\mathbf{A}_0(t) + \mathbf{A}_1(t) \cdot \alpha_t) - \text{tr} \mathbf{A}_1(t) \right] p_{\alpha_t \Theta_t}(\mathbf{x}),
\end{aligned}$$

and

$$\begin{aligned}
\frac{1}{2} \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} : \mathbf{D}_0(t) p_{\alpha_t \Theta_t}(\mathbf{x}) &= \frac{1}{2} \left[(\mathbf{x} - \alpha_t) \cdot \Theta_t^{-1} \cdot \mathbf{D}_0(t) \cdot \Theta_t^{-1} \cdot (\mathbf{x} - \alpha_t) \right. \\
& \left. - \text{tr} (\mathbf{D}_0(t) \cdot \Theta_t^{-1}) \right] p_{\alpha_t \Theta_t}(\mathbf{x}).
\end{aligned}$$

By comparing prefactors, we obtain the following evolution equations:

$$\dot{\alpha}_t = \mathbf{A}_1(t) \cdot \alpha_t + \mathbf{A}_0(t),$$

and

$$\dot{\Theta}_t = \mathbf{A}_1(t) \cdot \Theta_t + \Theta_t \cdot \mathbf{A}_1^T(t) + \mathbf{D}_0(t).$$

Exercise 2.8

In Mathematica $\text{\textcircled{R}}$:

```
Theta={{0.4,0.3},{0.3,0.6}}
invT=Inverse[Theta]
f[x1_,x2_] := Exp[-1/2 {x1,x2}.invT.{x1,x2}]/Sqrt[(2 Pi)^2 Det[Theta]]
Plot3D[f[x1,x2],{x1,-2,2},{x2,-2,2}]
```

The output is shown in Figure C.10.

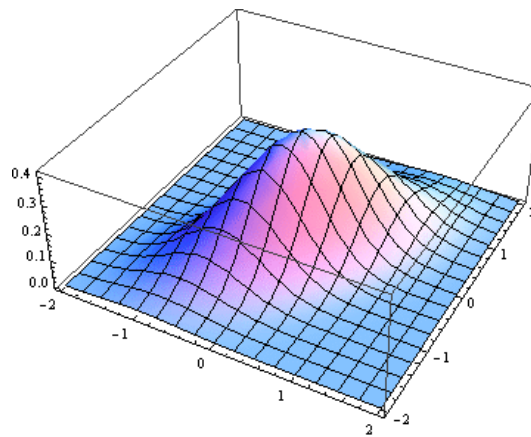


Figure C.10 Mathematica $\text{\textcircled{R}}$ output for the two-dimensional Gaussian of Exercise 2.8.

Exercise 2.9

The covariance matrix Θ is symmetric and can hence be diagonalized. By a linear transformation to suitable coordinates, Θ can hence be assumed to be diagonal. For diagonal Θ , the probability density in (2.39) indeed is the product of d one-dimensional Gaussians.

Exercise 3.1

To switch from a rectangular to a triangular initial distribution, we only need to change the stochastic initial condition. The curve for $t = 0.03$ is produced by the following MATLAB $\text{\textcircled{R}}$ code:

```
% Simulation parameters
```

```

NTRA=1000;NTIME=3;NHIST=100;DT=0.01;
XMIN=-1.;DX=0.05;XMAX=1.;
edges=XMIN:DX:XMAX;
centers=XMIN+DX/2:DX:XMAX-DX/2;

for K=1:NHIST
    % Generation of NTRA trajectories x
    y=random('Uniform',-1,1,[1,NTRA]); x=sign(y).*(1-sqrt(abs(y)));
    for J=1:NTIME
        x=x+random('Normal',0,sqrt(DT),[1,NTRA]);
    end
    % Collection of NHIST histograms in matrix p
    p(K,:)=histc(x,edges)/(DX*NTRA);
end

% Plot of simulation results
errorbar([centers NaN],mean(p),std(p)/sqrt(NHIST),'LineStyle','none')

```

Exercise 3.2

By integrating (3.19) over x , we obtain

$$1 - \int_0^{\infty} p_f(t, x) dx = \int_0^{\infty} \int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}} \exp\left\{-\frac{1}{2} \frac{(x+t-t')^2}{t-t'}\right\} dt' dx.$$

For the time derivative of the left-hand side of this equation, we obtain by means of the diffusion equation

$$-\frac{d}{dt} \int_0^{\infty} p_f(t, x) = \frac{1}{2} \frac{\partial p_f(t, x)}{\partial x} \Big|_{x=0} + p_f(t, 0).$$

The contribution to the time derivative of the right-hand side of the above equation resulting from the upper limit of the time integration is

$$a(t) \lim_{\epsilon \rightarrow 0} \frac{1}{\sqrt{2\pi\epsilon}} \int_0^{\infty} \exp\left\{-\frac{1}{2} \frac{(x+\epsilon)^2}{\epsilon}\right\} dx = \frac{1}{2} a(t),$$

where we can neglect the mean value $-\epsilon$ compared to the width $\sqrt{\epsilon}$ of the Gaussian distribution. For the time derivative of the Gaussian under the integral in the above equation, we can again use the diffusion equation to obtain

$$\int_0^{\infty} \int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}} \left(\frac{\partial}{\partial x} + \frac{1}{2} \frac{\partial^2}{\partial x^2} \right) \exp\left\{-\frac{1}{2} \frac{(x+t-t')^2}{t-t'}\right\} dt' dx = -\frac{1}{2} \int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}} e^{-(t-t')/2} dt'.$$

By equating the time derivatives of the left- and right-hand sides, we arrive at the desired result (3.20).

Exercise 3.3

Mathematica[®] code for the inverse Laplace transform using the Zakian method, adapted from the implementation `Zakian.nb` by Housam Binous in the Wolfram Library Archive (library.wolfram.com):

```
alph={12.83767675+I 1.666063445,
      12.22613209+I 5.012718792,
      10.9343031+I 8.40967312,
      8.77643472+I 11.9218539,
      5.22545336+I 15.7295290};
K={-36902.0821+I 196990.426,
    61277.0252-I 95408.6255,
    -28916.5629+I 18169.1853,
    4655.36114-I 1.90152864,
    -118.741401-I 141.303691};
abar[s_]=Exp[1-Sqrt[1+2s]]*(Sqrt[1+2s]+1)/(Sqrt[1+2s]-1);
a[t_]=2/t Sum[Re[K[[i]]abar[alph[[i]]/t]],{i,5}];
Plot[a[t],{t,0,5},PlotRange->{0,2.5}]
```

Mathematica[®] code for the evaluation of (3.19):

```
p[t_.,x_.]:= (1/Sqrt[2Pi t]) Exp[-0.5(x-1+t)^2/t]+
  NIntegrate[(a[tp]/Sqrt[2Pi(t-tp)]) Exp[-0.5(x+t-tp)^2/(t-tp)],{tp,0,t}]
Plot[p[0.3,x],{x,0,2}]
```

Exercise 4.1

From (4.15) and (4.21) we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{3N\tilde{R}}{2U}$$

which gives (4.22a). Similarly, from (4.16) and (4.21) we have

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N} = \frac{N\tilde{R}}{V}$$

which gives (4.22b). Finally, from (4.17) and (4.21) we have for a single-component fluid

$$-\frac{\tilde{\mu}}{T} = \left(\frac{\partial S}{\partial N} \right)_{U,V} = \tilde{s}_0 + \tilde{R} \ln \left[\left(\frac{U}{N\tilde{u}_0} \right)^{3/2} \left(\frac{V}{N\tilde{v}_0} \right) \right] - \frac{5}{2}\tilde{R}$$

Rearranging and using previous results, we can write

$$\tilde{\mu} = -T\tilde{s}_0 - \tilde{R}T \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{\tilde{R}T}{p\tilde{v}_0} \right) \right] + \frac{5}{2}\tilde{R}T$$

where we have used $\tilde{u}_0 = \frac{3}{2}\tilde{R}T_0$. Collecting all terms depending on T in $\tilde{\mu}^0(T)$ leads to (4.22c).

Exercise 4.2

We first invert (4.21) to obtain

$$U(S, V, N) = N\tilde{u}_0 \left(\frac{V}{N\tilde{v}_0} \right)^{-2/3} \exp \left\{ \frac{2}{3} \frac{S - N\tilde{s}_0}{N\tilde{R}} \right\}$$

as a starting point for our Legendre transformation. By differentiation with respect to S we obtain

$$T(S, V, N) = \frac{2\tilde{u}_0}{3\tilde{R}} \left(\frac{V}{N\tilde{v}_0} \right)^{-2/3} \exp \left\{ \frac{2}{3} \frac{S - N\tilde{s}_0}{N\tilde{R}} \right\},$$

and by inversion

$$S(T, V, N) = N\tilde{s}_0 + N\tilde{R} \ln \left[\frac{V}{N\tilde{v}_0} \left(\frac{3\tilde{R}T}{2\tilde{u}_0} \right)^{3/2} \right].$$

Now, from (4.24) the Helmholtz free energy is then given by $F(T, V, N) = U(S(T, V, N), V, N) - TS(T, V, N)$,

$$\begin{aligned} F(T, V, N) &= \frac{3}{2} N\tilde{R}T - N\tilde{s}_0T - N\tilde{R}T \ln \left[\frac{V}{N\tilde{v}_0} \left(\frac{3\tilde{R}T}{2\tilde{u}_0} \right)^{3/2} \right] \\ &= -N\tilde{R}T \ln \left[\frac{V}{N\tilde{v}_0} \left(\frac{3\tilde{R}T}{2\tilde{u}_0e} \right)^{3/2} \exp \left\{ \frac{\tilde{s}_0}{\tilde{R}} \right\} \right]. \end{aligned}$$

This expression can be simplified considerably by introducing a new constant c in terms of all the other constants,

$$c = \frac{1}{\tilde{v}_0} \left(\frac{3\tilde{R}}{2\tilde{u}_0e} \right)^{3/2} \exp \left\{ \frac{\tilde{s}_0}{\tilde{R}} \right\}.$$

Exercise 4.3

By integrating $p = N\tilde{R}T/V$ we find

$$F(T, V, N) = -N\tilde{R}T \ln \left[\frac{V}{C(T, N)} \right],$$

where $C(T, N)$ represents an additive integration constant. To obtain an extensive free energy, $C(T, N)$ must be of the form $C(T, N) = N\tilde{C}(T)$. Equation (4.25) then leads to the entropy

$$S(T, V, N) = N\tilde{R} \ln \left[\frac{V}{N\tilde{C}(T)} \right] - N\tilde{R}T \frac{1}{\tilde{C}(T)} \frac{d\tilde{C}(T)}{dT}.$$

For reproducing the ideal-gas entropy (see solution to Exercise 4.2) we need to choose

$$\frac{1}{\tilde{C}(T)} = cT^{3/2},$$

where c plays the role of a further integration constant. For a suitable matching of constants, the resulting Helmholtz free energy (4.39) coincides with the solution to Exercise 4.2.

Exercise 4.4

In terms of intensive quantities we can write (4.15) as $1/T = (\partial s/\partial u)_\rho$ and (4.17) as $-\hat{\mu}/T = (\partial s/\partial \rho)_u$. Applying these to (4.56) we obtain

$$\frac{1}{T} = \frac{3 k_B \rho}{2 m u}, \quad -\frac{\hat{\mu}}{T} = \frac{s}{\rho} + \frac{k_B}{m} \left[\frac{\partial \ln R_0(\rho)}{\partial \ln \rho} - \frac{5}{2} \right].$$

Combining these using the Euler equation (4.44) gives the following equations of state:

$$u = \frac{3 \rho k_B T}{2 m}, \quad p = \frac{\rho k_B T}{m} \left[1 - \frac{\partial \ln R_0(\rho)}{\partial \ln \rho} \right],$$

which match the equations of state for an ideal gas if $R_0(\rho)$ is constant.

Exercise 4.5

Using the Maxwell relation $(\partial \hat{s}/\partial \hat{v})_{T, w_\alpha} = (\partial p/\partial T)_{\hat{v}, w_\alpha}$ and definition for specific heat capacity $\hat{c}_{\hat{v}} = T(\partial \hat{s}/\partial T)_{\hat{v}, w_\alpha}$ in (4.49) gives

$$d\hat{u} = \hat{c}_{\hat{v}} dT + \left[T \left(\frac{\partial p}{\partial T} \right)_{\hat{v}, w_1} - p \right] d\hat{v} + \left[T \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, \hat{v}} + (\hat{\mu}_1 - \hat{\mu}_2) \right] dw_1.$$

Focusing on the last term in square brackets, we use (4.52) and write

$$T \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, p} = T(\hat{s}_1 - \hat{s}_2) = \hat{u}_1 - \hat{u}_2 + p(\hat{v}_1 - \hat{v}_2) - (\hat{\mu}_1 - \hat{\mu}_2),$$

which can be arranged to give

$$T \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, p} + (\hat{\mu}_1 - \hat{\mu}_2) = (\hat{h}_1 - \hat{h}_2).$$

Now, to change the independent variables in the derivative on the left-hand side, we write

$$\left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, p} = \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, \hat{v}} + \left(\frac{\partial \hat{s}}{\partial \hat{v}} \right)_{T, w_1} \left(\frac{\partial \hat{v}}{\partial w_1} \right)_{T, p} = \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, \hat{v}} + \left(\frac{\partial p}{\partial T} \right)_{\hat{v}, w_1} (\hat{v}_1 - \hat{v}_2),$$

where we have used the Maxwell relation and (4.52) to obtain the second equality. Combining the last two results, we obtain

$$T \left(\frac{\partial \hat{s}}{\partial w_1} \right)_{T, \hat{v}} + (\hat{\mu}_1 - \hat{\mu}_2) = (\hat{h}_1 - \hat{h}_2) + T \left(\frac{\partial p}{\partial T} \right)_{\hat{v}, w_1} (\hat{v}_1 - \hat{v}_2).$$

Substitution in the expression above for $d\hat{u}$ gives the result in (4.53).