Solutions to exercises

Exercise 1.1
The standard barrel of crude oil is 42 US gallons, that is, 42×3.785 litres $= 0.159\,\mathrm{m}^3$. The $100\,000\,\mathrm{m}^3$ 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

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

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

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

Exercise 2.3
In Mathematica:

```
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® 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.

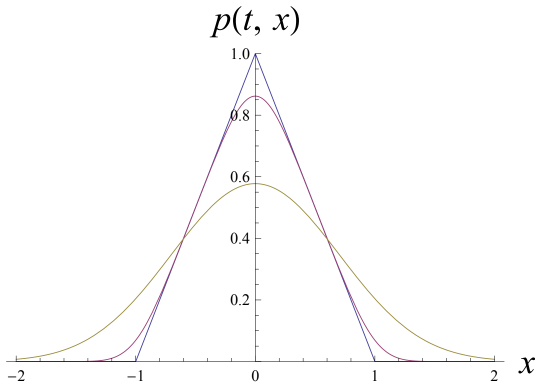

Figure C.9 Mathematica® output for the diffusion problem of Exercise 2.3.

Exercise 2.4

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

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

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,

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

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

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

Exercise 2.6

According to the respective definitions, we have

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

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

and

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

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

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

Exercise 2.7

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

$$\frac{\partial}{\partial t}p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})=\Bigg[\frac{1}{2}(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\dot{\boldsymbol{\Theta}}_t\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t)$$
$$+(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\dot{\boldsymbol{\alpha}}_t-\frac{1}{2}\,\mathrm{tr}\left(\dot{\boldsymbol{\Theta}}_t\cdot\boldsymbol{\Theta}_t^{-1}\right)\Bigg]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}),$$

$$-\frac{\partial}{\partial\boldsymbol{x}}\cdot\left[\boldsymbol{A}_0(t)+\boldsymbol{A}_1(t)\cdot\boldsymbol{x}\right]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})=$$
$$\Bigg[\frac{1}{2}(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot(\boldsymbol{\Theta}_t^{-1}\boldsymbol{A}_1(t)+\boldsymbol{A}_1^T(t)\cdot\boldsymbol{\Theta}_t^{-1})\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t)$$
$$+(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{A}_0(t)+\boldsymbol{A}_1(t)\cdot\boldsymbol{\alpha}_t)-\mathrm{tr}\boldsymbol{A}_1(t)\Bigg]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}),$$

and

$$\frac{1}{2}\frac{\partial}{\partial\boldsymbol{x}}\frac{\partial}{\partial\boldsymbol{x}}:\boldsymbol{D}_0(t)\,p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})=\frac{1}{2}\Big[(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\boldsymbol{D}_0(t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t)$$
$$-\,\mathrm{tr}\left(\boldsymbol{D}_0(t)\cdot\boldsymbol{\Theta}_t^{-1}\right)\Big]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}).$$

By comparing prefactors, we obtain the following evolution equations:

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

and

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

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.

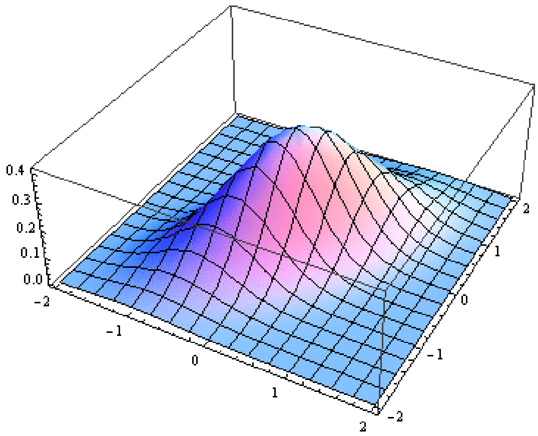

Figure C.10 Mathematica® output for the two-dimensional Gaussian of Exercise 2.8.

Exercise 2.9
The covariance matrix $\boldsymbol{\Theta}$ is symmetric and can hence be diagonalized. By a linear transformation to suitable coordinates, $\boldsymbol{\Theta}$ can hence be assumed to be diagonal. For diagonal $\boldsymbol{\Theta}$, 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:

```
% 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

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

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

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

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

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

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

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

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

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

and by inversion

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

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

$$F(T,V,N) = \frac{3}{2}N\tilde{R}T - N\tilde{s}_0T - N\tilde{R}T\ln\Big[\frac{V}{N\tilde{v}_0}\Big(\frac{3\tilde{R}T}{2\tilde{u}_0}\Big)^{3/2}\Big]$$
$$= -N\tilde{R}T\ln\Big[\frac{V}{N\tilde{v}_0}\Big(\frac{3\tilde{R}T}{2\tilde{u}_0 e}\Big)^{3/2}\exp\Big\{\frac{\tilde{s}_0}{\tilde{R}}\Big\}\Big].$$

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

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

Exercise 4.3
By integrating $p = N\tilde{R}T/V$ we find

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

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

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

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

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

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

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

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 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).