Solutions to exercises

Exercise 1.1
The standard barrel of crude oil is 42 US gallons, that is, \(42 \times 3.785 \text{ litres} = 0.159 \text{ m}^3\). The 100 000 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 \(p_{\alpha(t)}(x)\) defined in (2.16) give the following results:

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

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

and

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

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
\[
p(t, x) = \int_{-1/2}^{1/2} p_{01}(x - y)dy = \int_{(x-1/2)/\sqrt{2t}}^{(x+1/2)/\sqrt{2t}} p_{01/2}(z)dz
\]
\[
= \frac{1}{2} \left[ \text{erf} \left( \frac{x + 1/2}{\sqrt{2t}} \right) - \text{erf} \left( \frac{x - 1/2}{\sqrt{2t}} \right) \right].
\]

Exercise 2.3
In Mathematica:

\[
\text{convol}[x_, \text{sig}_1] = \\
\text{Integrate}[(1-t) \cdot \text{PDF}[\text{NormalDistribution}[t, \text{sig}_1], x], \{t, 0, 1\}] + \\
\text{Integrate}[(1+t) \cdot \text{PDF}[\text{NormalDistribution}[t, \text{sig}_1], x], \{t, -1, 0\}]
\]

\[
\text{Plot}[\{\text{Piecewise}[\{(1+x, -1 < x < 0), (1-x, 0 < x < 1)\}], 0\}, \\
\\text{convol}[x, \text{Sqrt}[0.03]], \text{convol}[x, \text{Sqrt}[0.3]], \{x, -2, 2\}, \\
\text{PlotRange} -> \{0, 1\}, \text{AxesLabel} -> \{\text{Text[Style[x, FontSize -> 20]],} \\
\\text{Text[Style[p[t, x], FontSize -> 20]]}\}]
\]

Notice that Mathematica® 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.

Exercise 2.4

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

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

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

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

**Exercise 2.6**

According to the respective definitions, we have

$$T - \exp\{M(t_1) + M(t_2)\} = 1 + M(t_1) + M(t_2).$$
By comparing prefactors, we obtain the following evolution equations:

\[ + \frac{1}{2} [M(t_1)^2 + M(t_2)^2] + M(t_2) \cdot M(t_1) \]
\[ + \frac{1}{6} [M(t_1)^3 + M(t_2)^3] + \frac{1}{2} [M(t_2) \cdot M(t_1)^2 + M(t_2)^2 \cdot M(t_1)] + \ldots, \]

and

\[ \exp\{M(t_1) + M(t_2)\} = 1 + M(t_1) + M(t_2) \]
\[ + \frac{1}{2} [M(t_1) + M(t_2)]^2 + \frac{1}{6} [M(t_1) + M(t_2)]^3 + \ldots. \]

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

\[ T - \exp\{M(t_1) + M(t_2)\} - \exp\{M(t_1) + M(t_2)\} = \frac{1}{2} C \]
\[ + \frac{1}{6} [C \cdot M(t_1) + M(t_2) \cdot C + M(t_2) \cdot M(t_1)^2 - M(t_1)^2 \cdot M(t_2) \]
\[ + M(t_2)^2 \cdot M(t_1) - M(t_1) \cdot M(t_2)^2] + \ldots. \]

**Exercise 2.7**

Straightforward differentiations of the probability density \( p_{\alpha t}(x) \) defined in (2.39) give the following results:

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

\[ - \frac{\partial}{\partial x} \cdot [A_0(t) \cdot A_1(t) \cdot x] p_{\alpha t}(x) = \]
\[ \left[ \frac{1}{2} (x - \alpha_t) \cdot \Theta_t^{-1} A_1(t) + A_1^T(t) \cdot \Theta_t^{-1} \cdot (x - \alpha_t) \right. \]
\[ + (x - \alpha_t) \cdot \Theta_t^{-1} \cdot (A_0(t) + A_1(t) \cdot \alpha_t) - \text{tr} A_1(t) \] \( p_{\alpha t}(x), \)

and

\[ \frac{1}{2} \frac{\partial}{\partial x} \frac{\partial}{\partial x} D_0(t) p_{\alpha t}(x) = \frac{1}{2} \left[ (x - \alpha_t) \cdot \Theta_t^{-1} \cdot D_0(t) \cdot \Theta_t^{-1} \cdot (x - \alpha_t) \right. \]
\[ \left. - \text{tr} \left( D_0(t) \cdot \Theta_t^{-1} \right) \right] p_{\alpha t}(x). \]

By comparing prefactors, we obtain the following evolution equations:

\[ \dot{\alpha}_t = A_1(t) \cdot \alpha_t + A_0(t), \]
and

\[ \dot{\Theta} = A(t) \cdot \Theta + \Theta \cdot A^T(t) + D_0(t). \]

**Exercise 2.8**

In Mathematica®:

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® output for the two-dimensional Gaussian of Exercise 2.8.](image)

**Exercise 2.9**

The covariance matrix \( \Theta \) is symmetric and can hence be diagonalized. By a linear transformation to suitable coordinates, \( \Theta \) can hence be assumed to be diagonal. For diagonal \( \Theta \), 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® code:

```matlab
% Simulation parameters
```
NTRA=1000;NTIME=1;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).*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

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

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

\[
-\frac{d}{dt} \int_0^\infty p(t,x)\,dx = \left. \frac{1}{2} \frac{\partial p(t,x)}{\partial x} \right|_{x=0} + p(t,0).
\]

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

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

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):

\[
\begin{align*}
\text{alph} &= 
\{12.83767675 + I 1.666063445, \\
&12.22613209 + I 8.40967312, \\
&8.77643472 + I 11.9218539, \\
&5.22545336 + I 15.7295290\}; \\
K &= 
\{-36902.0821 + I 196990.426, \\
&61277.0252 - I 95408.6255, \\
&-28916.5629 + I 18169.1853, \\
&4655.36114 - I 1.90152864, \\
&-118.741401 - I 141.303691\}; \\
\text{abar} &= \text{Exp}[1 - \sqrt{1+2s}] * (\sqrt{1+2s} + 1)/(\sqrt{1+2s} - 1); \\
\text{a} &= \frac{2}{t} \sum \Re[K[i] \text{abar[alph[i]]/t}], \{i,5\}; \\
\text{Plot}[a[t], \{t, 0, 5\}, \text{PlotRange} > \{0, 2.5\}] \\
\end{align*}
\]

Mathematica® code for the evaluation of (3.19):

\[
\begin{align*}
\text{p}[t, x] &= \frac{1}{\sqrt{2\pi t}} \exp\left[-0.5(x-1+t)^2/t\right] + \\
&\text{NIntegrate}\left[\left(\frac{a[t]}{\sqrt{2\pi(t-tp)}}\right) \exp\left[-0.5(x+t-tp)^2/(t-tp)\right], \{tp, 0, t\}\right] \\
\text{Plot}[p[0.3, x], \{x, 0, 2\}] \\
\end{align*}
\]

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

\[
p_T = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{N\tilde{R}}{V}
\]

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

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

Rearranging and using previous results, we can write

\[
\tilde{\mu} = -T\tilde{s}_0 - \tilde{R} T \ln \left[\left(\frac{T}{T_0}\right)^{3/2} \left(\frac{\tilde{R} T}{p_0}\right)\right] + \frac{5}{2} \tilde{R} T
\]

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
\[ F(T, V, N) = -N\tilde{R}T + N\tilde{s}_0 T - N\tilde{R} \ln \left[ \frac{V}{N\tilde{v}_0} \left( \frac{3\tilde{R}T}{2\tilde{u}_0} \right)^{3/2} \exp \left\{ \frac{\tilde{s}_0}{\tilde{R}} \right\} \right]. \]
This expression can be simplified considerably by introducing a new constant \( c \) in terms of all the other constants,
\[ c = \frac{1}{\tilde{v}_0} \left( \frac{3\tilde{R}}{2\tilde{u}_0 e} \right)^{3/2} \exp \left\{ \frac{\tilde{s}_0}{\tilde{R}} \right\}. \]

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:

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

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

**Exercise 4.5**

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

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

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

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

which can be arranged to give

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

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

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

where 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).