Excursions in Computing Science:
Book 9c. Heat: Histograms and Gases
Part III. Linear Thermodynamics.

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August 1, 2021

... a transport of delight

I. Prefatory Notes

1. Histograms.

2. Histogram arithmetic.

3. Distributions and densities.

4. Aggregates: the moments of distributions.

5. Quantum distributions: the density matrix.

6. The normal distribution.

7. Expectation, surprise and ignorance.

8. Does ignorance ever decrease?

9. Inside knowledge: the clients of Joe and Sue revisited.

10. Correlation and co-ignorance.

11. Conditional distributions and ignorance.

12. A gas simulation 1: the collisions

13. A gas simulation 2: statistics
14. The Boltzmann and Maxwell distributions.
15. Fluctuations, variations and samples.
16. Entropy.
17. Temperature.
18. Pressure.
19. State function for monatomic gases.
20. Thermostatic equations of state.
21. More on multivariate slopes.
22. Work and heat.

23. Correlation. Part II mainly discussed equilibrium thermodynamics, i.e, thermostatics, although we departed slightly from equilibrium in considering the Carnot cycle in Note 22. We now discuss transport phenomena, which depart from equilibrium, but still slightly enough that the departures are linear. So we leave thermostatics for thermodynamics, albeit linear thermodynamics.

First some general preliminaries concerning timeseries. We will need to understand cross-correlation, autocorrelation and convolution.

The "correlation" in the first two of these names rightly suggests statistics (see Note 10) but there is a twist: now we want to deal with *sequences*.
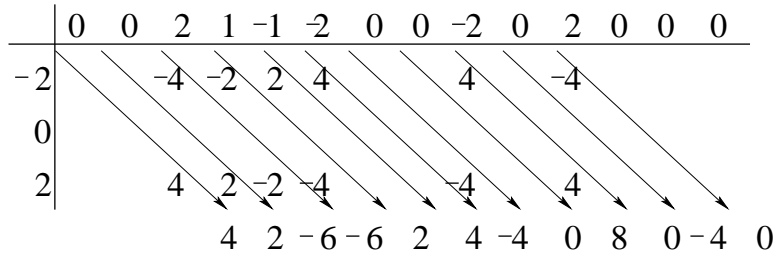
The *crosscorrelation* of two sequences provides a way of detecting similarities: one sequence is compared, at each position, to the other. The comparison is done by summing products between the two sequences.

Let's look for $-2, 0, 2$ as a subsequence of $2, 1, -1, -2, 0, 0, -2, 0, 2, 0$. Here is the explicit way of doing it.

```
         2    1   −1   −2    0    0   −2    0    2    0              lag   cc
  −2   0   2                                                        −2    4
       −2   0    2                                                  −1    2
            −2   0    2                                              0   −6
                 −2   0    2                                         1   −6
                      −2   0    2                                    2    2
                           −2   0    2                               3    4
                                −2   0    2                          4   −4
                                     −2   0    2                     5    0
                                          −2   0    2                6    8
                                               −2   0    2           7    0
                                                    −2   0   2       8   −4
                                                         −2   0   2  9    0
```

Note that the highest value in the result (column cc) gives the closest match, in this case an exact match. (The highest negative value gives the closest "antimatch".)

Here is a way which is easier for hand calculating. Make a "multiplication table" of the two sequences and then sum the diagonals.

```
        │ 0   0   2   1  −1  −2   0   0  −2   0   2   0   0   0
 ─────────────────────────────────────────────────────────────
  −2    │         −4  −2   2   4           4          −4
   0    │
   2    │         4   2  −2  −4          −4          4
              4   2  −6  −6   2   4  −4   0   8   0  −4   0
```

I'll use the symbol ⊘ to represent cross-correlation. Can you see from the multiplication table that the sequence $X \oslash Y$ is the reverse of $Y \oslash X$?

(In Note 26 I'll use Φ_{XY} to mean $X \oslash Y$ divided by the length of X or Y. In Note 24, Φ_X means Φ_{XX}.)

A program to calculate $C = X \oslash Y$ needs two loops after padding Y before and after with $|X| - 1$ zeros as above ($|X|$ is the size of X).

```
j = 1:|X| + |Y| - 1
    res = 0
    k = 1:|X|
        res = res + X(k)*Y(j+k-1)
    C(j) = res
```

Note that the result is a sequence involving only one subscript so it does not depend on k. In fact, if the sequences were infinitely long (say, if they were padded before and after with an infinite number of zeros) we could *translate* both sequences by changing k to $k' = k + \ell$ for any ℓ and the result would be the same.

We can normalize the crosscorrelation by dividing by the lengths of the sequences. I did not because the resulting fractions make the arithmetic less obvious.

<center>⊘ ⊘ ⊘ ⊘ ⊘</center>

A special case of crosscorrelation is the *autocorrelation* $x \oslash x$. This is clearly symmetric (i.e., invariant under time reversal if the sequences are "timeseries").
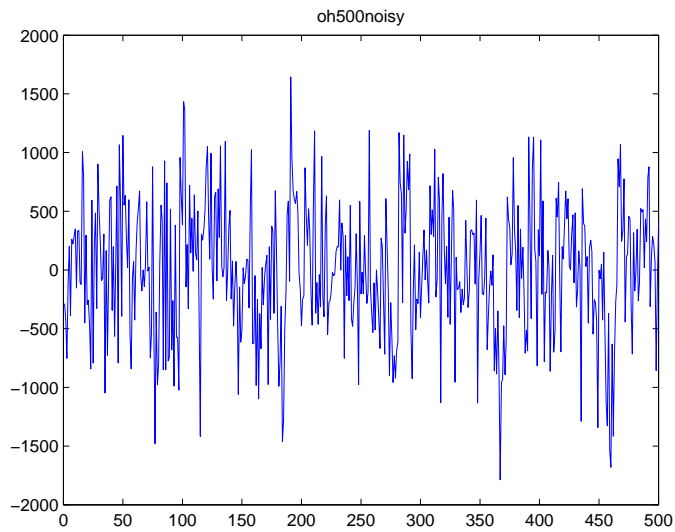
The autocorrelation can be used to discover periodic signals. Here is a portion of "oh" spoken by a man, and its autocorrelate.

<center>3</center>

oh(1006:1505)

Here's the result of applying the autocorrelation.
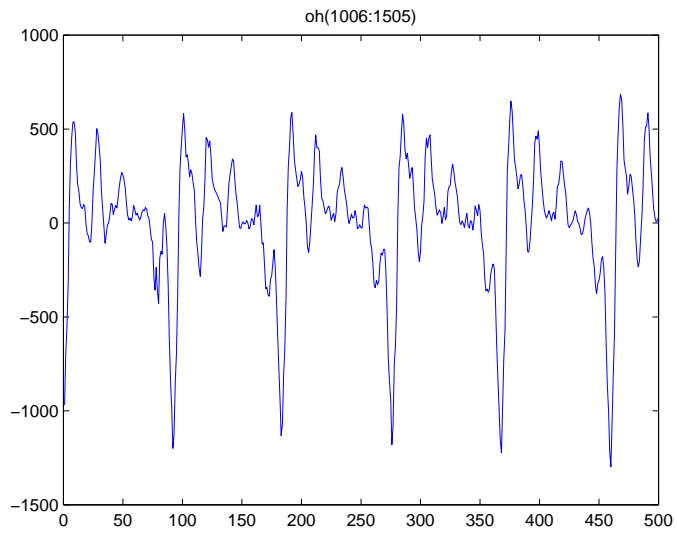
autocorrelation of oh500
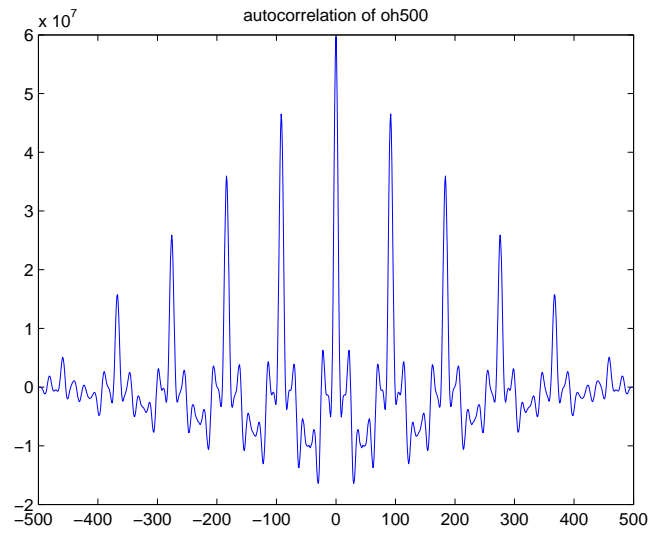
More practically, it can detect the period through noise.
```
oh500noisy = oh500 + random('normal',0,1,500,1)
```

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oh500noisy

This data is from the website for [GD99], which also provided the first crosscorrelation example in this Note.

Here's the result of applying the autocorrelation.

autocorrelation of oh500noisy
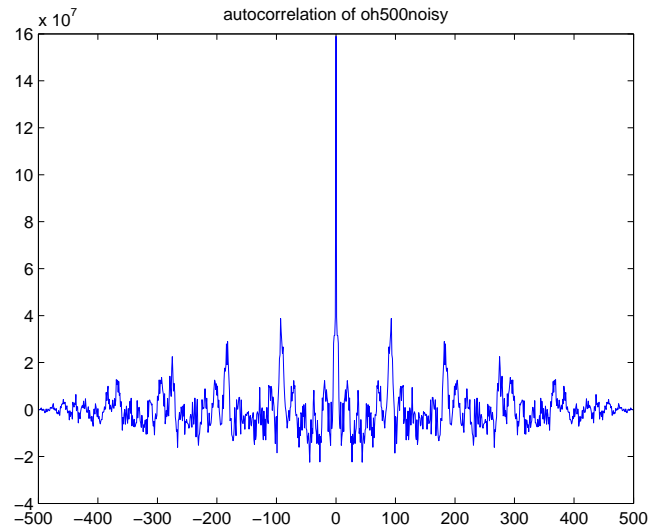
The reason for the diminution of the autocorrelation for lags away from 0 is due to the sample size. An infinitely long signal will not give such a decrease.

Periodic signals clearly correlate with themselves over arbitrary distances.

Pure noise, however, by definition, correlates with itself only at zero lag. Here is the autocorrelation of `random('normal',0,1,500,1)`

crosscorrel(noise500,noise500)
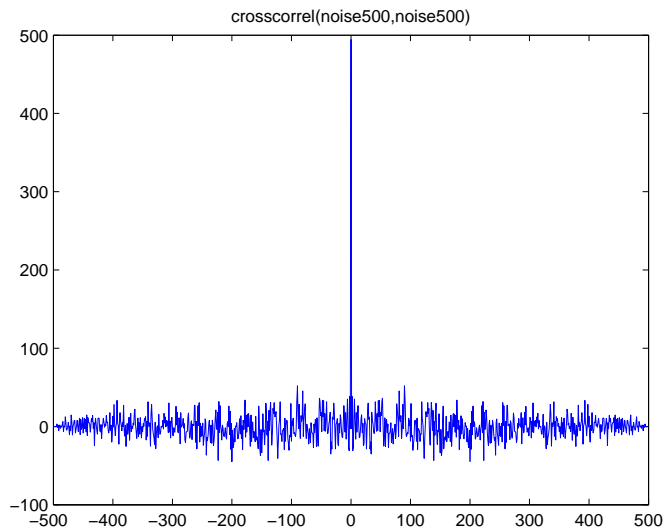
In between these two extremes, here are the autocorrelations of 500 a) ones, b) descending consecutive integers, and c) descending consecutive squares.


Autocorrelations of constant, linear and quadratic
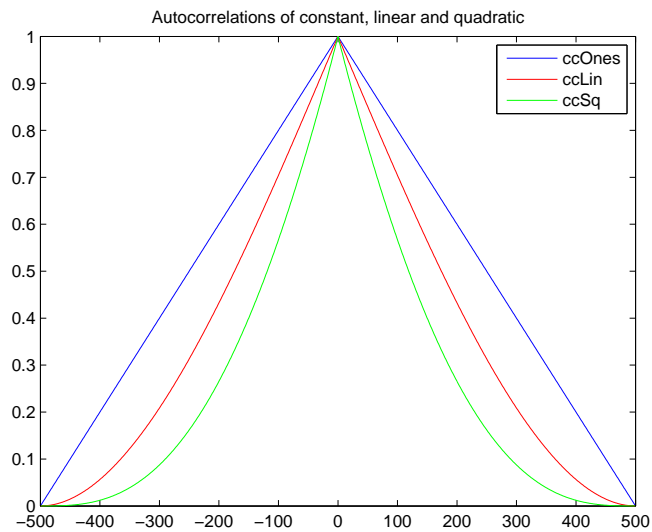
We can see from this plot that the autocorrelation "distances" of these functions get shorter as we progress from constant to linear to quadratic function. This can be linked to the idea of a range over which the functions somehow preserve "order". The infinite periodic function, and for that matter, an infinite constant function, is ordered "forever"—the autocorrelation never vanishes, no matter how far out we go. The finite functions lose autocorrelation with distance. A measure of all this is the simple sum of the autocorrelation, normalized to max = 1, from lag 0 to the length of the function. These are

```
ones   251
lin    188
sq     140
```

We can even find a special case in which the sum of the autocorrelation equals the mean distance over which the function correlates with itself. Let's talk in terms of "time", without loss of generality,

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to fix our ideas.

Imagine a timeseries which does not change for a time period τ, then changes to a new value "completely uncorrelated" with the first, holds that for another time period τ, and so on.
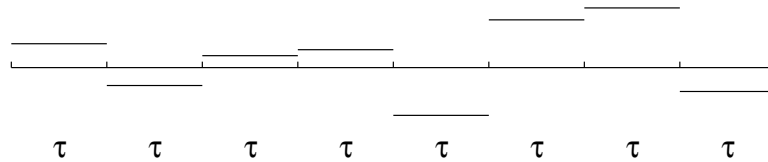
Of course, what I have drawn as straight lines only indicates the constancy of the series over time intervals τ. The positions of these lines are not meant to indicate specific values but only samples, drawn from, say, a normal random distribution of values.

Here is a way we might generate such a timeseries. For each time interval of length τ, sample a normal distribution and store this value in the next τ elements of the timeseries:

```
ts = randn(1);              % a single normal random value
for k = 1:tau
    timeseq(time) = ts;
    time = time + 1;
end % for k
```

When this is done for enough time intervals, say 100, calculate the autocorrelation, `ac`, of the resulting sequence (normalize `ac` so that its maximum value (i.e., at lag $= 0$) is 1), and then sum it `sum(ac)`.

Now, in fact, this will give the autocorrelation of only one sample sequence, so before doing the sum (and the normalization) of `ac` we should accumulate many of them, say 1000, so that the crosscorrelation from interval τ to other intervals do indeed average to 0.

Here's what I got. The sums are close to τ.

τ	1	2	5	10
`sum(ac)`	0.8943	2.1119	4.9263	10.0406

(We could also track standard deviations over the 1000 to check the statistical proximity of the results to τ.)

Here is a plot of the normalized autocorrelation for $\tau = 1$.

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average of 1000 autocorrelations of normal noise, width 1
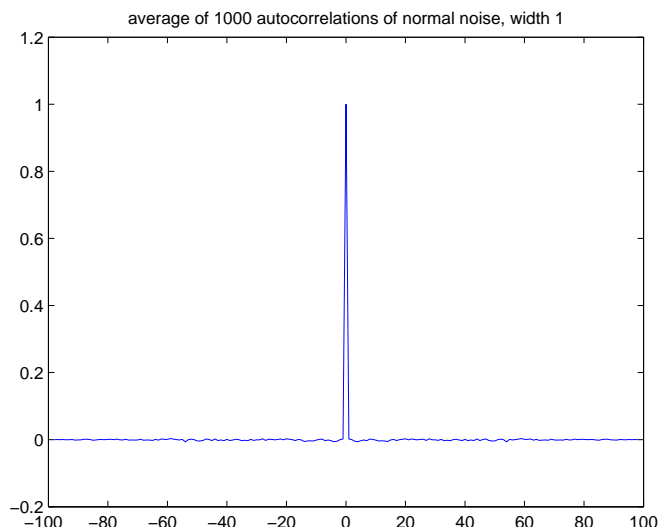
Of course, this is a standard result: the autocorrelation of pure noise is 1 at lag 0 and 0 elsewhere because any sequence correlates with itself (lag 0) but noise does not correlate with noise (lag $\neq 0$). But it is noteworthy that the plots look exactly the same for $\tau > 1$ with the important difference that they are widened by a factor τ, hence the results that I got for the sums.

There are only two things wrong with this simulation. First, if the intervals are not equally spaced but only *average* in duration to τ, we no longer get τ as the sum: in the program `oneMolecAvg()` in MATLABpak08cIII, I've included an internal parameter `mult = 1`. You can figure out how `mult = 2, 3, ..` changes the average duration of the interval, and run the modified program to get these poor results.

The second thing wrong with the above sum of the autocorrelation of fixed-length intervals is that the sum is from $-\infty$ to ∞ (well, -100 to 100). In physical applications, the autocorrelation of the negative values could be considered anticipatory because they involve negative time lags, and so may be unphysical.

So we next ask: is there a distribution of time intervals which will give us an autocorrelation whose sum a) over the non-negative lags gives us b) the mean interval length τ? (With the autocorrelation normalized to 1 at lag 0.)

The answer is yes. A distribution which does this is

$$\frac{e^{-t/\tau}}{\tau}$$

Since I didn't find a generator in MATLAB for this distribution, I wrote one using the *cumulative* distribution

$$\text{antislope}_{t'} \frac{e^{-t'/\tau}}{\tau}\bigg|_0^t = -e^{-t'/\tau}\bigg|_0^t = 1 - e^{-t/\tau}$$

If we plot this and sample the y-axis using a uniform distribution from 0 to 1, the corresponding x-value is distributed according to $e^{-t/\tau}/\tau$ from 0 to ∞:

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distribution generator using cumulative probability of $e^{-t/\tau}/\tau$
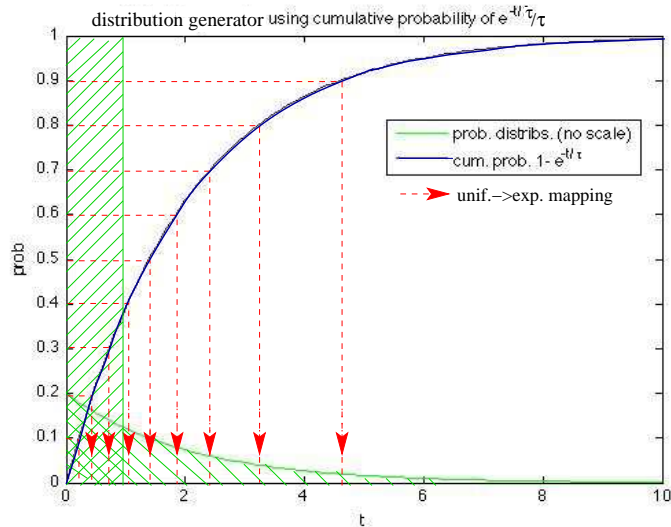
With different intervals selected according to this distribution—call them `tint`—we can do the same simulation as above for fixed time intervals.

```
ts = randn(1);              % a single normal random value
for k = 1:tint
    timeseq(time) = ts;
    time = time + 1;
end % for k
```

The results of this simply iterated, say 1000 times, have a large standard deviation, so I was more subtle and grouped the 1000 iterations into three nested levels of 10 each, taking the average of the 10 at each level up to the next level. Then the results are

τ	1	2	5	10
mean `sum(ac)`	0.9702	2.1610	5.5492	10.7972
stdev `sum(ac)`	0.1343	0.3261	0.6665	0.8271

We can do better by building into the code the assumption that the timesequence does not correlate with itself across time intervals and thereby dispense with generating the normally distributed noise.

The autocorrelation is constructed as follows, with exponentially distributed $t_j - t_{j-1}$

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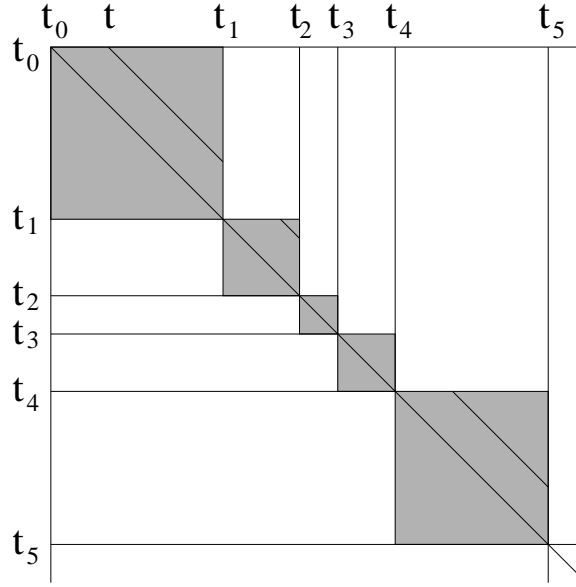
The diagonal line from $t_0 = 0$ gives the lag-0 autocorrelation. The diagonal line from t gives the lag-t autocorrelation. We assume the contributions not in the blocks down the diagonal are zero.

Thus for the timesequence with values

$$v_j \quad \text{for} \quad t_{j-1} \leq t < t_j \quad j = 1, ... \quad (t_0 = 0)$$

the lag-0 autocorrelation is

$$\Phi(0) = \sum_{j=1} v_j^2 (t_j - t_{j-1})$$

The lag-t autocorrelation for this sequence is

$$\Phi(t) = \sum_{j=1} v_j^2 (\text{if } t_j - t_{j-1} > t \text{ then } t_j - t_{j-1} - t \text{ else } 0)$$

A program to calculate this $\Phi(t)$ normalized to $\phi(t)$ with max 1 at $t = 0$ gives, for example (with 100 collisions and 100 timesteps dividing the maximum time interval generated)

τ	1	2	5	10
sum(ac)	0.9784	1.9390	5.2124	9.6615

Furthermore, each of these single runs (not averaged over many sets of 100 collisions) gives plots showing that the autocorrelation itself is exponential.

$$\phi(t) = e^{-t/\tau} \quad t \geq 0$$

Here is a good one for $\tau = 1$, and equally good ones turn up for other values of τ.

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idealized autocorrelation of intercollision times, mean =1
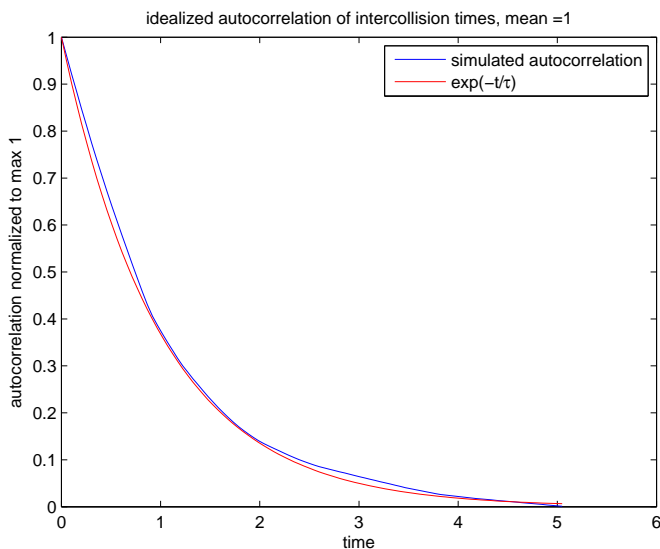
(Note that only non-negative values of t are plotted: by the symmetry of autocorrelation we should write

$$\phi(t) = e^{-|t|/\tau} \quad \text{all } t)$$

$\star\,\star\,\star\,\star\,\star$

On the other hand, the *convolution* is closely related to, but significantly different from the cross-correlation. It reverses the first sequence

$$(x \star y)(t) = ((\oslash x) \oslash y)(t)$$

where $\star$ is the convolution operator between two sequences x and y, and I've overloaded the $\oslash$ symbol by using it, as a unary operator, to reverse a sequence. (In this notation, thus, $y \oslash x = \oslash(x \oslash y)$.)

To calculate the convolution by hand, we do a simple modification to the hand-calculation of crosscorrelation. Here's an example, convolving $x = -1, 0, 1$ with $y = -2, -1, 0, 1, 2$.

x \ y	-2	-1	0	1	2
-1	2	1	0	-1	-2
0	0	0	0	0	0
1	-2	-1	0	1	2

These diagonals go in the other direction from the crosscorrelation. Summing along them gives the convolution.

$$x \star y = 2, 1, -2, -2, -2, 1, 2$$

Where have you seen this before?

The convolution has significant use in digital signal processing for implementing filters of a certain sort. (Week 9 has an Excursion on DSP filters which works out a lot of the detail.) Here is the result of filtering a constant sequence (`ones(1:1000)`) with an exponentially decaying filter (`exp(-(1:500)/100)`).

filter(exp(−1:500)/100,1,ones(1,1000)))
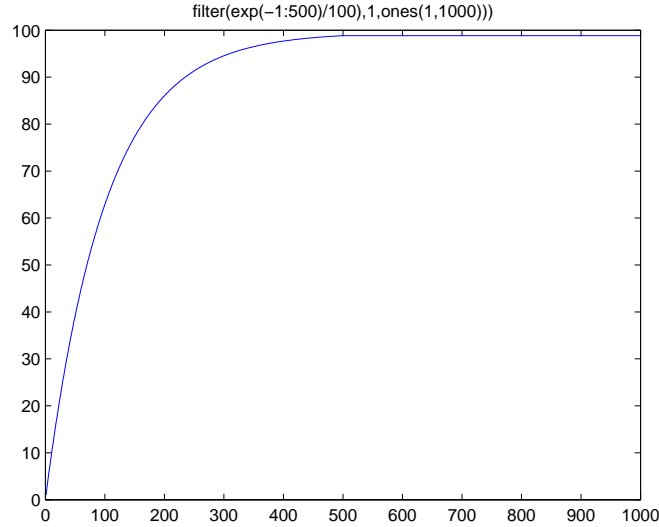
(There are continuous variants of convolution and crosscorrelation. They are not normalized. The continuous convolution has the form

$$(x \star y)(t) = \text{antislope}_{t'} x(t - t')y(t') \mid_{-\infty}^{\infty}$$

and this adds the physical dimension of t' (and t). For example, if x and y have physical dimension L (length, distance), $x \star y$, over time t, has physical dimension $L^2 T$. Or if x and y have physical dimension L/T (velocity), $x \star y$, over time t, has physical dimension L^2/T.)

24. Collision theory. Molecules in equilibrium have momenta which are normally distributed (the distribution of each component is the Maxwell distribution of Note 14 and Excursion *Maxwell distribution* for 2D and 3D respectively, in Part II, but without the p (p^2 in 3D) factor in front) but which are constant between collisions.

We will see in this Note that the intercollision time is distributed as $e^{-t/\tau}/\tau$ and so the autocorrelation of the momenta is, from Note 23, $\phi(t) = e^{-|t|/\tau}$.

We will show two theoretical results from this. First, the mean time between collisions (MTBC), or the mean free time (MFT)

$$\text{antislope}_t \phi(t)|_0^{\infty} = \text{antislope}_t e^{-t/\tau}\Big|_0^{\infty} = \tau$$

which immediately gives a meaning for τ.

The second theoretical result pertains when a force, $X(t)$, is applied which slightly perturbs the equilibrium state. The result is that the velocity $\dot{x}(t)$ of whatever particles in the medium are responding to this force, is the *convolution* of the force with the autocorrelation of the equilibrium velocities v of the molecules

$$\dot{x}(t) = \frac{1}{k_B T}\text{antislope}_{t'} X(t - t')\Phi_v(t')\Big|_0^{\infty}$$

where $\dot{x} = \text{slope}_t x$.

That is, the equilibrium autocorrelation acts as a *filter* on the applied force so that it produces, not an acceleration, as in free Newtonian objects, but a velocity.

These theoretical results are more useful for understanding than for calculation. Indeed, I have not attempted the difficult simulation of a force applied to a gas in equilibrium. The second will have

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one important practical consequence in the "Onsager relations" of Note 28.

It is significant that both of these results relate *non*-equilibrium properties (for instance, diffusion rates for the first result and drift speed for the second) to the (velocity) autocorrelation of the medium (e.g., gas) *in* equilibrium.

The first result is an instance of a "Green-Kubo formula" and the second of a "Kubo-Nyquist formula".

Feynman [FLS64, §43-1] shows that if τ is the mean time between collisions in a gas in equilibrium then the probability of the next collision happening in time t is $e^{-t/\tau}$. This will establish the first theoretical result above, so here is the argument.

1. The number of collisions a single molecule has in time interval Δt is $\Delta t/\tau$: this number of collisions must be proportional to the amount of time during which we are counting, and the constant of proportionality must be $1/\tau$ so that on average there is one collision when $\Delta t = \tau$.

2. Of N_0 molecules in a container, let $N(t)$ be the number that have *not had a collision* after a length of time t. Then in time interval Δt this number will be reduced by $\Delta t/\tau$ for each molecule, or, if Δt is small enough, by $N(t)\Delta t/\tau$ for all $N(t)$ molecules.

3. But this new value of $N(t)$, namely $N(t) - N(t)\Delta t/\tau$, is just $N(t+\Delta t) = N(t) + \text{slope}_t(N(t))\Delta t$. So

$$\text{slope}_t N(t) = -N(t)/\tau$$

and thus

$$N(t) = N_0 e^{-t/\tau}$$

where I've put in the total number N_0 of molecules as the constant of integration, since $N(0) = N_0$.

The *probability* that a single molecule has not collided in time t is $e^{-t/\tau}$: just divide by N_0.

4. The cumulative probability distribution of molecules that *have* had a collision by time t is $1 - e^{-t/\tau}$. So the probability density is

$$
\begin{aligned}
\text{prob. coll. during } t \text{ to } t + \Delta t \;\; &= \;\; \Delta\,\text{slope}_t(1 - e^{-t/\tau}) \\
&= \;\; \Delta t \frac{e^{-t/\tau}}{\tau}
\end{aligned}
$$

Feynman uses this to show the surprising result that τ is not only the mean time between collisions under this distribution but τ also is the mean time *until the next collision* at any point in time: the mean time until a collision is the sum of t weighted by the probability, i.e.,

$$
\begin{aligned}
\text{antislope}_t t \frac{e^{-t/\tau}}{\tau} \;|_0^\infty \;\; &= \;\; \tau\,\text{antislope}_{t/\tau} \frac{t}{\tau} e^{-t/\tau} \;|_0^\infty \\
&= \;\; \tau\,\text{antislope}_x x e^{-x} \;|_0^\infty \\
&= \;\; \tau(-x e^{-x} - \text{antislope}(-e^{-x})) \;|_0^\infty \\
&= \;\; \tau(e^{-x}(-1 - x)) \;|_0^\infty \\
&= \;\; \tau
\end{aligned}
$$

where integrating by parts (see Note 6 in Part I or Note 37, Book 8c, Part IV) using $u = -x$ and $v = e^{-x}$ reduces $\text{antislope}_x x e^{-x}$ to the line following it above.

Furthermore, τ is also the mean time *since the previous* collision. This is easy to see for molecules because the microscopic physics of collisions is time-reversible. So, running time backwards just swaps "next collision" with "previous collision".

Microscopic time reversibility is going to help us again later, specifically in deriving the Onsager relations of Note 28.

This establishes the intercollision distribution as $e^{-t/\tau}/\tau$ and so the normalized autocorrelation is

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$e^{-t/\tau}$ from Note 23, and we have our first theoretical result

$$\tau = \text{antislope}_t \phi(t) \mid_0^\infty$$

The unnormalized autocorrelation $\Phi(t)$ is just $\phi(t)$ times $\Phi(0)$, the value of $\Phi(t)$ at lag 0. But this is just the sum of squares of whatever $\Phi(t)$ is autocorrelating, say the velocities: v^2 summed over the length of the entire sequence being autocorrelated.

I will define $\Phi(t)$ to include a further implicit normalization, namely it is divided by the length of the sequence. Hence $\Phi_v(0) = \overline{v^2}$, the mean square velocity, and

$$\Phi_v(t) = \overline{v^2} \phi(t)$$

(I don't need to subscript the $\phi(t)$ with a v because the velocities have been normalized out—it could be an autocorrelation of momenta or velocities— but we'll understand that velocities are being autocorrelated from now on.)

This is handy for the second theoretical result because $\overline{v^2}$ is closely related to the mean energy as we saw in Note 18 of Part I.

For the first result it did not matter what quantity we autocorrelate, as long as it is effectively noise, but fixed over time intervals distributed as $e^{-t/\tau}$. It also does not matter how many dimensions we are measuring: 1, 2 or 3 dimensional autocorrelations (we take the vector dot product for more than 1 dimension) all normalize to 1 at lag 0.

The second theoretical result is 1-dimensional. It applies to each component of the force and of the resulting induced velocity. In 1 dimension, the energy $m\overline{v^2}/2 = k_B T/2$ (Note 18, Part II) so $m\overline{v^2} = k_B T$.

To derive it, let's start with the acceleration $a(t)$ that might be caused by an external force $X(t)$. (Newton says $a(t) = X(t)/m$ where m is the mass of whatever is being accelerated by $X(t)$: Note 37 of Book 8c Part IV.)

Suppose that the previous collision was time t_c ago and we're now at time t. Suppose that the particle being accelerated lost all its velocity at that collision and so is now being accelerated from scratch. (This assumption becomes plausible when many particles are considered: the collisions have given them random velocities in all directions, which average out to 0. However, the particle being accelerated is not necessarily one of the molecules of the medium. If it is much more massive than those molecules, it will take several collisions to randomize its velocity [FLS64, §43-3] and we'll have to redefine τ.)

Since acceleration is the rate of change of velocity, i.e., its slope, the velocity will be given by the antislope of the acceleration, and in particular during the time t_c (and the sum is approximated by an antislope).

$$
\begin{aligned}
< v(t) > &= (\text{antislope}_{t_c} \frac{e^{-t_c/\tau}}{\tau} (\text{antislope}_{t'} a(t')) \mid_{t-t_c}^t) \mid_0^\infty \\
&= (\text{antislope}_{t'} a(t')(\text{antislope}_{t_c} \frac{e^{-t_c/\tau}}{\tau}) \mid_{t-t'}^\infty) \mid_0^t
\end{aligned}
$$

I've done some mathemagics[1] here so let's pause to discern the sleight-of-hand. The swapping of the antislopes and the corresponding changes to the limits are consequences of antislopes being areas or, approximately, sums. The two combined antislopes above are a two-dimensional sum, and the following diagram shows why and how they can be swapped.

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[1] "Mathematics" is pluralized because of its many facets. "Mathemagics" has at least two facets. The first is the sleight-of-hand I'm doing here and will do a few more times in this Note. The second is the wonder of results such as the multitude of infinities, $e^{i\pi} + 1 = 0$, and that, due to the Fourier transform, a piece of paper can sound like a bell. (Just play a recording of the 1812 Overture through a loudspeaker!)
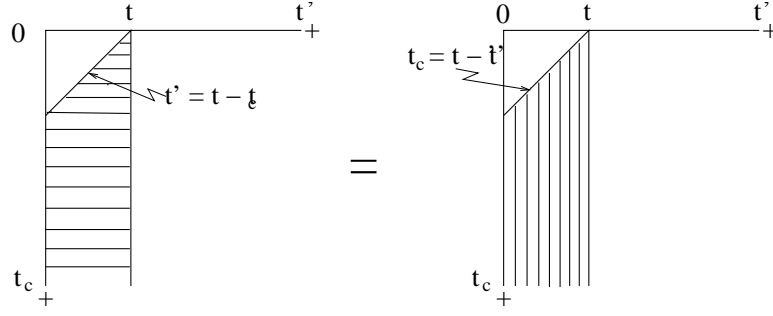
From this

$$\text{antislope}_{t_c}(\text{antislope}_{t'} f(t', t_c) \mid_{t-t_c}^{t}) \mid_0^{\infty} = \text{antislope}_{t'}(\text{antislope}_{t_c} f(t', t_c) \mid_{t-t'}^{\infty}) \mid_0^{t}$$

for any $f(t', t_c)$ which vanishes for negative t'. (Please note that I've plotted t_c here with positive going *downwards*, not the conventional upwards. This is to make more obvious the connection with convolution—next.)

The inner antislope we can do

$$\text{antislope}_{t_c} \left. \frac{e^{-t_c/\tau}}{\tau} \right|_{t-t'}^{\infty} = -e^{-t_c/\tau} \mid_{t-t'}^{\infty}$$
$$= e^{-(t-t')/\tau}$$
$$= \phi(t - t')$$

where the last line follows from $\phi(t) = e^{-t/\tau}$.

So now we have

$$\text{antislope}_{t'} a(t')\phi(t - t') \mid_0^t$$

and this is almost the convolution of $a(t)$ and $\phi(t)$.

A little more mathemagics. Since $\phi(t - t')$ goes from $e^{-0} = 1$ at $t' = t$ to $e^{-t/\tau}$ at $t' = 0$, for large enough $t \gg \tau$ we could carry on to $t' = -\infty$, where $\phi(t - t') = 0$, without too much disturbance.

Then we can change variable to $t'' = t - t'$ so $t' = t - t''$ and $\Delta t' = -\Delta t''$.

$$\text{antislope}_{t'} a(t')\phi(t - t') \mid_0^t \approx \text{antislope}_{t'} a(t)\phi(t - t') \mid_{-\infty}^t$$
$$= -\text{antislope}_{t'} a(t)\phi(t - t') \mid_t^{-\infty}$$
$$= \text{antislope}_{t''} a(t - t'')\phi(t'') \mid_0^{\infty}$$

and this *is* the convolution of $a(t)$ and $\phi(t)$.

Now switch back to forces, $X(t) = ma(t)$, and to the full velocity autocorrelation $\Phi_v(t) = \overline{v^2}\phi(t)$. And call the result $\dot{x}(t)$ since the average $< v(t) >$ was taken over all intercollision times and this is invisible macroscopically.

$$\dot{x}(t) = \text{antislope}_{t'} a(t - t')\phi(t') \mid_0^{\infty}$$
$$= \frac{1}{m\overline{v^2}}\text{antislope}_{t'} X(t - t')\Phi_v(t') \mid_0^{\infty}$$
$$= \frac{1}{k_B T}\text{antislope}_{t'} X(t - t')\Phi_v(t') \mid_0^{\infty}$$

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Thus the velocity of some special particle acted on by a force $X(t)$ in a medium, whose *equilibrium* velocity autocorrelation is $\Phi_v(t)$, is the convolution of the force with the autocorrelation divided by $k_B T$.

For a constant force (or one which changes slowly with respect to the mean time between collisions, τ) we can take it out of the antislope and get

$$
\begin{aligned}
\dot{x} &= \frac{X}{k_B T} \text{antislope}_t \Phi_v(t) \mid_0^\infty \\
&= \frac{X}{m} \text{antislope}_t \phi_v(t) \mid_0^\infty \\
&= X \frac{\tau}{m}
\end{aligned}
$$

That is, the resulting velocity is linear in the applied force. The constant of proportionality is called the *mobility*

$$
\mathcal{M} = \frac{\tau}{m}
$$

(A more conventional symbol is μ, but we've already used μ twice, for statistical moments and for chemical potential.)

If we were to express $\dot{x}$ in terms of the momentum $p_x = m\dot{x}$ of the particle, we would have (for future reference)

$$
\frac{p_x}{\tau} = X
$$

25. Mobility, diffusivity and Brownian motion. The mobility of a particle immersed in a medium in equilibrium describes its response to an *external* force

$$
\dot{x} = \mathcal{M} X
$$

The *diffusivity* $\mathcal{D}$ gives the response of a set of particles in a medium to the *internal* "force" induced by a gradient in concentration or density. The medium need not be a gas. If it were a liquid, we are all familiar with the gradual spreading of a dollop of milk in a cup of tea or coffee, even without stirring.

Because we must deal with concentration of the milk, which is the amount of milk per unit volume, instead of individual particles, it is appropriate to switch from velocities to *current density*. The concentration in general is a function $c(x, y, z)$ of all coordinates, but let's simplify to a 1-dimensional concentration

slope$_x$ c is concentration gradient   current
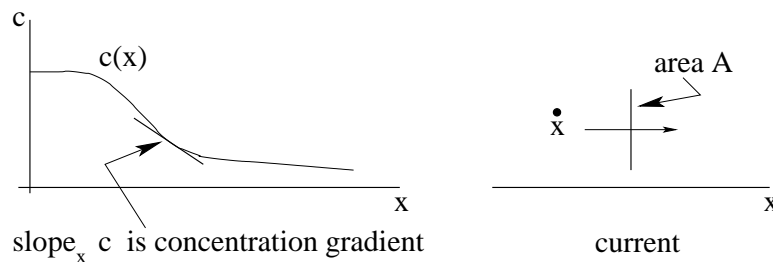
The current density is the net flow of milk per unit area per unit time, so it is the amount of milk per unit volume times the velocity

$$
j_x = c(x)\dot{x}
$$

Fick's first law says that the diffusion current is proportional to the gradient of the concentration

$$
j_{\text{diff}} = -\mathcal{D}\, \text{slope}_x c
$$

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which defines the diffusivity $\mathcal{D}$ as the constant of proportionality. Let's relate this to the mobility.

Here is Feynman's argument [FLS64, §43-5]. Imagine an external force X which just stops the diffusion. Thus, X holds the milk-and-coffee mixture in equilibrium.

So the Boltzmann distribution (Note 14, Part II) applies and the concentration

$$c = c_0 e^{-U/(k_b T)}$$

for some constant c_0 (which is going to disappear) and for potential energy $U(x)$. Now the force is the negative slope of the potential energy, $X(x) = -\text{slope}_x U(x)$, so

$$\begin{aligned} \text{slope}_x c &= c_0 e^{-U/(k_B T)} \left(-\frac{1}{k_B T} \right) \text{slope}_x U \\ &= \frac{c}{k_B T} X \end{aligned}$$

But under this force X the drift velocity would be $\dot{c} = \mathcal{M}X$ so the drift current would be

$$\begin{aligned} j_{\text{drift}} &= c\dot{x}_{\text{drift}} \\ &= c\mathcal{M}X \\ &= c\mathcal{M}\frac{k_B T}{c}\text{slope}_x c \end{aligned}$$

Now for the balance: the net current $j_{\text{diff}} + j_{\text{drift}}$ must be 0 so

$$0 = -\mathcal{D}\,\text{slope}_x c + \mathcal{M}k_B T\text{slope}_x c$$

with the result that

$$\mathcal{D} = \mathcal{M}k_B T$$

This relationship between diffusivity and mobility was discovered by Nernst in 1884 and rediscovered by Einstein in his Brownian motion paper of 1905; it is known as the Einstein relation, or, more fairly, as the Nernst-Einstein relation.

Brownian motion is a third transport phenomenon connected with mobility $\mathcal{M}$ and diffusivity $\mathcal{D}$. In 1827 Robert Brown noticed in his microscope a perpetual jiggling of pollen particles in water. He avoided dismissing this phenomenon as due to life in the pollen and showed true scientific colours by finding the same motion in water trapped in quartz millions of years old.

Einstein in 1905 and Smoluchowski in 1916 finally analyzed this problem and showed that the random bombardment of the pollen particle by the water molecules causes the pollen to move, on average, away from its starting point in such a way that its mean squared displacement $< r^2(t) >= 6\mathcal{D}t$ where t is the time since the "starting point" and $\mathcal{D}$ is the diffusivity.

This result was important because one can *measure* how far the pollen gets, on average, per unit time, and so can measure $\mathcal{D} = \mathcal{M}k_B T$. One can also measure the mobility $\mathcal{M}$ by measuring drift velocity per unit force. Finally the temperature T can be measured. All these measurements allowed k_B to be found for the first time, and since $N_A k_B = R$ for a mole of gas, and R is known from $PV = RT$, the ideal gas law, thus finally, for the first time, Avogadro's number N_A, the number of molecules in a mole, was worked out.

That's a long chain of measurements to get something that everybody knows. Only in 1905 nobody knew N_A. Furthermore, there was serious criticism, from very distinguished physicists, of the very notion of molecules. Physics had been able to do so much thermodynamics with the continuous math of partial slopes—as we did a little in Notes 19 and 20, Part II—that the idea of discreteness

just seemed messy. Too bad. Ernst Mach, at least, had the scientific grace to admit the error of his opposition, eventually.

(Like special relativity, the determination of N_A by Einstein in 1905 was too controversial for the Nobel committee, which eventually awarded his prize for his third great paper of that year.)

So let's find $< r^2(t) >= 6\mathcal{D}t$. We start with the Langevin equation of motion for a Brownian particle

$$\dot{\vec{p}} = -\frac{\vec{p}}{\tau} + \vec{F}(t)$$

where $\vec{p}$ is the momentum and $\dot{\vec{p}}$ its rate of change, where the drag force $-\vec{p}/\tau$ is the resistance to this momentum, given at the end of Note 24, and where $\vec{F}(t)$ is the time-varying "force" on the particle of all those molecules bouncing off it.

The statistics are such that $< \vec{F}(t) >= 0$, the average force, and $< \vec{r}.\vec{F} >= 0$, no particular direction is favoured by the force on average. The Brownian particle does not have to forget its previous motion after every collision: its motion is modelled as if it went in a straight line for some enormous number of collisions, say 10^{12}—a tera-collision—in $1/100$ sec. Beyond such periods it certainly will forget its previous motion.

In this way, Brownian motion may be imagined to be a "Markovian random walk"—a drunk milling around a lamp post outside the pub with each step totally independent in direction and magnitude of the previous step.

We want to find $< r^2 >=< \vec{r}.\vec{r} >$ somewhere in the Langevin equation, so we might try taking the dot product of the whole equation with $\vec{r}$ to see what that gets us.

Here are some identities

$$\begin{aligned}
\text{slope}_t r^2 &= \text{slope}_t \vec{r}.\vec{r} = 2\dot{\vec{r}}.\vec{r} = \frac{2}{m}\vec{p}.\vec{r} \\
\text{slope}_t^2 r^2 &= \text{slope}_t \frac{2}{m}\vec{p}.\vec{r} = \frac{2}{m}(\dot{\vec{p}}.\vec{r} + \vec{p}.\dot{\vec{r}})
\end{aligned}$$

So

$$\begin{aligned}
\vec{p}.\vec{r} &= \frac{m}{2}\text{slope}_t r^2 \\
\dot{\vec{p}}.\vec{r} &= \frac{m}{2}\text{slope}_t^2 r^2 - m\dot{\vec{r}}.\dot{\vec{r}} \\
&= \frac{m}{2}(\text{slope}_t^2 r^2 - 2v^2)
\end{aligned}$$

So the dot-multiplied Langevin equation becomes

$$\frac{m}{2}(\text{slope}_t^2 r^2 - 2v^2) = -\frac{m}{2\tau}\text{slope}_t r^2 + \vec{F}.\vec{r}$$

and, averaged (and note that slopes, averages, antislopes and sums can all be interchanged—why?)

$$\frac{m}{2}\text{slope}_t^2 r^2 - m < v^2 >= -\frac{m}{2\tau}\text{slope}_t < r^2 >$$

and since $< v^2 >= 3k_B T/m$ in 3 dimensions

$$\text{slope}_t^2 r^2 + \frac{1}{\tau}\text{slope}_t < r^2 > -\frac{6k_B T}{m} = 0$$

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This is a differential equation in $<r^2>$ and you can check that it is satisfied by

$$
\begin{aligned}
<r^2> &= 6k_B T \frac{\tau}{m}(t - \tau(1 - e^{-t/\tau})) \\
&= 6\mathcal{D}(t - \tau(1 - e^{-t/\tau}))
\end{aligned}
$$

This is not exactly what we want, but for time much greater than the MTBC, $t \gg \tau$, we get

$$
<r^2> = 6\mathcal{D}t
$$

as requested.

The Kubo-Nyquist formula of Note 24 thus has given us the transport properties of mobility and diffusion, and these two explain Brownian motion in terms of molecules and lead to a value for Avogadro's number.

Ohm's law of electrical conductivity is also directly related to mobility. An *electric field $E(x, y, z)$* is a function defined in space as the force exerted on a unit charge, $E = F/q$. The *electric current density $i(x, y, z)$* is a charge current, so if each carrier has charge q, $i = cqv$ where c is the concentration of carriers in space and v is their drift velocity under the force. So

$$
\frac{i}{cq} = v = \mathcal{M}F = \mathcal{M}Eq
$$

giving the *conductivity $\mathcal{K} = \mathcal{M}cq^2$* so that

$$
i = \mathcal{K}E
$$

In a wire of length ℓ and cross-sectional area A the *potential difference* between the ends is $\mathcal{E} = E\ell$ and the *current $I = iA$* (assuming i is constant across the disc of the wire): it's the rate of charge $\dot{q}$ crossing an imaginary disc across the wire. So

$$
\frac{I}{A} = i = \mathcal{M}cq^2 E = \mathcal{M}cq^2 \frac{\mathcal{E}}{\ell}
$$

giving the *resistance $R = \ell/(\mathcal{M}cq^2 A)$* so that

$$
\mathcal{E} = IR
$$

(Note that $\mathcal{E} = F\ell/q$ is measured in Volts, q in Coulombs, and $F\ell$ is an energy. If $\mathcal{E}$ were one Volt and $F\ell$ were one "electron Volt" then q would be the charge on the electron.

The above is called Ohm's law, and the resistance R is measured in Ohms.)

Many other transport properties can be derived from Kubo-Nyquist formulae. Properties such as viscosity, heat conduction and thermal diffusion are expressed as suitable coefficients times gradients.

26. Three potentials and dissipation.

> *Folks like us could never fuss*
> *With schools and books and learning.*
> *Still we've gone from A to Z,*
> *Doing what comes naturally.*
> Irving Berlin "Annie Get Your Gun"
> (But see other verses for the dissipative
> effect of this disdain for learning.)

Having discussed diffusion we can arrive at a better understanding of the chemical potential introduced in Note 19 of Part II. We will also in this Note put the electric potential into its place in the

thermodynamics equation of state (Note 20 of Part II), and then combine the two in a discussion of the Nernst potential across biological membranes.

Out of each of these comes the notion of dissipation.

We can define the *chemical potential* μ as the potential energy responsible for diffusion. Then the "force" in the x direction is $\mathrm{slope}_x\mu$ and so, using diffusivity $\mathcal{D}$ and mobility $\mathcal{M}$,

$$
\begin{aligned}
-\mathcal{D}\,\mathrm{slope}_x c &= j_{\text{diff}} \\
&= c\dot{x}_{\text{diff}} \\
&= c\mathcal{M}\,\mathrm{slope}_x\mu \\
&= -c\frac{\mathcal{D}}{k_B T}\mathrm{slope}_x\mu
\end{aligned}
$$

So

$$
\frac{\mathrm{slope}_x c}{c} = \frac{1}{k_B T}\mathrm{slope}_x\mu
$$

and thus

$$
\mu - \mu_0 = k_B T \ln\frac{c}{c_0}
$$

where μ_0 and c_0 are the (arbitrary) constants we get when we take the antislopes of the two sides.

This connects chemical potential μ with concentration c as a result of considering Fick's law of diffusion as being caused by a potential difference rather than by a concentration gradient.

In the equations of state of Note 20 (Part II) we had

$$
T\Delta S = \Delta U + P\Delta V - \mu\Delta N
$$

and we see that there is a negative sign on the μ term. This makes sense if we think about "doing what comes naturally": entropy S always increases, so $\Delta S > 0$, on the way to equilibrium; but a concentration excess will decrease, so $\Delta N < 0$, as concentration evens out. Similarly, volume will increase under internal pressure, so $\Delta V > 0$.

This explains the difference in signs on $P\Delta V$ and $\mu\Delta N$.

It also allows us to infer the signs of additional contributions to the energy, such as electric charge q and *electric potential* $\mathcal{E}$. Under an electric potential a current will flow so as to reduce the charge, $\Delta q < 0$, so this term has a negative sign

$$
T\Delta S = \Delta U + ... - \mathcal{E}\Delta q
$$

and $\mathcal{E} = \mathrm{slope}_q(\text{energy})$ has a positive sign.

The *Nernst potential* is the electric potential which arises when the force that balances diffusion is electric in Feynman's argument of Note 25: $F = Eq = q\,\mathrm{slope}_x\mathcal{E}$. Then

$$
\mathcal{E} - \mathcal{E}_{\prime} = -\frac{k_B T}{q}\ln\frac{c}{c_0}
$$

by simple adjustment of the relationship above between μ and c, but negative because it *counters* the diffusion.

As a biological application, imagine a membrane bounding a cell or some organelle within a cell. There is a concentration c_i of ions (charged molecules) inside and a concentration c_o outside.
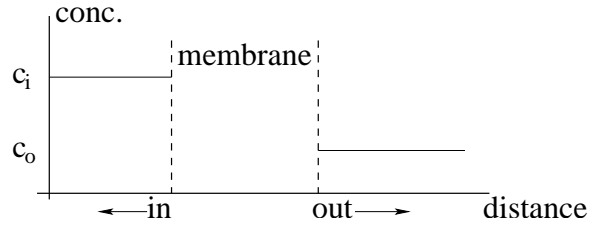
Thus for equilibrium, the Nernst potential

$$\Delta\mathcal{E}_n = \mathcal{E}_i - \mathcal{E}_o = -\frac{k_B T}{q}\ln\frac{c_i}{c_o} = \frac{k_B T}{q}\ln\frac{c_o}{c_i}$$

where q is the (positive) charge on each ion.

What might cause such a potential and hold the concentration of ions different on either side of a membrane without a compensating diffusive flow? *Donnan equilibrium* is an example.

Imagine an equal concentration of ordinary salt, NaCl, on either side of the membrane. The salt dissociates into Na^+ ions and Cl^- ions, each with the same initial concentrations on both sides. Now add on the in-side a compound PNa of sodium (Na^+) and something big, such as a protein (P^-) to which the membrane is *impermeable*.

Since the PNa dissociates into ions, there is now a greater concentration of sodium inside than outside so it will start to diffuse through the membrane. This will set up an electric potential which will cause chlorine to diffuse through the membrane, also from inside to outside. Things get complicated now, but at the end, when everything has settled into (Donnan) equilibrium, both sides will be electrically neutral but the inside concentrations of Na^+ and Cl^- will be a little less and the outside concentrations a little more, by the same amount, than they were at the start.

Let's use notation $[Na^+]$ to be the concentration of Na^+, etc.

	Inside		Outside	
	initial	equilibrium	initial	equilibrium
$[P]$	c_2	c_2	0	0
$[Na^+]$	$c_2 + c_1$	$c_2 + c_1 - \gamma$	c_1	$c_1 + \gamma$
$[Cl^-]$	c_1	$c_1 - \gamma$	c_1	$c_1 + \gamma$

We can find γ by realizing that the Nernst potential must balance in the final, equilibrium state. Na^+ and Cl^- each contribute additively and P^- does not contribute because it does not diffuse.

$$k_B T\ln[Na^+]_i + k_B T\ln[Cl^-]_i = k_B T\ln[Na^+]_o + k_B T\ln[Cl^-]_o$$

so

$$
\begin{aligned}
(c_2 + c_1 - \gamma)(c_1 - \gamma) &= [Na^+]_i[Cl^-]_i \\
&= [Na^+]_o[Cl^-]_o \\
&= (c_1 + \gamma)(c_1 + \gamma)
\end{aligned}
$$

This gives an equation for γ in terms of the initial concentrations of salt, c_1, and PNa, c_2, and we can solve it

$$\gamma = \frac{c_1 c_2}{4c_1 + c_2}$$

Thus the Nernst potential is the electric potential across the membrane caused by equilibrium of different ions.

• • • • •

Finally we can introduce the idea of dissipation by going back to our discussion of the equation of state, which, including electric effects, now is

$$T\Delta S = \Delta U + P\Delta V - \mu\Delta N - \mathcal{E}\Delta q$$

After the application of any of these potentials, P, μ or $\mathcal{E}$, it is a flow, or current, which attempts to restore equilibrium after the application of the potential. These flows are called dissipative because they raise the entropy. The rate of loss of useful energy is called the dissipation function σ

$$
\begin{aligned}
\sigma &= T\mathrm{slope}_t S \\
&= T\dot{S} \\
&= \dot{U} + P\dot{V} - \mu\dot{N} - \mathcal{E}\dot{q}
\end{aligned}
$$

still using $\dot{x}$ for $\mathrm{slope}_t x$ for all the various quantities U, V, N and q.

But these dotted quantities are just the flows. The rate of decrease of charge, $-\dot{q}$, is just the total current I flowing out of the area of charge concentration. Thus the dissipation caused by an electric potential $\mathcal{E}$ alone is

$$\mathcal{E}I = I^2 R = \mathcal{E}^2/R$$

where we can use the resistance R to give the alternatives in terms of I alone or $\mathcal{E}$ alone.

Similarly the rate of decrease of numbers of special molecules (e.g., molecules of milk in coffee), $-\dot{N}$, is just the total current j flowing away from the concentrated region, so dissipation due to diffusion is

$$\mu J = J^2 \frac{\ell}{c A \mathcal{M}} = \mu^2 \frac{c A \mathcal{M}}{\ell}$$

for a flow along distance ℓ of cross-sectional area A if we make assumptions similar to the electrical case discussed in Note 25, that the force is a constant, $\mathrm{slope}_x\mu = \Delta\mu/\ell$, over the distance ℓ.

In both cases the first results are free of assumptions and are that *dissipation is the product of potential difference and total flow, or current.*
$$\sigma = \mathcal{E}I \qquad\qquad \text{or} \qquad\qquad \sigma = \mu J \qquad\qquad \text{etc.}$$

27. Active transport and biochemistry. As we saw in Note 26, given concentrations inside and outside a membrane, we can calculate the resulting Nernst potential needed to stop diffusion. For potassium, K^+, $q = +1$ and observed concentrations for relaxed nerve and muscle cells at 300°K are $c_i = 15$ mMoles/litre and $c_o = 140$ mMoles/litre. (Moles and litres are the units normally used for quantity and volume, respectively, in this discipline. We haven't encountered them before but, since concentrations appear only as ratios in the potential calculations of Note 26, we can just accept their use up to when we get to cancel them.)

Thus $\Delta\mathcal{E}_N = -92$ mV for potassium: check this using Note 26.

For sodium, Na^+, $q = +1$ and at 300°K, $c_i = 135$ and $c_o = 4$ giving $\Delta\mathcal{E}_N = 58$ mV.

Unfortunately, for these same resting nerve and muscle cells, the observed electric potential difference is about -80 mV, so we have some explaining to do.

Let's combine the currents I_{Na^+} and I_{K^+}. I_{Na^+} is the current of Na^+ from outside to inside caused by the potential $\mathcal{E}_{Na} = -92$ mV across a resistor which we'll call R_{Na}. I_{K^+} is the current of K^+ from outside to inside caused by the potential $\mathcal{E}_K = 58$ mV across a resistor which we'll call R_K. These two resistors reflect the electrical resistance of the membrane to the passage of these two ions, and measurements have determined that $R_{Na} = 10R_K$.

in i

I_{Na} R_{Na} I_K R_K I_{SS} $- \,\mathcal{E}_{SS}$
$-\, +\, \mathcal{E}_{Na}$ $-\,+\, \mathcal{E}_K$ $+$

out o
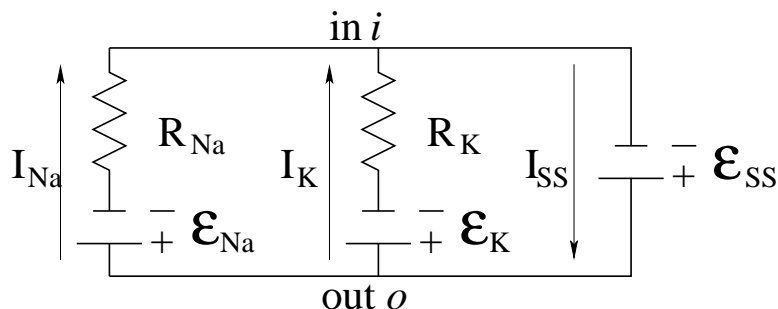
For steady state the total current must be 0, and we'd like to find the electric potential $\mathcal{E}_{ss}$ needed to make this so by opposing both $\mathcal{E}_{Na}$ and $\mathcal{E}_K$. From Ohm's law (Note 25)

$$
\begin{aligned}
0 &= I_{SS} = I_{Na} + I_K \\
&= (\mathcal{E}_{Na} - \mathcal{E}_{SS})/R_{Na} \\
&\quad + (\mathcal{E}_K - \mathcal{E}_{SS})/R_K \\
\mathcal{E}_{SS} &= \frac{\mathcal{E}_{Na} + \mathcal{E}_K(R_{Na}/R_K)}{1 + (R_{Na}/R_K)} \\
&= \frac{58 - 10 * 92}{11} \\
&= -78\mathrm{mV}
\end{aligned}
$$

which is essentially what is observed.

What might cause this "steady-state" electric potential $\mathcal{E}_{SS}$? It is like an extra battery supplying energy to the Na^+/K^+ transport system.

There is in fact an Na^+/K^+ "pump" which does just this. It adds $58 + 78 = 136$ meV to each Na^+ ion and transfers it from inside to outside the membrane against the passive diffusion. And it adds $92 - 78 = 14$ meV to each K^+ ion and transfers it from outside to inside, again against the passive diffusion. This mechanism is called "active transport".

This pump takes chemical energy from an ATP, adenosine triphosphate, molecule by "phosphorylating" it to ADP, adenosine diphosphate, to do this. (ATP is the biochemical energy currency . It is made (by "cellular respiration") in mitochondria from ADP (so completing a cycle) and glucose. Glucose is made in the chloroplasts of algae and green plants, which animals must eat, directly or indirectly.)

The mechanism of this Na^+/K^+ pump illustrates fundamental principles of biochemistry. It uses an enzyme-like protein. (An enzyme is a protein which catalyzes chemical reactions by providing "sites" whose geometry attracts the reactants so they are brought together to react.) This protein resides in the membrane and has sites for ATP and for three Na^+ ions. It causes the ATP to phosphorylate and uses the resulting energy to transport the Na^+ ions against the 136 mV potential from inside to outside. (The ADP resulting from the phosphorylation remains on the in-side.) But phosphorylation changes the shape of the membrane protein so that it has more affinity for two K^+ ions than for the three Na^+ ions. These it picks up, changing its shape back to the original, and transfers from outside to inside against the 14 mV potential. The shape now prefers Na^+ to K^+ so the two K^+ get dropped and three new Na^+ get picked up, and the cycle repeats, using $3 \times 136 + 2 \times 14 = 436$ eV of energy each time.

This explains and elaborates the presence of an approximately 80 mV potential across resting nerve and muscle cell walls. This potential is itself a form of energy storage—a battery as we called it earlier. Energy in this form is much more responsive than energy stored in ATP, so can be used for contracting muscles or propagating nerve impulses which must be quick.

The membrane protein serves as a "channel" along which the ions pass in a complicated way which

keeps the channel in one shape as long as it is transporting Na^+ and in the other while transporting K^+.

There are thus three different transport mechanisms for "diffusion" across biological membranes. Ordinary diffusion is sometimes called "passive" to distinguish it from the others. "Facilitated diffusion" uses channels, as above, or "carrier" molecules which overcome resistance to the passage of target molecules or ions. Finally, active transport is driven by pumps such as the above Na^+/K^+ pump in nerve and muscle cells, or by "proton pump" (H^+ ions) in mitochondria.

28. Combined transport. The Kubo-Nyquist formula (Note 24)

$$\dot{x}(t) = \frac{1}{k_B T} \text{antislope}_{t'} X(t - t') \Phi_{\dot{x}\dot{x}}(t') \mid_0^\infty$$

applies to any complementary pair x and X defined as $X = \text{slope}_x U$ for potential energy $U(x)$. Thus

$$\dot{y}(t) = \frac{1}{k_B T} \text{antislope}_{t'} Y(t - t') \Phi_{\dot{y}\dot{y}}(t') \mid_0^\infty$$

(I've written the autocorrelation symbol Φ with two identical subscripts to prepare for the cross-correlation to follow.)

We can generalize these Kubo-Nyquist formulae to handle a flow of x caused by Y: replace the autocorrelation by the cross-correlation ([Wan87, p.501])

$$\dot{x}(t) = \frac{1}{k_B T} \text{antislope}_{t'} Y(t - t') \Phi_{\dot{x}\dot{y}}(t) \mid_0^\infty$$

Now we can use both mathematics and physics to replace $\Phi_{\dot{x}\dot{y}}$ by $\Phi_{\dot{y}\dot{x}}$. First, cross-correlation is (mathematically) invariant under translation of both sequences.

$$
\begin{aligned}
\Phi_{\dot{x}\dot{y}}(t) &= \text{antislope}_{t'} \dot{x}(t + t') \dot{y}(t) \\
&= \text{antislope}_{t'} \dot{x}(t + t' + a) \dot{y}(t + a)
\end{aligned}
$$

and if we let $a = -t'$

$$\Phi_{\dot{x}\dot{y}}(t) = \text{antislope}_{t'} \dot{x}(t) \dot{y}(t - t')$$

Second, the whole system is invariant (physically) under time-reversal at the microscopic level; if we run time backwards, all the velocities will be reversed, but their cross-correlation will not change.

$$
\begin{aligned}
\Phi_{\dot{x}\dot{y}}(t) = \Phi_{\dot{x}\dot{y}}(-t) &= \text{antislope}_{t'} \dot{x}(-t) \dot{y}(-t - t') \\
&= \text{antislope}_{t'} \overset{.}{-}x(t) \overset{.}{-}y(t + t') \\
&= \text{antislope}_{t'} \dot{y}(t + t') \dot{x}(t) \\
&= \Phi_{\dot{y}\dot{x}}
\end{aligned}
$$

This symmetry was discovered by Lars Onsager in 1931. It is useful in the case of linear response (essentially constant forces) when transport is due to combined mechanisms.

For example, suppose now that the flow $\dot{x}(t)$ is due both to X and Y

$$
\begin{aligned}
\dot{x}(t) &= \frac{1}{k_B T} \text{antislope}_{t'} (X(t - t') \Phi_{\dot{x}\dot{x}}(t') + Y(t - t') \Phi_{\dot{x}\dot{y}}(t')) \mid_0^\infty \\
\dot{y}(t) &= \frac{1}{k_B T} \text{antislope}_{t'} (X(t - t') \Phi_{\dot{y}\dot{x}}(t') + Y(t - t') \Phi_{\dot{y}\dot{y}}(t')) \mid_0^\infty
\end{aligned}
$$

If X and Y change slowly enough, we can, as in Note 24, take them out of the antislopes

$$
\begin{aligned}
\dot{x}(t) &= \frac{X}{k_B T} \text{antislope}_{t'} \Phi_{\dot{x}\dot{x}}(t') \big|_0^\infty + \frac{Y}{k_B T} \text{antislope}_{t'} \Phi_{\dot{x}\dot{y}}(t') \big|_0^\infty \\
&= \mathcal{L}_{\dot{x}\dot{x}} X + \mathcal{L}_{\dot{x}\dot{y}} Y \\
\dot{y}(t) &= \frac{X}{k_B T} \text{antislope}_{t'} \Phi_{\dot{y}\dot{x}}(t') \big|_0^\infty + \frac{Y}{k_B T} \text{antislope}_{t'} \Phi_{\dot{y}\dot{y}}(t') \big|_0^\infty \\
&= \mathcal{L}_{\dot{y}\dot{x}} X + \mathcal{L}_{\dot{y}\dot{y}} Y
\end{aligned}
$$

In the resulting matrix equation, Onsager says that the matrix is symmetrical

$$
\mathcal{L}_{\dot{y}\dot{x}} = \mathcal{L}_{\dot{x}\dot{y}}
$$

We can make use of the Onsager relations to work out the thermodynamics of combined transport. For example, a family of effects in thermocouples involving entropy flow (heat flow) and electric current flow use the complementary pairs S and T, and q and $\mathcal{E}$: entropy, whose flow is $\dot{S}$, with temperature difference, and charge, whose flow is $\dot{q}$, with electric potential difference.

Here are the respective roles of these variables, showing also x and X for analogy.

independent	dependent	
x	X	$X = \text{slope}_x \text{energy}$
S	T	$T = \text{slope}_S \text{energy}$
q	$\mathcal{E}$	$\mathcal{E} = \text{slope}_q \text{energy}$

for some suitable form of energy (see Note 20 Part II for possibilities).

We translate the Onsager relations into these variables, but using ΔT and $\Delta \mathcal{E}$ to emphasize that it is temperature *difference* and electric potential *difference* that act as the driving "forces".

Note that these Onsager coefficients $\mathcal{L}$ have an implicit inverse dependence on temperature T through the $k_B T$ factor. *Ratios* of two $\mathcal{L}$s will usually not depend on temperature.

Now some physics. A thermocouple is a juncture of wires of two different conducting metals. The juncture is held at a temperature T_J while the free ends are held at temperature T_F, generally lower, so that $\Delta T = T_J - T_F \geq 0$. There may be a voltmeter across the two free ends of the thermocouple or there may be a battery of e.m.f. ("electomotive force", electric potential difference) $\mathcal{E}$. (Actually, voltmeter or battery will have copper leads which themselves make junctions with the free ends, but both at the same temperature T_F. With voltmeter or battery at T_F these copper leads do not influence the thermocouple.)

The *Seebeck effect* uses the voltmeter to observe an electric potential generated by the thermocouple due to a nonzero temperature difference ΔT. Because voltmeters in principle have infinite resistance, no charge is flowing in the circuit: $\dot{q} = 0$. So from the second Onsager equation, the Seeback coefficient, which is the ratio of voltage to temperature, is

$$
\frac{\Delta \mathcal{E}}{\Delta T} = -\frac{\mathcal{L}_{\dot{q}\dot{S}}}{\mathcal{L}_{\dot{q}\dot{q}}}
$$

The *Peltier effect* uses the battery to observe a heat flow generated by the electric current caused by the battery, even when $T_J = T_F$, i.e., at $\Delta T = 0$. The two Onsager equations together give the Peltier coefficient, which is the ratio of heat flow to current. First, entropy flow

$$
\frac{\dot{S}}{\dot{q}} = \frac{\mathcal{L}_{\dot{S}\dot{q}}}{\mathcal{L}_{\dot{q}\dot{q}}}
$$

By the Onsager symmetry, the two coefficients are the negatives of each other. Going from entropy to heat, $Q = ST$, the real Peltier coefficient is T times this, so the Peltier coefficient is T times the Seebeck coefficient.

This relationship was deduced by Kelvin using arguments, now controversial, assuming reversibility in the thermocouple.

By the way, $\mathcal{L}_{\dot{S}\dot{S}}$ is related to the thermal conductivity and $\mathcal{L}_{\dot{q}\dot{q}}$ to the electrical condictivity, so the thermocouple measurements plus these give the value for $\mathcal{L}_{\dot{S}\dot{q}} = \mathcal{L}_{\dot{q}\dot{S}}$. For instance, from the second Onsager equation when temperature is uniform, i.e., the difference $\Delta T = 0$, we have $\mathcal{E}/R = \dot{q} = \mathcal{L}_{\dot{q}\dot{q}}\mathcal{E}$ so resistance

$$R = \frac{1}{\mathcal{L}_{\dot{q}\dot{q}}}$$

The dependence of resistance on temperature is implicit in this because of the above-mentioned temperature dependence of the Onsager coefficients.

This ratio $\mathcal{L}_{\dot{S}\dot{q}}/\mathcal{L}_{\dot{q}\dot{q}}$ is significant for the thermocouple: when $\Delta T = 0$ this is $\dot{S}\dot{q}$ (from the Onsager equations) which is the amount of entropy "carried along" by a unit of current. The ratio is thus called the *entropy transport parameter* S^*, a symbol which suggests both entropy S and Seeback's name (the Seebeck coefficient is $-S^*$).

All the theory so far pertains to one type of material. The Onsager coefficients and S^* in particular, will depend on the material. Thus the e.m.f. $\Delta\mathcal{E}$ of a thermocouple, made, say, of copper and nickel wires, will be given by the difference of *two* entropy transport parameters,

$$\frac{\Delta\mathcal{E}}{\Delta T} = -(S^*_{\text{Cu}} - S^*_{\text{Ni}})$$

and similarly for the Peltier effect

$$\frac{\dot{Q}}{\dot{q}} = T(S^*_{\text{Cu}} - S^*_{\text{Ni}})$$

Here and above, T is temperature of the material at which the temperature difference ΔT is observed. So ΔT must be small compared to T, and the theory best applies in the limit that $\Delta\mathcal{E}/\Delta T$ becomes $\text{slope}_T\mathcal{E}$.

29. Phase transitions.

30. Phase transitions in random graphs.

31. Point-to-point resistance in a network.

32. Van der Waals.

33. Sublimation.

34. Ferromagnets.

35. Particle individuality and Bose-Einstein condensation.

II. **The Excursions**
You've seen lots of ideas. Now *do* something with them!

1. Write program `C = crosscorrel(X,Y)` outlined in Note 23.

2. Write a program `echo = radar(signal, noise, delay)` which, given a `signal`, a `noise` level and a `delay` returns the delayed signal obscured by Gaussian white noise (use `randn()`). Then use your `crosscorrel()` program to detect the signal in the echo: it should appear at the specified delay. Thus, `signal = sine(20,1)` and `echo = radar(signal,0.5,10)` followed by `crosscorrel(signal,echo)` will give

signal = sine(20,1)
echo = radar(signal,0.5,10)
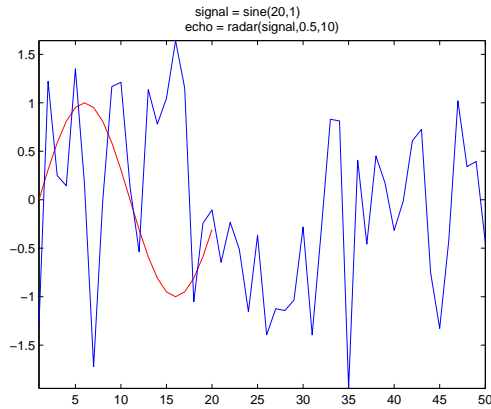
3. Invent a crosscorrelation-like method to detect the character sequence `baa` in the text `baa, baa, black sheep`. How would you detect the pattern `b*a` where `*` is the *wildcard* symbol, matching any single character?

4. Use your program `crosscorrel(X,Y)` to test translation invariance as discussed in Note 23: invent some `X` and `Y` and run, then run again with both `X` and `Y` prefixed by the same number of zeros. For example

```
>> crosscorrel([-2,0,2],[2,1,-1,-2,0,0,-2,0,2,0])
        4    2   -6   -6    2    4   -4    0    8    0   -4    0
>> crosscorrel([0,0,-2,0,2],[0,0,2,1,-1,-2,0,0,-2,0,2,0])
    0    0    4    2   -6   -6    2    4   -4    0    8    0   -4    0    0    0
```

5. **Least squares filter.** Cross-correlations can be used to design filters (see Excursion *DSP filters* in Week 9) to imitate "black boxes". (Reproducing some unknown system is the exercise of "reverse engineering".)

Suppose the black box outputs a sequence y on receiving sequence x. An FIR filter—one with no poles except at 0—generates sequence $h^* \star x$ on input of x. We can minimize the sum of squares of the differences between these two outputs by setting h to satisfy

$$(x \oslash x)h = x \oslash y$$

Let's work an example where h has three elements which we'll label starting at 0: h_0, h_1, h_2.
a) Show that the sum to be minimized is (let's leave out the first values of y to allow the system to settle down)

$$
\begin{aligned}
& (y_3 - (h_0 x_3 + h_1 x_2 + h_2 x_1))^2 \\
+\ & (y_4 - (h_0 x_4 + h_1 x_3 + h_2 x_2))^2 \\
+\ & (y_5 - (h_0 x_5 + h_1 x_4 + h_2 x_3))^2 \\
+\ & (y_6 - (h_0 x_6 + h_1 x_5 + h_2 x_4))^2 \\
+\ & \ ...
\end{aligned}
$$

b) Do the algebra to show that setting to 0 the slopes of this with respect to h_0, h_1 and h_2 gives

$$
\begin{pmatrix}
(x \oslash x)_0 & (x \oslash x)_1 & (x \oslash x)_2 \\
(x \oslash x)_{-1} & (x \oslash x)_0 & (x \oslash x)_1 \\
(x \oslash x)_{-2} & (x \oslash x)_{-1} & (x \oslash x)_0
\end{pmatrix}
\begin{pmatrix}
h_0 \\
h_1 \\
h_2
\end{pmatrix}
=
\begin{pmatrix}
(x \oslash y)_0 \\
(x \oslash y)_1 \\
(x \oslash y)_2
\end{pmatrix}
$$

c) Use this to derive the filter $h = (2, 1, -1)$ if the "impulse function" $x = (1, 0, 0, 0, 0, 0, 0, 0, 0)$ causes the black box to output $y = (2, 1, -1, -2, 0, 0, -2, 0, 2)$. Is this plausible?

d) Work a second example with the same output y, for input $x = (1, 1, 1, 1, 0, 0, 0, 0, 0)$. How good does this look?

6. The descending consecutive integers and descending consecutive squares whose autocorrelations are plotted in Note 23 were defined

$$\texttt{lin500 = 500:-1:1}$$

and

$$\texttt{sq500 = lin500}^2$$

Show that the ascending definitions

$$\texttt{lin500 = 1:500}$$

and

$$\texttt{sq500 = lin500}^2$$

give the identical autocorrelations, respectively. Why?

7. What are we dividing by when we normalize an autocorrelation so that its maximum value is 1?

a) Show that we divide by the sum of the squares of the sequence being autocorrelated.

b) A sequence is said to be "centred" by subtracting from each term the average of the whole sequence. The autocorrelation could have been defined as in Note 23 but divided by the length of the sequence. With these two changes, show that the autocorrelation is normalized to a maximum of 1 by dividing by the variance of the sequence.

8. The program `oneMolecExpAvg()` in MATLABpak08cIII calculates the non-negative sum of the autocorrelation of normally distributed noise held constant for intervals of time which are distributed as $e^{-t/\tau}$.

Show that it produces standard deviations nearly as large as the means. Modify it to calculate a hierarchy of means in order to reduce the standard deviation at the top level. Hint: a recursive routine invoking this program will allow you to specify the number of levels when you run it.

9. Use your function `crosscorrel()` and the MATLAB function `wrev()` to implement the convolution of $x = [-1, 0, 1]$ and $y = [-2, -1, 0, 1, 2]$. (Note 23.) (This is slightly perverse. Normally the convolution is basic and the crosscorrelation would be expressed in terms of the convolution.) Why is your result just the negative of the crosscorrelation?

10. Show that the convolution is commutative, $x \star y = y \star x$.

11. I made this plot using `myFilter()` —see Excursion *DSP filters* from Week 9—instead of using `crosscorrel()`, above. Why do they give different results? How different?

crosscorrel(exp(−1:500)/100),ones(1,1000)))
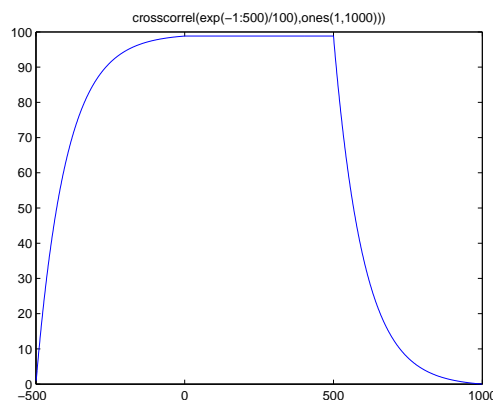
12. a) Use convolution to multiply two polynomials, e.g., $(1 + 2x)(1 + 2x + 3x^2)$.
b) Use convolution to multiply terms of the binomial expansion,
e.g., $(a^2 + 2ab + b^2)(a^3 + 3a^2b + 3ab^2 + b^3)$

13. a) What is the relationship between the Fourier transform of the convolution $X \star Y$ and the Fourier transforms of X and Y? Use your programs to find out.
b) Why would the Fourier transform of an autocorrelation be the same as its cosine transformation?

14. Check the physical dimensions of the equations relating velocity, force and autocorrelation in Note 24.

15. Look up Ryogo Kubo (1920–95) and "linear response". Look up Harry Theodor Nyquist (1889–1976). What is Johnson noise? What are Nyquist plots?

16. Show that $\text{antislope}_y\text{antislope}_x \, |_0^y|_0^\infty = \text{antislope}_x\text{antislope}_y \, |_x^\infty|_0^\infty$, basing your argument on the antislope swap of Note 24.

17. You can check directly that the following solves the Langevin equation in Note 25 (or compare it to the convolution result in Note 24).

$$\vec{p}(t) = \vec{p}(0)e^{-t/\tau} + e^{-t/\tau}\left(\text{antislope}_{t'}e^{t'/\tau}F(t')\right)_0^t$$

18. If $t \ll \tau$ in the Einstein equation for $< r^2 >$ (Note 25) show that $< r^2 >=< v^2 > t^2$, i.e., $r_{\text{rms}} = v_{\text{rms}}t$, so the Brownian particle has an instantaneous velocity appropriate to its thermal energy.

19. **Kirchhoff circuits.** Here is an electric circuit from [Mas12, KVL, KCL in "Basic Concepts Chapter"], who provides a friendly on-line introduction to "Kirchhoff's Laws".
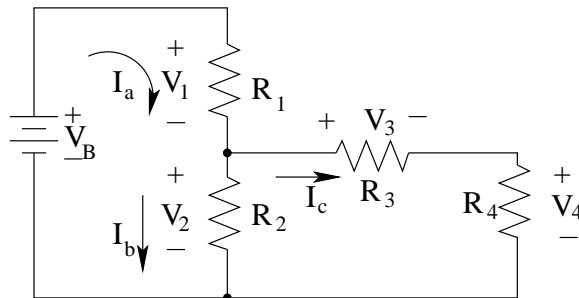
These laws are
KVL (Kirchhoff's Voltage Law): the sum of the voltages around a closed loop vanishes;
KCL (Kirchhoff's Current Law): the sum of the currents at a junction vanishes. (Junctions are shown as bullets in the figure.)
a) For voltages V_k measured from $-$ to $+$ across each resistor R_k, show that this means

$$\begin{aligned} -V_B + V_1 + V_2 &= 0 \\ -V_2 + V_3 + V_4 &= 0 \\ -V_B + V_1 + V_3 + V_4 &= 0 \end{aligned}$$

and show that the third equation adds nothing new to the first two.
b) For currents flowing as indicated by the arrows from $+$ to $-$, show also that it means

$$\begin{aligned} I_a - I_b - I_c &= 0 \\ I_c + I_b - I_a &= 0 \end{aligned}$$

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c) Use Note 25 to show (the voltages V_k are equivalent to e.m.f.)

$$
\begin{aligned}
V_1 &= I_a R_1 \\
V_2 &= I_b R_2 \\
V_3 &= I_c R_3 \\
V_4 &= I_c R_4
\end{aligned}
$$

d) Turn the above into four equations in four unknown voltages, assuming the resistances R_k and the voltage V_B of the battery are known.
What would happen if R_3 and R_4 were changed without changing $R_3 + R_4$?
Instead of the four voltages, try solving for the three currents.
e) Solve these to find the voltages in Volts and the currents in Amperes given the resistances in Ohms as $R_1 = 4$, $R_2 = 3$, $R_3 = 2$, $R_4 = 1$ and the battery voltage in Volts as $V_B = 11$.
f) Note that the directions of the currents and voltages shown are arbitrary. Reverse some of them, adjust the equations and solve again.
g) Relate KVL to conservation of energy. Relate KCL to another form of conservation. Find out about circuit elements (other than resistors and batteries) which cause exceptions to either of these two laws.
h) Look up Gustav Robert Kirchhoff, 1824–87. What is Kirchhoff's law of thermal radiation?

20. **Resistors in series and parallel.** Here are two special resistance circuits, where the battery is not shown but a voltage V is understood to be applied from node a to node c in each part of the diagram.
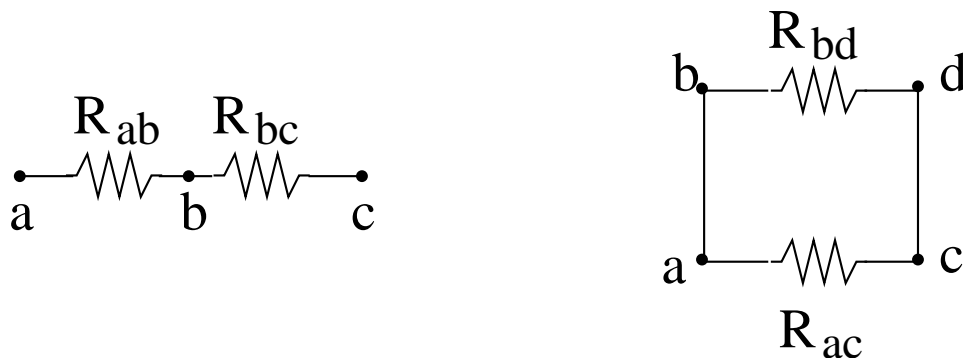
Show that the effective resistance between a and c is, for the circuit on the left (resistances in *series*), $R_1 + R_2$, and, for the circuit on the right (resistances in *parallel*),

$$
\frac{1}{\frac{1}{R_1} + \frac{1}{R_2}}
$$

a) Series. The path from a to c is abc, consisting of two edges ab and bc and one intermediate node b. The voltage law gives, in terms of currents I_{ab} and I_{bc} (not shown), for path abc

$$
R_{ab} I_{ab} + R_{bc} I_{bc} = V
$$

The current law gives, for the one node b, apart from a and c themselves

$$
I_{ab} - I_{bc} = 0
$$

(Note that current entering the node is taken to be positive and current leaving is negative: this convention could be reversed without harm.)
The equation to be solved is

$$
\begin{pmatrix} R_{ab} & R_{bc} \\ 1 & -1 \end{pmatrix} \begin{pmatrix} I_{ab} \\ I_{bc} \end{pmatrix} = \begin{pmatrix} V \\ 0 \end{pmatrix}
$$

Show that the solution is

$$\frac{V}{R_{ab} + R_{bc}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

and hence, by looking either at the total current flowng from a or the total current flowing into c, that the effective resistance between a and c is

$$R_{ac} = R_{ab} + R_{bc}$$

Is this what it should be?

b) Parallel. Show that the matrix and its solution is

$$\begin{pmatrix} I_{ac} \\ I_{ab} \\ I_{bd} \\ I_{dc} \end{pmatrix} = \begin{pmatrix} R_{ac} & & & \\ & R_{bd} & & \\ & 1 & -1 & \\ & & 1 & -1 \end{pmatrix} \backslash \begin{pmatrix} V \\ V \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} V/R_{ac} \\ V/R_{bd} \\ V/R_{bd} \\ V/R_{bd} \end{pmatrix}$$

Hence show that the effective resistance between a and c is the fraction of fractions given at the begining of thie Excursion.

c) These two rules are not always easy to apply, and the full Kirchoff rules must be used. For example, assume $R_{ab} = r, R_{ac} = 1, R_{bc} = 1, R_{bd} = 1, R_{cd} = 1$ and $V_{ad} = 1$, and find the effective resistance from a to d in
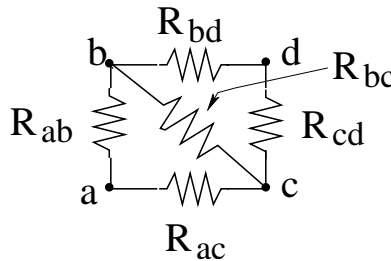
Check that

$$\begin{pmatrix} I_{ab} \\ I_{ac} \\ I_{bc} \\ I_{bd} \\ I_{cd} \end{pmatrix} = \begin{pmatrix} r & & 1 & & \\ & 1 & & & 1 \\ r & 1 & & & 1 \\ 1 & -1 & -1 & & \\ & 1 & 1 & & -1 \end{pmatrix} \backslash \begin{pmatrix} 1 \\ 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \frac{1}{5r+3} \begin{pmatrix} 4 \\ 3r+1 \\ 1-r \\ r+3 \\ 2r+2 \end{pmatrix}$$

i.e., that the above matrices represent the problem and that they solve as shown. Check that, of the two alternate paths $abcd$ and $acbd$, one of them is redundant in the context of all the Kirchoff equations.

What happens when $r = 1, r = 2$ or $r = 1/2$?

Show that the effective resistance from a to d is

$$\frac{3r + 5}{5r + 3}$$

How does this compare with the combined series-parallel rules above applied to the three paths abd, acd and $abcd$?

21. **Kirchoff lattices: relations and operators.** Write a MATLAB program to generate the Kirchoff equations, and solve them, for an m-by-n lattice of resistors. For example, the 1-by-2 square and triangular lattices:
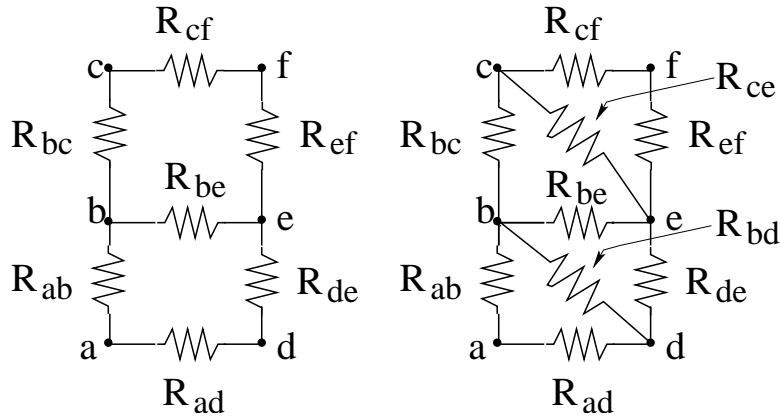
We will assume all resistances are equal in any lattice, and that the edges are *directed* to remove ambiguities about currents flowing in two different directions along the same edge. (A current flowing in the direction of the edge will have a positive sign; one flowing contrasens will be negative.) So we can avoid drawing and labelling the resistors.
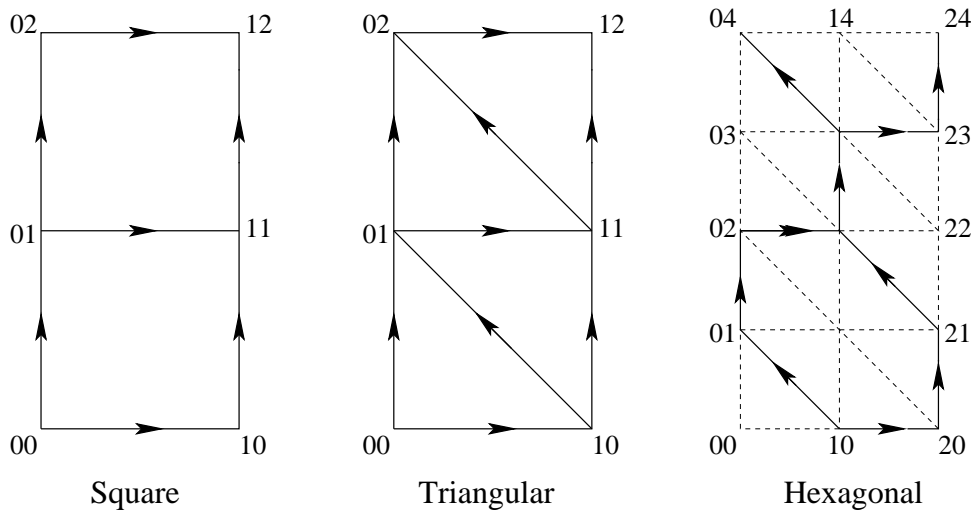
The third lattice in this figure is a 1-by-2 hexagonal lattice with dashed edges showing what was removed from a 2-by-4 triangular lattice to make it. Note that the geometric names (square, triangular, hexagonal) refer to the shape of the basic unit of the lattice, not of the lattice itself.

a) Write a MATLAB function, `crystal2(m,n,f)`, which generates all the edges of an `m`-by-`n` lattice with *fanout* `f` giving the unit shape: `f = 4` for square, `f = 6` for triangular and `f = 3` for hexagonal. The invocation `edgs = crystal2(1,2,f)` should give the edges as pairs of coordinate pairs:

$f=4$			
0	0	1	0
0	0	0	1
0	1	1	1
0	1	0	2
0	2	1	2
1	0	1	1
1	1	1	2

$f=6$			
0	0	1	0
0	0	0	1
0	1	1	1
0	1	0	2
0	2	1	2
1	0	1	1
1	0	0	1
1	1	1	2
1	1	0	2

$f=3$			
0	1	0	2
0	2	1	2
1	0	2	0
1	0	0	1
1	2	1	3
1	3	2	3
1	3	0	4
2	0	2	1
2	1	1	2
2	3	2	4

What is the condition on the coordinates j, k of any *vertex* that will exclude that vertex from participating in the hexagonal case?

It will also be handy for `crystal2()` to return the individual vertices of the lattice: `[edgs,vertices] = crystal2(m,n,f)`. And it is also useful if `crystal2()` draws the resulting lattice as a figure.

Now we must do two things with these edges: find all paths between the two vertices to which the voltage is applied (for the Voltage law), and find all edges containing each vertex except these end-points (for the Current law).

b) Write MATLAB code to combine `edgs`, generated in (a) by `crystal2()`, into paths between every possible pair of vertices.

(This exercise is more general than we need for this Excursion, which seeks only to find the effective resistance between two *specified* vertices, but we'll see that more general is, in this case, easier than less.)

We start with the idea of a *natural join* between two *relations*. First, a *relation* is, like a matrix or array, a collection of data. We can visualize a relation as a set of identically-structured rows. An illustration is the set of edges of the 1-by-2 square lattice from (a) above.

edges1by2square

x_1	y_1	x_2	y_2
0	0	1	0
0	0	0	1
0	1	1	1
0	1	0	2
0	2	1	2
1	0	1	1
1	1	1	2

where the relation *name*, edges1by2square, and its four *attributes* are also shown. The attributes, and hence the number of attributes, are an intrinsic part of the relation. The rows (technically known as *tuples*, as in the 4-tuples ("quadruples") of the example) provide the data and are not fixed in number; they must all be distinct.

Without the name and attributes, this relation can be represented in MATLAB as a 7-by-4 array of integers.

Here are two more relations, R(X,Y) and S(Y,Z), this time using letters instead of integers as data.

	R(X	Y)		S(Y	Z)		R⋈S(X	Y	Z)

R(X Y)

X	Y
a	a
b	a
c	a
a	b
c	b

S(Y Z)

Y	Z
a	a
a	b
b	a
c	a
c	b

R⋈S(X Y Z)

X	Y	Z
a	a	a
a	a	b
b	a	a
b	a	b
c	a	a
c	a	b
a	b	a
c	b	a

The third relation is the *natural join* of R and S, the natural join operator written as a bow tie. You can see that R and S are matched on their *common attribute* Y: wherever Y from R equals Y from S, the two tuples (rows) are combined. So, since there are three "a"s in Y from R and two "a"s in Y from S, the join will have six tuples with "a"s under its Y attribute. Similarly, it will have $2 \times 1 = 2$ tuples with "b"s under its Y attribute, and none with "c"s. The simplest way to implement a natural join is with a double loop: compare every tuple in R with every tuple in S. The extreme case is a join of an m-tuple R with an n-tuple S giving an mn-tuple join: create an example of this extreme. The other extreme is an empty join: create an example of that.

(By the way, the relations R and S above are *the same relation* apart from their names and attributes: the *order of the tuples* doesn't matter. This abstraction away from tuple order gives relations and their operators a great deal of power. Relations were first used for databases on computer secondary storage [Cod70, Mer99].)

The natural join can help us find paths through a lattice. We join the to-vertex of each edge with the from-vertex of each edge to get paths of length 2 (three vertices: start, middle, end). Then we join this result, via its start vertex, to the original edges relation, via its to-vertex, to get paths of length 3 (four vertices), and so on.

The joins, being on vertices, are on *pairs* of attributes instead of single attributes, extending the above join rules marginally.

Here is the join of edges1by2square with itself (after suitable renaming of attributes to make x_2 and y_2 common, and after rearranging tuples to make the join easier to do by hand).

edges1by2square

x_1	y_1	x_2	y_2
0	0	0	1
0	1	0	2
0	0	1	0
0	1	1	1
1	0	1	1
0	2	1	2
1	1	1	2

edges1by2square

x_2	y_2	x_3	y_3
0	0	1	0
0	0	0	1
0	1	1	1
0	1	0	2
0	2	1	2
1	0	1	1
1	1	1	2

x_1	y_1	x_2	y_2	x_3	y_3
0	0	0	1	1	1
0	0	0	1	0	2
0	1	0	2	1	2
0	0	1	0	1	1
0	1	1	1	1	2
1	0	1	1	1	1

Check that the paths of length 2 given by the join are indeed those that you can find in the diagram.

One more join, again with attributes suitably renamed and tuples reordered, gives the longest paths in the 1-by-2 square lattice example.

x_1	y_1	x_2	y_2
0	0	0	1
0	1	0	2
0	0	1	0
0	1	1	1
1	0	1	1
0	2	1	2
1	1	1	2

x_2	y_2	x_3	y_3	x_4	y_4
0	0	0	1	1	1
0	0	0	1	0	2
0	0	1	0	1	1
0	1	0	2	1	2
0	1	1	1	1	2
1	0	1	1	1	1

x_1	y_1	x_2	y_2	x_3	y_3	x_4	y_4
0	0	0	1	0	2	1	2
0	0	0	1	1	1	1	2
0	0	1	0	1	1	1	2

Any further join will produce an empty result.

Now we specialize this by supposing that two endpoints are specified. For example, to find the effective resistance between (0,0) and (1,2) we must specify these as the endpoints of the paths. All these paths have the same length, 3, and so are given in the last join, above.

Another example is endpoints (0,0) and (0,2). Now we can find only one path in the above joins, the second tuple in the length-2 result above, 00 01 02. This omits paths of length 4 such as 00 10 11 12 02 or 00 01 11 12 02 or, for that matter, 00 10 11 01 02.

To include these paths we must do more work. We must combine edges1by2square with its own *transpose*, i.e., swapping vertices, before we do the joins. Let's illustrate with only the bottom square of the Square figure.

x_1	y_1	x_2	y_2	x_3	y_3	
0	0	0	1	0	0	←
0	0	0	1	1	1	
0	0	1	0	0	0	←
0	0	1	0	1	1	
0	1	0	0	0	1	←
0	1	0	0	1	0	
0	1	1	1	0	1	←
0	1	1	1	1	0	
1	0	0	0	0	1	
1	0	0	0	1	0	←
1	0	1	1	0	1	
1	0	1	1	1	0	←
1	1	0	1	0	0	
1	1	0	1	1	1	←
1	1	1	0	0	0	
1	1	1	0	1	1	←

edges1by2square

x_1	y_1	x_2	y_2
0	0	0	1
0	0	1	0
0	1	1	1
1	0	1	1
0	1	0	0
1	0	0	0
1	1	0	1
1	1	1	0

Show that the six-column relation above is the natural join with itself of the transpose-extended edges1by2square. Note that this join is a lot larger than the self-join we had earlier of edges1by2square alone. Convince yourself furthermore that the next join will be even bigger. So specifying simply that the last join be empty will no longer stop the iteration of natural joins.

The trick is to get rid of the tuples marked by arrows: these all show *cyclic* paths, e.g., from 00 back to 00.

To do this, we must modify the join implementation to a *no-overlap* join:

Write a MATLAB function `T = nolapjoin2D(R,S)` which performs a natural join matching the last two columns of R with the first two columns of S (both R and S may have any even number of columns, with all data assumed to be of the same type, e.g., integers) but detects and rejects any tuples containing the same coordinate pair more than once—i.e., tuples with self-overlap.

Now the code to find all paths is the simple loop

```
paths = [edgs;[edgs(:,3:4),edgs(:,1:2)]];  % add in the transpose
pathsInit = paths;
while ~isempty(paths)
  % do something here to select paths between the two specified endpoints
  paths = nolapjoin2D(pathsInit,paths);
end % while ~isempty()
```

The `do something here` comment needs some discussion. First, confirm that the `while` loop above will produce the following paths.

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paths							
$(x_1$	y_1	x_2	y_2	x_3	$y_3)$		
0	0	1	0	1	1		
0	0	0	1	1	1		
0	1	1	1	1	0		
1	0	1	1	0	1		
1	0	0	0	0	1		
0	1	0	0	1	0		
1	1	0	1	0	0		
1	1	1	0	0	0		

paths							
$(x_1$	y_1	x_2	y_2	x_3	y_3	x_4	$y_4)$
0	0	1	0	1	1	0	1
0	0	0	1	1	1	1	0
0	1	1	1	0	0	0	0
1	0	1	1	1	1	0	0
1	0	0	0	1	1	1	1
0	1	0	0	0	0	1	1
1	1	0	1	0	0	1	0
1	1	1	0	0	0	0	1

and subsequent joins will be empty. Thus, for endpoints 00 and 01, we can select a path of length 1 (from the original edges) 00 01, and a path of length 3 (from the last non-empty join) 00 10 11 01.

The discussion we needed is to note that the paths between two endpoints are not necessarily all the same length. Each path can be stored as a row vector in MATLAB, but the collection of paths, all between the same two endpoints, must be managed as a MATLAB cell array of such vectors. So the `do something here` comment must build up elements of a cell array.

Check that your assembled procedure will find all the paths between any given two endpoints in all the above lattices and their extensions to any sizes.

c) Now that we can generate lattices and paths through them, we must figure out how to generate and solve the Kirchoff equation matrices. Write a MATLAB function
`effResist = buildSolveKirchoff(paths)` which, given the cell vector `paths` of all paths between one pair of endpoints (`paths` contains one relation for each path length, holding all paths of that length), uses it finally to calculate the effective resistance between those two points.

The Kirchoff matrix has a row for each path and for each node interior to any path, and it has a column for each edge that appears in some path. Thus, for paths 00 01 and
00 10 11 01 between nodes 00 and 01, the matrix rows and columns would be labelled

$$
\begin{pmatrix}
& 0001 & 0010 & 1011 & 1101 \\
0001 & & & & \\
00101101 & & & & \\
10 & & & & \\
11 & & & &
\end{pmatrix}
$$

So write a MATLAB function `[edgs,nodes] = paths2edgesNinnerNodes(paths)` which extracts all the paths from a MATLAB cell and finds all edges in any of those paths and all nodes interior to any of those paths. (The invocation for the above example is

    [edgs,nodes] = paths2edgesNinnerNodes({[0,0,0,1],[0,0,1,0,1,1,0,1]})

where you see the two row vectors in the cell.)

The next job is to populate the matrix: in the rows for paths, with 1 under every column that is an edge in that path; in the rows for inner nodes, with 1 under every column that is an edge ending in this node, and a -1 under every column that is an edge beginning with this node; and 0 everywhere else. For example

$$
\begin{pmatrix}
& 0001 & 0010 & 1011 & 1101 \\
0001 & 1 & & & \\
00101101 & & 1 & 1 & 1 \\
10 & & 1 & -1 & \\
11 & & & 1 & -1
\end{pmatrix}
$$

This job is part of your function `buildSolveKirchoff()`, which should also invoke `paths2edgesNinnerNodes()`.

At the same time, the Kirchoff vector of voltages must be built up: 1s for rows labelled with paths and 0s for rows labelled with nodes. This is also part of `buildSolveKirchoff()`. Solving for currents uses a MATLAB matrix operator, say

$$\texttt{currents = matKirchoff}\backslash\texttt{vecKirchoff}$$

For example

$$\begin{pmatrix} 1 & & & \\ & 1 & 1 & 1 \\ & 1 & -1 & \\ & & 1 & -1 \end{pmatrix} \backslash \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 1/3 \\ 1/3 \\ 1/3 \end{pmatrix}$$

The total current out of the first node in all the paths (into the lattice) can be found from this, and the effective resistance is the reciprocal of this total. In the example, the total current out of 00 into the lattice is $4/3$ (as is the total current from the lattice into 01) so the effective resistance is $3/4$.

This package of functions will be useful in Part IV.

22. Show that $(\text{slope}_x c)/c = \text{slope}_x \ln c$ for any function $c(x)$. Hint: $\text{slope}_x c^{-1}(x) = 1/\text{slope}_c x(c)$ and $\text{slope}_x e^x = e^x$.

23. In Note 26 we found the relationship between chemical potential μ and concentration c

$$\mu - \mu_0 = \frac{1}{k_B T} \ln \frac{c}{c_0}$$

Chemical potential is a form of energy, which is in most cases a *relative* quantity, so let's take the "base energy" $\mu_0 = 0$. And let's turn the equation around

$$\frac{c}{c_0} = e^{\mu/(k_B T)}$$

In [FLS64, §4-1], Feynman gives a direct argument to work out the density of the atmosphere as a function of height

$$\frac{c}{c_0} = e^{-mgh/(k_B T)} = e^{-U/(k_B T)}$$

for potential energy U. (This also is a direct consequence of the Boltzmann distribution (Note 13, Part II). Why is the sign on U negative while the sign on μ is positive?

24. **Viscosity and heat conduction.** All transport mechanisms can be seen as conveying a current (or current density) of some sort across an imaginary surface dividing the gas into two regions. Diffusion is a current of molecules themselves, or a current density of their concentration. Viscosity is a current of momentum, which I'll explain shortly. Heat conduction is a current of energy. Each of these currents is driven by a gradient. So the laws governing these transport mechanisms have the appearance

$$\text{current density} = \text{coefficient} \times \text{gradient}$$

All the transport is conveyed by molecules crossing the dividing surface between one region and the other.
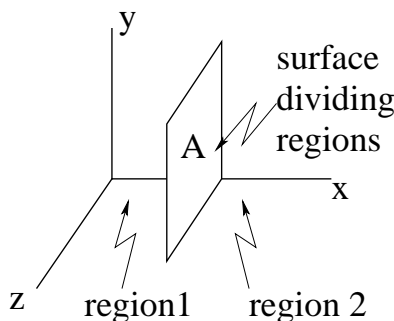
a) So we must first figure out how many molecules are going, say, from region 1 to region 2. That will be all those molecules with positive x-velocity, v_x.

We get the distribution of velocities from Boltzmann's distribution (Note 14, Part II)

$$e^{-K/(k_B T)}$$

where K is the kinetic energy $K = mv^2/2$, $v^2 = v_x^2 + v_y^2 + v_z^2$, and I've now put $1/(k_B T)$ for β as we found out in Note 17 (Part II).

Because of the v^2 this is a normal distribution in v and we must normalize it to make it a probability distribution (Note 6, Part I). This is the same for each of v_x, v_y and v_z, so, for example

$$\text{prob. density for } v_x = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_x^2}{2 k_B T}}$$

and for v is just the product of all three with $e^{-av_x^2} e^{-av_y^2} e^{-av_z^2} = e^{-av^2}$.

The total positive velocity is

$$\left(\text{antislope}_{v_z} \left(\text{antislope}_{v_y} \left(\text{antislope}_{v_x} v_x (\frac{m}{2\pi k_B T})^{\frac{3}{2}} e^{-\frac{m v^2}{2 k_B T}} \right)_0^\infty \right)_{-\infty}^\infty \right)_{-\infty}^\infty$$

(Note that the limits for v_x are non-negative.)

Since

$$\left(\text{antislope}_{v_z} \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_z^2}{2 k_B T}} \right)_{-\infty}^\infty = 1$$

and similarly for v_y, and since

$$\left(\text{antislope}_{v_x} v_x \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_x^2}{2 k_B T}} \right)_0^\infty = \sqrt{\frac{m}{2\pi k_B T}} \frac{k_B T}{m} = \sqrt{\frac{k_B T}{2\pi m}}$$

(just change variables in antislope $e^{-bs^2/2}$ to $t = s^2/2$ and work out $\text{antislope}_t e^{-bt}$) this is

$$\text{total } x_+ \text{ velocity} = \sqrt{\frac{k_B T}{2\pi m}} = \frac{\overline{v}}{4}$$

where I've used the mean velocity of a 3D Maxwell distribution (Excursion for Note 14, Part II), $\overline{v} = \sqrt{8 k_B T/(\pi m)}$, as a shorthand for this result.

To work with particle concentration c we multiply so that the total particle concentration crossing the dividing surface is

$$\text{particle current density} = \frac{c\overline{v}}{4}$$

b) Here's a direct way to relate the current density of whatever is being transported to a gradient. Unfortunately it is a little too simple and requires "kludge factors", which we'll call κ, to adjust it to empirical observations.

Suppose the quantity being transported is q. The q varies across the surface dividing the regions. It is plausible to suppose that region 1 "extends" into region 2 by the distance of the mean free path, or mean distance between collisions, λ, and vice-versa.

This mean distance between collisions must be the mean time between collisions, τ, times the mean velocity

$$\lambda = \overline{v}\tau$$

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but I'll wait a few lines before plugging this in.

However, because of the looseness of this argument, we multiply λ by the kludge factor κ. So we need to know quantity q not at the dividing surface, $q = q_0$, but at a distance $\pm \kappa \lambda$ on either side of it. This can be approximated—here comes the gradient of q—by

$$q_0 \pm \kappa \lambda \, \text{slope}_x q$$

Putting these together, the total current density for q, $c\bar{v}q/4$, is the difference from $-$ (the q leaving region 1 for region 2) to $+$ (the q leaving region 2 for region 1)

$$
\begin{aligned}
\frac{1}{4}c\bar{v}((q_0 - \kappa\lambda\,\text{slope}_x q) \quad &- \quad (q_0 + \kappa\lambda\,\text{slope}_x q)) \\
&= \quad -\frac{1}{2}c\bar{v}\kappa\lambda\,\text{slope}_x q \\
&= \quad -\frac{1}{2}\kappa c\bar{v}^2\tau\,\text{slope}_x q \\
&= \quad -\frac{1}{2}\kappa cm\bar{v}^2\mathcal{M}\,\text{slope}_x q \\
&= \quad -4\kappa c\frac{k_B T}{\pi}\mathcal{M}\,\text{slope}_x q \\
&= \quad -\frac{4}{\pi}\kappa c\mathcal{D}\,\text{slope}_x q
\end{aligned}
$$

where the last three lines use the mobility $\mathcal{M} = \tau/m$, the Maxwell mean velocity (above) and the diffusivity $\mathcal{D} = k_B T \mathcal{M}$.

c) Apply this to viscosity. The quantity being transported is momentum in some direction perpendicular to x, say y. It is conventional to work with velocity, so I'll use for q

$$q = p_y = mv_y$$

Here's a picture for the case of "laminar flow" in a gas. In laminar flow the y-velocity depends only on x—I've plotted it in the example of a pipe of radius r (with $v_y = 0$ at the walls of the pipe) but for the moment notice only that v_y depends only on x. (Laminar: from lamina, Latin for plate or layer. Contrasted with turbulent flow which has eddies and circular components.)
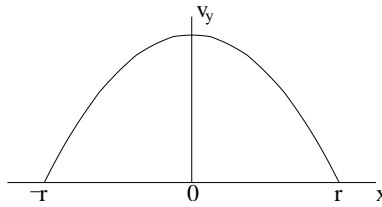
In detail, we can imagine two adjacent "slabs" of gas, each moving at a uniform speed but slightly different from its neighbour.
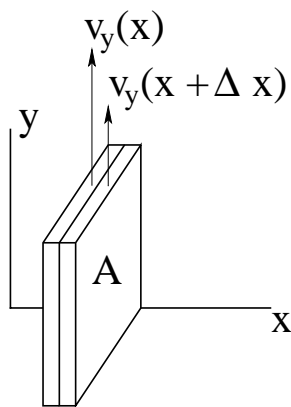
The faster slab is losing momentum to the slower slab because of the presence of "its" molecules a distance $\kappa\lambda$ into the slower slab. Correspondingly the slower slab gains momentum from the faster. The analogy has been made with two coal trains on parallel tracks going in the same direction side by side but at different speeds. Two gangs are shovelling coal laterally from each train to the other: the faster coal imparts forward momentum to the slower train and vice versa.

Back to the theory. The momentum current

$$\frac{c\bar{v}q}{4} = \frac{c\bar{v}mv_y}{4} \approx -\frac{4}{\pi}\kappa cm\mathcal{D} \text{ slope}_x v_y$$

and the term multiplying the gradient is the coefficient of viscosity

$$\eta = \frac{4}{\pi}\kappa cm\mathcal{D}$$

(Yes: Wannier also drops the minus sign: why?)

The concentration times the mass is just the density, $cm = \rho$, and observation makes κ very close to 1, so

$$\eta = \frac{4}{\pi}\rho\mathcal{D}$$

This depends on temperature (because of the $k_B T$ in $\mathcal{D}$) but not on pressure, a result which surprised Maxwell when he first deduced it from his kinetic theory.

The momentum current, which is a rate of transfer per unit area, is just a force per unit area, in the form of a shearing stress. So we can write

$$F = \eta A \text{ slope}_x v_y$$

d) Apply it to heat conduction. Here q is energy being transported across the dividing surface due to a temperature gradient, which relates to energy via the specific heat at constant volume per molecule (Note 22, Part II)

$$\text{slope}_x \text{energy/molecule} = c_V \text{ slope}_x T$$

and where this time the kludge factor κ checks out to be rather further from 1 than in (c) because the more energetic molecules cross the dividing plane more rapidly. Does the heat conductivity depend on the pressure? On the temperature?

e) Apply it to transport of concentration (diffusion). By comparison with the diffusivity we got in Note 25, what is κ this time?

f) Is there a useful way to invent "potentials" corresponding to the flow of momentum in viscosity or to the flow of energy in heat conduction, as we did for concentration and chemical potential, so that a better theory can be made? Such potentials would be the slopes of energy with respect to the quantities that are flowing. What would the physical dimensions be?

25. **"Ohm's law" for viscosity.** a) Using $F = \eta A \, \text{slope}_x v_y$ (previous Excursion) in a circular pipe of radius r and length ℓ, with pressure P applied at the bottom (and ignoring gravity), show that the velocity distribution is parabolic in x (see drawing in previous Excursion), being 0 at the pipe wall and maximum in the middle:

$$v_y(x) = \frac{P}{4\eta\ell}(r^2 - x^2)$$

Note that the force due to P is $P\pi r^2$ where the area of cross-section of the pipe, πr^2, is not the area $A = 2\pi x\ell$ of the boundary of the slab of a given velocity $v_y(x)$. Note also that, since a slab is moving at uniform velocity $v_y(x)$, there is no net force on it:

$$P\pi x^2 + \eta 2\pi x\ell \, \text{slope}_x v_y = 0$$

b) show that the total volume flow

$$\dot{V} = \text{antislope}_x 2\pi x v_y(x) \, |_0^r$$

is Poiseuille's formula

$$\dot{V} = \frac{\pi P}{8\eta\ell} r^4$$

so there is a simple relationship between the total "volume current" $\dot{V}$ and the "potential difference P: $P = \dot{V}R$ where the "resistance"

$$R = \frac{8\eta\ell}{\pi r^4}$$

c) What is the maximum fluid velocity? show that this is twice the average velocity.

26. **Elasticity and viscosity: stress, strain and flow tensors.** The science of rheology (Greek $\rho\epsilon o\sigma$ stream, current) was introduced to me as a graduate student, when the science was half its present age, by a demonstration in a laboratory of Royal Dutch Shell, who were supporting me on a scholarship. A cylindrical pot of some goopy oil product was mounted on a turntable. As the turntable span, the goop span with the pot, but also rose up in the centre into an appreciable and mystifying mound.
a) Reproduce this demonstration with a pot of honey on some kind of turntable which you can safely spin up to a few tens of revolutions per minute. (I have not tried it. Honey might *not* bulge up. Why?)
b) This behaviour is due to "Poisson's ratio" ν which arises in flows and elastic strains in more than one dimension. We must consider tensors (see Note 4 of Week 7c) of stress and of the deformations resulting from strain.
Start with stress. In the previous two Excursions on viscosity we had relationships among force F, area A, viscosity η and deformation $d_{xy} = \text{slope}_x v_y$ (this deformation is a flow; deformations can also be elastic strains which we'll encounter later in this Excursion)

$$F = \eta A d_{xy}$$

The area A was imagined in those Excursions to be that of a surface orthogonal to the x-direction, so we could call it, more generally, A_x.[2]

---

[2]In two dimensions, the "area" would be a length, but we'll call it "area" anyhow. In three dimensions it would be, not a vector as suggested by the subscript x but a "pseudovector" (see Note 5 of Week 7c) because it changes sign depending on whether we are looking at the "front" or the "back" of the area. Since Newton's third law makes the sign of a force a physical consideration, we can get away with pretending the area is a vector and adjusting the sign to suit the physics.

The force F was imagined to be in the y direction, so F_y.

The *stress*, like pressure, is F/A, so with the above discussion we have a stress *tensor* $s_{yx} = F_y/A_x$. (It must be a tensor because it is a physical quantity independent of the coordinate system, $x, y, ..$, although its components in different coordinate frames will have different values.)

The deformation d_{xy}, having been written above as the x-gradient of a y-flow, is also a tensor. And the viscosity relationship between s_{yx} and d_{xy} is not a simple $s_{yx} = \eta d_{xy}$ but in general requires a *viscosity tensor*

$$s_{yx} = \eta_{xx'yy'} d_{x'y'}$$

with repeated ("dummy") indices to be summed over (see Excursion *.. tensor notation ..* in Week 7c: but I'm going to change to matrix notation now, and that excursion will not be a prerequisite for this one).

c) I think elasticity is easier to start with than viscosity. The difference is not in the stress but in the deformation. Elastic deformation is a restorable displacement of the parts of the body under stress, while viscous deformation is a flow. (There is also plastic deformation, which is elastic up to a certain stress then flows. I'll mention plasticity again later in this Excursion, but will not analyze it.)

An easy elastic deformation to study is *shear strain*. We are familiar with it from Week iv Note 9 and Week 3 Note 9 where it was the Lorentz transformation. The shear transformation is a matrix of the form

$$\frac{1}{\sqrt{c_2}} \begin{pmatrix} c & s \\ s & c \end{pmatrix}$$

where $c = \cos\theta$, $s = \sin\theta$ and $c_2 = \cos 2\theta = c^2 - s^2$ so that the determinant of the matrix is 1. The angle θ is the symmetric distortion so that a right angle is deformed into $\pi/2 - 2\theta$
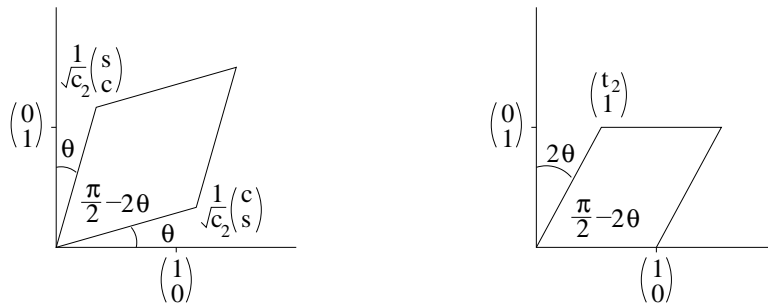
The left side of the diagram show this. But physical shear experiments usually look like the right side of the diagram, where $t_2 = \tan 2\theta$: the transformation is

$$\begin{pmatrix} 1 & t_2 \\ 0 & 1 \end{pmatrix}$$

whose determinant is also 1.

But this transformation has a component of rotation in it and rotation does not *deform* a body but moves it rigidly. We can find the rotation part mathematically by looking for a rotation matrix hidden in the transformation. Before we go on, there is another "But!".

But a deformation also is a *relative* displacement $x' - x$ and $y' - y$ where x' and y' are the transformed x and y. That is, in pictures
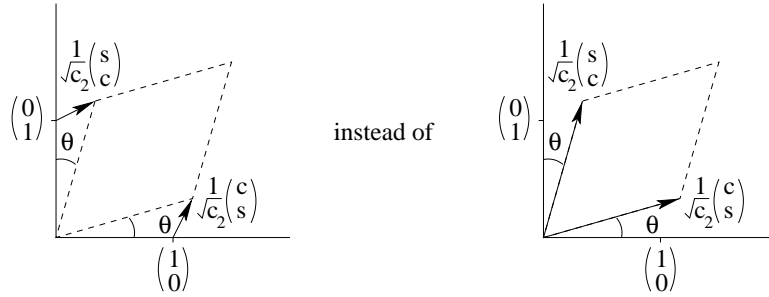
So where a transformation T maps x and y into x' and y' respectively, the relative transformation R maps x and y into $x' - x$ and $y' - y$ respectively. Show that

$$R = T - I$$

and so for shear

$$\frac{1}{\sqrt{c_2}} \begin{pmatrix} c & s \\ s & c \end{pmatrix} \quad \text{becomes} \quad \frac{1}{\sqrt{c_2}} \begin{pmatrix} c - \sqrt{c_2} & s \\ s & c - \sqrt{c_2} \end{pmatrix}$$

and

$$\begin{pmatrix} 1 & t_2 \\ 0 & 1 \end{pmatrix} \quad \text{becomes} \quad \begin{pmatrix} 0 & t_2 \\ 0 & 0 \end{pmatrix}$$

One final "But!": elasticity does not apply to large deformations, so we are going to work with infinitesimal (very small) deformations. For shear, this means very small angles θ.

$$\frac{1}{\sqrt{c_2}} \begin{pmatrix} c & s \\ s & c \end{pmatrix} \quad \text{becomes} \quad \frac{1}{\sqrt{c_2}} \begin{pmatrix} 1 & \theta \\ \theta & 1 \end{pmatrix} \quad \text{and, relatively,} \quad \frac{1}{\sqrt{c_2}} \begin{pmatrix} 0 & \theta \\ \theta & 0 \end{pmatrix}$$

and

$$\begin{pmatrix} 1 & t_2 \\ 0 & 1 \end{pmatrix} \quad \text{becomes} \quad \begin{pmatrix} 1 & 2\theta \\ 0 & 1 \end{pmatrix} \quad \text{and, relatively,} \quad \begin{pmatrix} 0 & 2\theta \\ 0 & 0 \end{pmatrix}$$

Now we can return to the first "But!", getting rid of the rotation.

$$\begin{pmatrix} 0 & 2\theta \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \theta \\ \theta & 0 \end{pmatrix} + \begin{pmatrix} 0 & \theta \\ -\theta & 0 \end{pmatrix}$$

and the second part of this breakdown is the relative transformation giving the an infinitesimal rotation about the negative angle $-\theta$. Removing this, we are left with the relative transformation for an infinitesimal *symmetric* shear, the one we got originally from Weeks iv and 3.

The reason for going through this there-and-back-again discussion of shear is that it applies to any deformation: we must write the relative version of the transformation, we consider infinitesimal deformations, and we must get of any rigid rotations by symmetrizing the matrix. We do not need to symmetrize the stress matrix because we will just assume it is symmetrical: any antisymmetric part of it would describe a *torque*, and torque causes rigid rotations without deforming the body.

We can add one final consideration before writing down the general form of the "rheological equation". This is the separation into *isotropic* and *anisotropic* components, and applies both to stress and to deformation.

For example, before we apply shear, let's shrink the body by factors h_x and h_y (actually these will be < 1 for a shrink and > 1 for an expansion, but I'll call them h for s*h*rink anyway.)

$$\begin{pmatrix} 1 & t_2 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} h_x & \\ & h_y \end{pmatrix} = \begin{pmatrix} h_x & t_2 h_y \\ 0 & h_y \end{pmatrix}$$

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or

$$\frac{1}{\sqrt{c_2}} \begin{pmatrix} c & s \\ s & c \end{pmatrix} \begin{pmatrix} h_x & \\ & h_y \end{pmatrix} = \frac{1}{\sqrt{c_2}} \begin{pmatrix} ch_x & sh_y \\ sh_x & ch_y \end{pmatrix}$$

that is

$$\begin{pmatrix} 1 & \theta \\ \theta & 1 \end{pmatrix} \begin{pmatrix} h_x & \\ & h_y \end{pmatrix} = \begin{pmatrix} h_x & \theta h_y \\ \theta h_x & h_y \end{pmatrix} \rightarrow \begin{pmatrix} h_x - 1 & \theta h_y \\ \theta h_x & h_y - 1 \end{pmatrix}$$

where the $\rightarrow$ is the process of relativizing the shear.

Now suppose this shrink is *isotropic*—it is the same in all directions—that is $h_x = h_y = h$.

$$\begin{pmatrix} h - 1 & \theta h \\ \theta h & h - 1 \end{pmatrix} = \begin{pmatrix} h - 1 & \\ & h - 1 \end{pmatrix} + \begin{pmatrix} & \theta h \\ \theta h & \end{pmatrix}$$

and I've separated the isoptropic part, just a constant diagonal matrix, from the anisotropic part, i.e., all the rest.

Even if the shrink were not isotropic, it can be considered to have an isotropic part.

$$\begin{pmatrix} h_x - 1 & \theta h_y \\ \theta h_x & h_y - 1 \end{pmatrix} = \begin{pmatrix} \frac{h_x + h_y}{2} - 1 & \\ & \frac{h_x + h_y}{2} - 1 \end{pmatrix} + \begin{pmatrix} \frac{h_x - h_y}{2} & \theta h_y \\ \theta h_x & -\frac{h_x - h_y}{2} \end{pmatrix}$$

where the isotropic part of an infinitesimal relative transformation, R, is just half its trace times the unit matrix

$$R_{\text{iso}} = \frac{\text{tr}(R)}{2} I$$

(In three dimensions, this would change to one third of the trace.)

In general, any matrix can be broken down into a multiple of I, a symmetric part and an antisymmetric part

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = \frac{a + 2}{2} \begin{pmatrix} 1 & \\ & 1 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} a - d & b + c \\ b + c & d - a \end{pmatrix} + \frac{b - c}{2} \begin{pmatrix} & -1 \\ 1 & \end{pmatrix}$$

If the matrix describes a deformation, the antisymmetric part must be removed, and if it describes an infinitesimal relative transformation, the multiple of I is the isotropic part and the rest is the anisotropic part.

d) **Hookean solid.** Robert Hooke announced in 1676 that force is proportional to extension for an elastic solid. This is not universally true, so by definition a Hookean solid responds (strain, i.e., elastic deformation) to stress linearly in two ways.

If the isotropic stress (hydrostatic pressure) and the corresponding strain are

$$s_{\text{iso}} = \begin{pmatrix} -p & \\ & -p \end{pmatrix} ; \quad d_{\text{iso}} = \begin{pmatrix} h & \\ & h \end{pmatrix}$$

these are related by the *bulk modulus K* as $-p = K(2h)$ where $2h = \text{tr}(d_{\text{iso}})$ is the *volume dilatation*. (In 3D $-p = K\text{tr}(d_{\text{iso}}) = K(3h)$.)[3]

If the anisotropic stress and the corresponding strain are

$$s_{\text{aniso}} = \begin{pmatrix} & \sigma \\ \sigma & \end{pmatrix} ; \quad d_{\text{aniso}} = \begin{pmatrix} & \gamma/2 \\ \gamma/2 & \end{pmatrix}$$

these are related by the *shear modulus G* as $\sigma = 2G(\gamma/2)$. (This is the same in 3D.)

In general

$$s_{\text{iso}} = KI\,\text{tr}(d_{\text{iso}})$$

---

[3]Actually any substance, not just Hookean solids, show volume dilatation under hydrostatic pressure, so this discussion applies to liquids, for instance, as well.

Since $s = s_{\text{iso}} + s_{\text{aniso}}$ and $d = d_{\text{iso}} + d_{\text{aniso}}$ we have the following *rheological equations* (in 2D)

$$s_{11} = K(d_{11} + d_{22}) + 2G(d_{11} - \frac{1}{2}(d_{11} + d_{22}))$$

$$s_{22} = K(d_{11} + d_{22}) + 2G(d_{22} - \frac{1}{2}(d_{11} + d_{22}))$$

$$s_{12} = 2Gd_{12}$$

Although s and d are tensors (square matrices, symmetric by the discussion in (c)) we can write them as column vectors and get a matrix form for the *elasticity tensor*

$$\begin{pmatrix} s_{11} \\ s_{22} \\ s_{12} \end{pmatrix} = \begin{pmatrix} K+G & K-G & \\ K-G & K+G & \\ & & 2G \end{pmatrix} \begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix}$$

or, inverting,

$$\begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix} = \frac{1}{4GK} \begin{pmatrix} G+K & G-K & \\ G-K & G+K & \\ & & 2K \end{pmatrix} \begin{pmatrix} s_{11} \\ s_{22} \\ s_{12} \end{pmatrix}$$

We use the latter form to find out what happens under "simple pull"

$$s = \begin{pmatrix} s_{11} & 0 \\ 0 & 0 \end{pmatrix}$$

so

$$\begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix} = \frac{s_{11}}{4GK} \begin{pmatrix} G+K \\ G-K \\ 0 \end{pmatrix}$$

Simple pull has historically been described in terms of the *tensile modulus* E (usually named after Thomas Young although he was anticipated by a century)

$$s_{11} = Ed_{11}$$

so this gives E in terms of K and G

$$E = \frac{4KG}{G+K}$$

We see, moreover, that pulling a Hookean solid in one direction leads to its contraction in the other direction(s) by a ratio named for Siméon Poisson

$$\nu = -\frac{d_{22}}{d_{11}} = \frac{K-G}{K+G}$$

These four historical measures of elasticity depend on any two of them as follows (in 2D)

	K, G	K, E	K, ν	G, E	G, ν	E, ν
K				$\frac{GE}{4G-E}$	$\frac{1+\nu}{1-\nu}G$	$\frac{E}{2(1-\nu)}$
G		$\frac{KE}{4K-E}$	$\frac{1-\nu}{1+\nu}K$			
E	$\frac{4KG}{K+G}$		$2K(1-\nu)$		$2G(1+\nu)$	
ν	$\frac{K-G}{K+G}$	$\frac{2K-E}{2K}$		$\frac{E-2G}{2G}$		

For a Hookean solid in 3D show that

$$
\begin{pmatrix} s_{11} \\ s_{22} \\ s_{33} \end{pmatrix} = \begin{pmatrix} K + \frac{4}{3}G & K - \frac{2}{3}G & K - \frac{2}{3}G \\ K - \frac{2}{3}G & K + \frac{4}{3}G & K - \frac{2}{3}G \\ K - \frac{2}{3}G & K - \frac{2}{3}G & K + \frac{4}{3}G \end{pmatrix} \begin{pmatrix} d_{11} \\ d_{22} \\ d_{33} \end{pmatrix}
$$

and $s_{jk} = 2G d_{jk}$ when $j \neq k$. Thus show

$$
\begin{pmatrix} d_{11} \\ d_{22} \\ d_{33} \end{pmatrix} = \frac{1}{6GK} \begin{pmatrix} \frac{2}{3}G + 2K & \frac{2}{3}G - K & \frac{2}{3}G - K \\ \frac{2}{3}G - K & \frac{2}{3}G + 2K & \frac{2}{3}G - K \\ \frac{2}{3}G - K & \frac{2}{3}G - K & \frac{2}{3}G + 2K \end{pmatrix} \begin{pmatrix} s_{11} \\ s_{22} \\ s_{33} \end{pmatrix}
$$

and, for simple pull,

	K, G	K, E	K, ν	G, E	G, ν	E, ν
K				$\frac{GE}{9G-3E}$	$\frac{2G(1+\nu)}{3(1-2\nu)}$	$\frac{E}{3(1-2\nu)}$
G		$\frac{3KE}{9K-E}$	$\frac{3K(1-2\nu)}{2(1+\nu)}$			$\frac{E}{2(1+\nu)}$
E	$\frac{9KG}{3K+G}$		$3K(1-2\nu)$		$2G(1+\nu)$	
ν	$\frac{3K-2G}{6K+2G}$	$\frac{3K-E}{6K}$		$\frac{E-2G}{2G}$		

The Poisson ratio has a small range. Because all the moduli must be non-negative, $-1 \leq \nu \leq 1$ in 2D and $-1 \leq \nu \leq 1/2$ in 3D. The upper value in each range corresponds to $K = \infty$, the *incompressible* solid. For real substances (in 3D) rubber has $\nu = 1/2$ and cork has $\nu = 0$. Why are wine bottles stoppered with cork? What would happen if you tried to push in a rubber "cork"?

e) **Newtonian liquid.** For liquids, which show viscosity rather than elasticity (except that they have a bulk modulus, infinite if the liquid is incompressible), the deformation is a flow, relating to the stress by the viscosity η, which we have already discussed for 1D in the previous Excursions.

If the liquid is compressible we have both strain deformation, which I'll write ϵ, and a flow deformation, which I'll write f. The rheological equation is

$$
s = K \operatorname{tr}(\epsilon) + 2\eta f
$$

by exact analogy with what we had for elasticity with G instead of η. The analogue of E is Trouton's *coefficient of viscous traction*, λ_T, and, just as $E = 2G(1 + \nu)$ above, so

$$
\lambda_T = 2\eta(1 + \nu)
$$

That viscous substances resist pull can be seen in the following cultural vignette. The French for "pull" is "tirer" and in Québec, "la tire" is the name for a concentration of maple syrup boiled further to almost the crystallization point and then poured on snow to make spring-time taffy enjoyed during "sugaring off". Such sugar taffy also narrows as it elongates—there's a wonderful illustration of this in Jacques Tati's film "Les Vacances de M. Hulot"—which is evidence for positive ν.

Thus there is a Poisson ratio for viscosity too, and this can explain my experience in the Shell lab: a negative ν would mean that pulling the goop in one direction (horizontal-tangential to the surface of the rotating pot) would fatten it in the other directions (radial and vertical-tangential) and force it to pile up somewhere away from the edge, i.e., in the centre.

Now you can say if the experiment on honey that I suggested at the beginning of this Excursion will reproduce this effect.

For incompressible liquids, the assumption of classical hydrodynamics, the strain $\epsilon = 0$, leaving only flows, f, to be determined. The above relationship gives $\lambda_T = 3\eta$ in 3D since

$\nu = 1/2$ for incompressible substances.

f) The rheological equation is generally the relationship between stresses, s, and deformation, d, for substances which are not necessarily ideal Hookean solids or Newtonian liquids. Even more ideal are i) the rigid Euclidean solid, which does not deform at all, so its rheological equation is

$$d = 0$$

and ii) the Pascalian liquid which is superfluid and supports no stress

$$s = 0$$

In addition to elasticity and viscosity, substances exhibit *plasticity*. The idealization of plasticity is the St. Venant body, which is defined to be rigid up to a certain stress after which it flows with no further increase in stress.

Thus we have three idealizations: the Hookean (H) solid, which can be symbolized by a pure spring; the Newtonian (N) liquid, which can be symbolized by a "dash pot" like the shock absorber on a car; and the St.Venant (V) body, which can be symbolized by a block on a surface supposedly having static friction to be overcome to start the block moving, and (lower) kinetic friction resisting its continued motion.

These three idealizations can be used to model different non-ideal bodies by constructs called "rheological trees", which are the parsings of expressions such as

$$K = H \mid N$$

(a "Kelvin body" is a parallel combination of Hooke and Newton, in which $s = s_H + s_N = 2GE + 2\nu f$),

$$M = N - -H$$

(a "Maxwell body" is a series combination of Newton then Hooke),

$$B = H - -(V \mid N)$$

(a "Bingham plastic", named after Eugene Bingham who with the help of Markus Reiner coined the term "rheology", is a series combination of Hooke with a parallel combination of St. Venant and Newton), and so on.

g) My source for this Excursion has been primarily Reiner [Rei71] whom I have rephrased. Among the many topics you can follow up while checking what I've made of it all, above, is his discussion of the helical spring in section 14 of part II.

To show

$$k = \frac{r^5}{2R^3\ell}G$$

for the spring constant k (I've used it for instance in Notes 12 and 39 of Book 8c and particularly in the Excursion *Forces and deformations* of Book 8c, Part IV) in terms of the length of the spring ℓ, the radius R of its coils and the radius r of the wire it is made of, you will need to follow Reiner's use of cylindrical coordinates which needs the full effects of tensor notation.

h) **Principle axes.** Because both stress and deformation are symmetric matrices they have "principle axes" along which they can be diagonalized (see Week 8, Note 1). What are the eigenvectors of

$$\begin{pmatrix} a & b \\ b & d \end{pmatrix}$$

and what is the diagonal matrix it rotates to? (Hint. For eigenvector $(x, y)^{\mathrm{T}}$

$$\begin{pmatrix} a & b \\ b & d \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \lambda \begin{pmatrix} x \\ y \end{pmatrix}$$

for some "eigenvalue" λ to be discovered. So

$$\begin{pmatrix} a - \lambda & b \\ b & d - \lambda \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \lambda \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

and for nonzero $(x, y)^{\mathrm{T}}$ the determinant

$$0 = \begin{vmatrix} a - \lambda & b \\ b & d - \lambda \end{vmatrix} = \lambda^2 - (a + b)\lambda + ad - b^2$$

which is the *characteristic polynomial* of the matrix, whose roots are its eigenvalues. (Notice that the coefficients of the characteristic polynomial of, matrix M, apart from 1, are $\mathrm{tr}(M)$ and $\det(M)$, respectively. Why does this mean the trace and the determinant are invariant under the rotations of M?)
If $d = a$ you may also be able to guess the two eigenvectors from the discussion of Week 3, Note 6.)
What are the diagonal forms of

$$\begin{pmatrix} 1 & -\nu \\ -\nu & 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & -\nu & -\nu \\ -\nu & 1 & -\nu \\ -\nu & -\nu & 1 \end{pmatrix}?$$

But will both stress and deformation diagonalize together, i.e., have the same principle axes? And, if they do, will they relate to each other via a scalar, or even a diagonal tensor?

27. **Lattice statics and dynamics.** How can we model elasticity at the atomic level? We imagine a lattice of atoms connected by springs and we start with two ideas, (a) and (b) below.
a) Given the strain ("deformation")

$$D = \begin{pmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{pmatrix}$$

show from the discussion of parts (c) and (d) of the previous Excursion that lattice positions are moved to

$$P'_{xy} = (I + D)P_{xy}$$

where

$$P_{xy} = \begin{pmatrix} x \\ y \end{pmatrix}$$

is the priginal position.
Write a MATLAB program to explore this, which is the *assumption* that the microscopic structure deforms *homogeneously* with macroscopic strain. In particular you should be able to generate the pictures
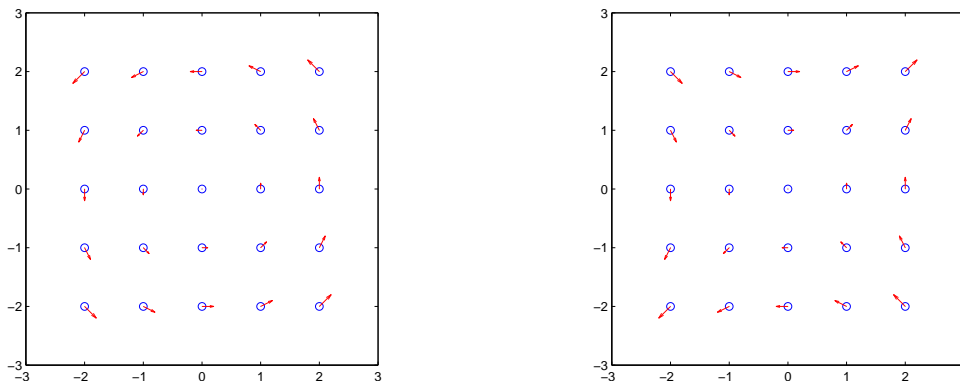
(Here the first is a rotation and not acceptable by the discussion of part (c) of the previous excursion. We'll restrict ourselves from now on to symmetric D matrices, such as the shear in the second picture.)

b) From Note 37 of Book 8c (Part IV), force is the slope of the Lagrangian, or, in a static situation, of the negative of the potential energy U.

$$F = -\text{slope}_x U$$

Since stress $s = F/A$ (part (b) of the previous excursion) where A is the surface area to which the force is applied, and since strain $d = x\ell$, the displacement *relative* to position ℓ, persuade yourself that

$$s = -\frac{1}{V}\text{slope}_d U$$

relates stress s, deformation d, and the volume V of the deformed sample. (U/V is the potential *energy density*, the energy per unit volume.) More specifically, each element of the stress tensor is related this way to the corresponding element of the strain tensor

$$s_{jk} = -\frac{1}{V}\text{slope}_{d_{jk}} U$$

The negative sign indicates that the force is the *restoring force*, which tries to return the sample to its original configuration. If the force we mean is causing the deformation then the restoring force is the "equal and opposite" reaction, and so for the causing stress we drop the negative sign.

For a "cube" of side ℓ this is

$$\begin{aligned}
\text{in 3D} \quad S_{jk} &= \frac{1}{\ell^3}\text{slope}_{d_{jk}} U \quad j,k = x,y,z \\
\text{in 2D} \quad S_{jk} &= \frac{1}{\ell^2}\text{slope}_{d_{jk}} U \quad j,k = x,y \\
\text{in 1D} \quad S &= \frac{1}{\ell}\text{slope}_d U
\end{aligned}$$

Now let's apply these two ideas to a 2D square lattice of "atoms" connected by springs. Suppose that each spring has the same constant, k_S
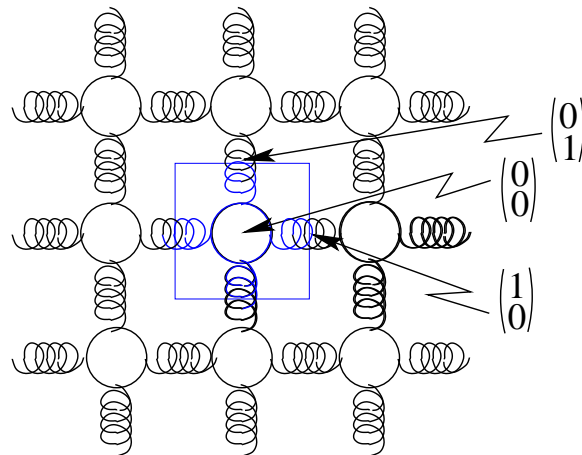
The "unit cell" is shown in blue: repetition of this unit cell in both directions eventually gives the whole lattice. By the assumption of homogeneous deformation, we can work solely with

the unit cell, applying the deformation matrix D to all of the points in it.
In fact, we need only two points for this configuration of springs,

$$P_{10} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad P_{01} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

since

$$P_{\bar{1}0} = \begin{pmatrix} -1 \\ 0 \end{pmatrix} \quad \text{and} \quad P_{0\bar{1}} = \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$

will behave in exactly the opposite way, and their contributions to the potential energy will be exactly the same.
The origin

$$P_{00} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

remains fixed. So the potential energy depends only on the changes in length of the springs

$$
\begin{aligned}
U &= \frac{k_S}{2}((|\ P'_{10}\ | - |\ P_{10}\ |)^2 + (|\ P'_{\bar{1}0}\ | - |\ P_{\bar{1}0}\ |)^2 + (|\ P'_{01}\ | - |\ P_{01}\ |)^2 + (|\ P'_{0\bar{1}}\ | - |\ P_{0\bar{1}}\ |)^2) \\
&= k_S 2((|\ P'_{10}\ | - |\ P_{10}\ |)^2 + (|\ P'_{01}\ | - |\ P_{01}\ |)^2)
\end{aligned}
$$

where k_S is the spring constant.
c) Show that

$$|\ P'_{10}\ | - |\ P_{10}\ | = \sqrt{1 + 2d_{11} + d_{11}^2 + d_{12}^2} - 1$$

and use the binomial series (Note 7 of Week ii) to show that, to second powers

$$|\ P'_{10}\ | - |\ P_{10}\ | \approx d_{11} + \frac{1}{2}d_{12}^2$$

Similarly show

$$|\ P'_{01}\ | - |\ P_{01}\ | \approx d_{22} + \frac{1}{2}d_{12}^2$$

remembering $d_{21} = d_{12}$.
d) Thus show that, again to second powers,

$$U = k_S(d_{11}^2 + d_{22}^2)$$

Use (b) to give

$$
\begin{aligned}
s_{11} &= 2k_S d_{11} \\
s_{22} &= 2k_S d_{22} \\
s_{12} &= 0
\end{aligned}
$$

or

$$\begin{pmatrix} s_{11} \\ s_{22} \\ s_{12} \end{pmatrix} = \frac{k_S}{2} \begin{pmatrix} 1 & & \\ & 1 & \\ & & 0 \end{pmatrix} \begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix}$$

(Remember to divide by V, the "volume" of the unit cell.)
Compare this 3-by-3 matrix of elastic coefficients with part (d) of the previous excursion: is this a hookean solid? What is the shear resistance? The Poisson ratio?

e) A more ambitious structure also connects *second* nearest-neighbours. Add springs of constant k_S from $(0,0)^{\mathrm{T}}$ to $(1,1)^{\mathrm{T}}$, $(-1,-1)^{\mathrm{T}}$, $(1,-1)^{\mathrm{T}}$ and $(-1,1)^{\mathrm{T}}$ and extend your calculations of (d) to show

$$
\begin{pmatrix} s_{11} \\ s_{22} \\ s_{12} \end{pmatrix} = \frac{k_S}{2} \begin{pmatrix} 2 & 1 & \\ 1 & 2 & \\ & & 4 \end{pmatrix} \begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix}
$$

If the $x\overline{y}$ springs are eliminated in this analysis, show that

$$
\begin{pmatrix} s_{11} \\ s_{22} \\ s_{12} \end{pmatrix} = \frac{k_S}{4} \begin{pmatrix} 3 & 1 & 2 \\ 1 & 3 & 2 \\ 2 & 2 & 4 \end{pmatrix} \begin{pmatrix} d_{11} \\ d_{22} \\ d_{12} \end{pmatrix}
$$

f) Born and Huang [BH54, §11] provide the formalism for a more general lattice structure. In particular they show that "homogeneous deformation" can include a fixed relative displacement of two or more *sub*lattices if each unit cell contains two or more atoms. Examples are the "face-centred cubic" structure of 2 atoms per unit cell or a related structure with two different types of atom and in which the atoms are not "centres of symmetry".
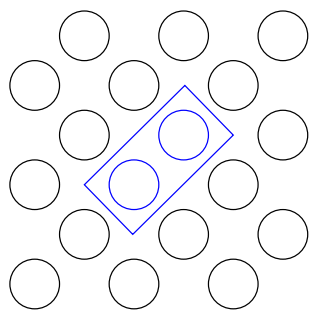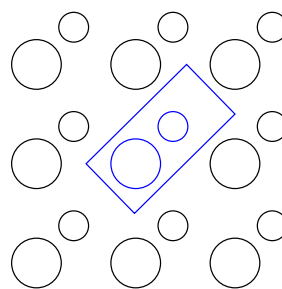
"Face–centred cubic" in 2D   No centres of symmetry

(By the way, the "face-centred cubic" in 2D can be seen as a regular lattice with one atom per unit cell, so working with this example will add nothing new. Can you see this lattice? Look up face-centred- and body-centred-cubic lattices in 3D.)

What are the "Cauchy relations" and how would they appear in 2D?

In [BH54, §25] Born and Huang show that the method of homogeneous deformations works only if the forces between the atoms are central (which our springs were in the two examples, radiating outwards from each atom). For the general case they develop the method of long waves, in which the modes and energies of vibration of the atoms in our model must be calculated and compared, in the case of long wavelength (small wavenumber) with the corresponding vibrations of a continuous elastic solid. This is beyond our present capabilities. In particular it involves examining small wavenumbers in the continuous Fourier transform—as opposed to the discrete Fourier transform, which we know—and tangling with the difficulty that there is no limiting energy as a function of wavenumber—because it depends on the direction of the wave.

That was lattice statics, or equilibrium. To move on to lattice dynamics, or how lattice atoms move, we must explore the connection between the Fourier transform and the waves $e^{-i(\omega t - kx)}$ of Note 2 of Week 6.

First let's check that the 2-dimensional discrete Fourier transform (from the Excursion of that name in Week 9) diagonalizes the matrices describing the 2D lattices of parts (c), (d) and (e) above when they are formulated with periodic boundary conditions (Note 22 of Book 8c, Part II)—which is what we would expect from the symmetry discussions of that Book.

g) For a 3-by-3 square lattice with first-nearest-neighbours connected by springs all with

spring constant k_S ((c) and (d) above), show that periodic boundary conditions give the matrix

$$\mathcal{K}_1 = \begin{pmatrix}
2K & -K_y & -K_y & -K_x & & & -K_x & & \\
-K_y & 2K & -K_y & & -K_x & & & -K_x & \\
-K_y & -K_y & 2K & & & -K_x & & & -K_x \\
-K_x & & & 2K & -K_y & -K_y & -K_x & & \\
& -K_x & & -K_y & 2K & -K_y & & -K_x & \\
& & -K_x & -K_y & -K_y & 2K & & & -K_x \\
-K_x & & & -K_x & & & 2K & -K_y & -K_y \\
& -K_x & & & -K_x & & -K_y & 2K & -K_y \\
& & -K_x & & & -K_x & -K_y & -K_y & 2K
\end{pmatrix}$$

where

$$K_x = k_S \begin{pmatrix} 1 & \\ & 0 \end{pmatrix} \qquad K_y = k_S \begin{pmatrix} 0 & \\ & 1 \end{pmatrix} \qquad K = k_S \begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$$

and where the nine rows and columns of $\mathcal{K}_1$ describe the connections among the positions (x, y) in the following order

$$(-1,-1),\ (-1,0),\ (-1,1),\ (0,-1),\ (0,0),\ (0,1).\ (1,-1),\ (1,0),\ (1,1)$$

Then show that the 2-D Fourier transform(Excursion, Week 9)

$$\frac{1}{3} e^{-2\pi i (j_x k_x + j_y k_y)/3} \begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$$

diagonalizes $\mathcal{K}_1$, giving diagonal elements associated with the different waves (Note 22, Book 8c) as follows

diagonal	0,0	3,0	3,0	0,3	3,3	3,3	0,3	3,3	3,3
wave	00	10	20	01	11	21	02	12	22
	•	– –	–	‖	//	\\	|	/	\

where the first row of "wave" gives the wavenumber's x- and y-directions and the second row gives the same schematically, with double symbols meaning long wavelengths (small wavenumbers)—see the figure in Note 22 of Book 8c.

Thus there is no resistance in this lattice to translation (wavenumber 00), to y-waves (transverse) in the x-direction (wavenumbers 10, 20), or to x-waves in the y-direction (01, 02).

h) For the same with second-nearest-neighbour connections added ((e) above) show that the matrix is

$$\mathcal{K}_2 = \begin{pmatrix}
4K & -K_y & -K_y & -K_x & -K_{xy} & -K_{x\bar{y}} & -K_x & -K_{x\bar{y}} & -K_{xy} \\
-K_y & 4K & -K_y & -K_{x\bar{y}} & -K_x & -K_{xy} & -K_{xy} & -K_x & -K_{x\bar{y}} \\
-K_y & -K_y & 4K & -K_{xy} & -K_{x\bar{y}} & -K_x & -K_{x\bar{y}} & -K_{xy} & -K_x \\
-K_x & -K_{x\bar{y}} & -K_{xy} & 4K & -K_y & -K_y & -K_x & -K_{xy} & -K_{x\bar{y}} \\
-K_{xy} & -K_x & -K_{x\bar{y}} & -K_y & 4K & -K_y & -K_{x\bar{y}} & -K_x & -K_{xy} \\
-K_{x\bar{y}} & -K_{xy} & -K_x & -K_y & -K_y & 4K & -K_{xy} & -K_{x\bar{y}} & -K_x \\
-K_x & -K_{xy} & -K_{x\bar{y}} & -K_x & -K_{x\bar{y}} & -K_{xy} & 4K & -K_y & -K_y \\
-K_{x\bar{y}} & -K_x & -K_{xy} & -K_{xy} & -K_x & -K_{x\bar{y}} & -K_y & 4K & -K_y \\
-K_{xy} & -K_{x\bar{y}} & -K_x & -K_{x\bar{y}} & -K_{xy} & -K_x & -K_y & -K_y & 4K
\end{pmatrix}$$

with K_x, K_y and K as before, and

$$K_{xy} = \frac{k_S}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \qquad K_{x\bar{y}} = \frac{k_S}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

Show that the 2-D Fourier transform does not quite diagonalize this:

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diagonal	0,0	3,6	3,6	6,3	$\frac{1}{2}\begin{pmatrix} 9 & 3 \\ 3 & 9 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 9 & -3 \\ -3 & 9 \end{pmatrix}$	6,3	$\frac{1}{2}\begin{pmatrix} 9 & -3 \\ -3 & 9 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 9 & 3 \\ 3 & 9 \end{pmatrix}$
wave	00	10	20	01	11	21	02	12	22
	•	$--$	$-$	$||$	$//$	$\backslash\backslash$	$|$	$/$	$\backslash$

so that the diagonal waves coupling x and y must combine x and y equally

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

since

$$\frac{1}{2}\frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 9 & 3 \\ 3 & 9 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} 3 & \\ & 6 \end{pmatrix} \quad \frac{1}{2}\frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 9 & -3 \\ -3 & 9 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} 6 & \\ & 3 \end{pmatrix}$$

Only translation is now unresisted.

We must now look at how the atoms move in time as these waves pass over them. We can learn enough in one dimension, and it's simpler.

The discrete Fourier transform $(1/n)e^{2\pi ijk/n}$ is *spatial*, in that j indexes the atoms of the lattice, whose positions $x_j = ja$, where the atoms are spaced a nanometers apart. So we can express the wavenumber $\nu_k = k/(na)$ in numbers of waves across the crystal size na: note that this is discrete in a crystal lattice. (And notice that the k in this treatment is not the k in Week 7a: I won't use k in that sense at all here, but you can work out how they relate to each other by using ν.)

So the Fourier transform is equivalently $(1/n)e^{2\pi ix\nu}$. If we expand this to include time as in Note 2 of Week 7a we will be able to work out how the atoms move in time:

$$e^{2\pi i(x\nu - ft)} = e^{2\pi ix\nu - i\omega t} = e^{2\pi ijk - i\omega t}$$

where it is handy to use the last form with the time dimension in terms of the angular frequency but the space dimension in terms of integers j and k. And I've dropped the normalizing $1/n$ which is irrelevant for waves.

It is particularly interesting to see what happens in a *diatomic* lattice with two different types of atoms per unit cell, and this is still easy in one dimension.

Let's follow Born & Huang [BH54, §5] to find the relationship between ω and k in the 1-D diatomic lattice. Note that for ordinary waves we expect this relationship to be *linear*: the wave

$$e^{2\pi ijk - i\omega t}$$

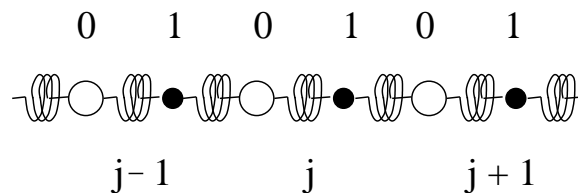has the same phase, say phase $= 0$, at positions j and time t satisfying

$$2\pi jk - \omega t = \text{phase} = 0$$

or

$$\omega = 2\pi jk$$

On the other hand, for a *particle*, since energy $E = \hbar\omega$ and momentum $p = h\nu$ (Week 6), and since also $E = p^2/2$, there is a *parabolic* relationship between ω and k.

i) Which of these applies to lattice vibrations? Write the masses and displacements of the two types of atom as m^0, m^1, u^0 and u^1, respectively.

Then since $H = m\ \mathrm{slope}_t\mathrm{slope}_t u$ (Newton's second law: Note 37, Book 8c (Part IV)—acceleration $a = \mathrm{slope}_t v$ and velocity $v = \mathrm{slope}_t u$) and $\ddot{u}$ is the usual abbreviation of $\mathrm{slope}_t\mathrm{slope}_t u$, the *equations of motion* are

$$m^0\ddot{u}_j^0 = -k_S((u_j^0 - u_{j-1}^1) + (u_j^0 - u_j^1))$$
$$m^1\ddot{u}_j^1 = -k_S((u_j^1 - u_j^0) + (u_j^1 - u_{j+1}^0))$$

If we take the expanded Fourier transform

$$u_j^0 = u^0 e^{2\pi ijk - i\omega t}$$
$$u_j^1 = u^1 e^{2\pi ijk - i\omega t}$$

show that the equation of motion becomes

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 2k_S - \omega^2 m^0 & -k_S(1 + e^{-2\pi ik}) \\ -k_S(1 + e^{-2\pi ik}) & 2k_S - \omega^2 m^1 \end{pmatrix} \begin{pmatrix} u^0 \\ u^1 \end{pmatrix}$$

and thence that

$$\frac{m^0\omega^2}{k_S} = \frac{1}{\mu}\left((\mu + 1) \pm \sqrt{(\mu+1)^2 - 4\mu\sin^2(\pi k)}\right)$$

where $\mu = m^0/m^1$ is the ratio of the two masses.
Plot the right-hand side of this as functions of k with different values for the parameter μ.

Dispersion for diatomic lattice: acoustic below, optical above
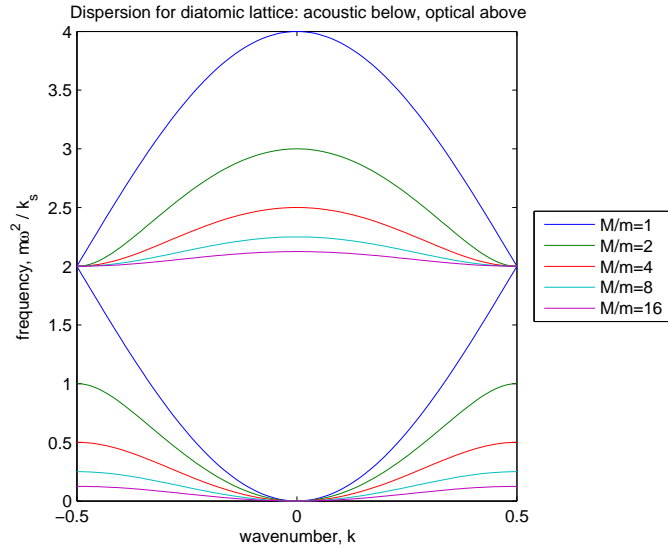
Why need we consider only $-1/2 \le k \le 1/2$?
Before you go to Born & Huang to compare plots, work out that

$$\frac{1}{\mu}\left((\mu + 1) \pm \sqrt{(\mu+1)^2 - 4\mu\sin^2(\pi k)}\right) = \begin{cases} \left.\begin{matrix} 2(1 + \frac{1}{\mu}) \\ 0 \end{matrix}\right\} & k = 0 \\[2ex] \left.\begin{matrix} 2 \\ 2/\mu \end{matrix}\right\} & k = \frac{1}{2} \\[2ex] 2 \pm 2\sqrt{\cos(\pi k)} & \mu = 1 \end{cases}$$

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and use $\cos x = 1 - x^2/2$ and $\sqrt{y} = 1 + y/2$ to show that the latter is

$$\begin{cases} 4 - (\pi k)^2/2 \\ (\pi k)^2/2 \end{cases}$$

From this, does the second solution for $\mu = 1$ describe a "wave" or a "particle"?

The relationship between wavenumber and frequency is called the *dispersion*.

j) So the atoms in the diatomic linear chain oscillate as $e^{\iota\omega t}$ with phases differing from their nearest neighbours by $\pm 2\pi k$. The solutions in (i) give two distinct sets of dispersions. How do these appear in the motions of the atoms?

Show that

$$\begin{aligned}
\frac{u^0}{u^1} &= \frac{k_S(1 + e^{-2\pi k})}{2k_S - m^0\omega^2} \\
&= \frac{k_S(1 + e^{-2\pi k})}{2k_S - k_S\frac{\mu m^1\omega^2}{k_S}} \\
&= \frac{1 + e^{-2\pi k}}{2 - \frac{\mu m^1\omega^2}{k_S}}
\end{aligned}$$

and that if $k = 0$

$$\begin{aligned}
\frac{u^0}{u^1} &= \frac{2}{2 - \begin{cases} 2(\mu - 1) \\ 0 \end{cases}} \\
&= \begin{cases} -1/\mu \\ 1 \end{cases}
\end{aligned}$$

For the modes shown lower in the plot above ($-$ of the $\pm$) $\mu^0 = \mu^1$ meaning that the atoms vibrate together. For the upper modes ($+$ of the $\pm$) $\mu^0 m^0 + \mu^1 m^1 = 0$: the atoms vibrate in opposition in proportion to their masses.

Because the two different atoms in a diatomic chain could have opposite charges, because an opposing oscillation of different charges will generate an electromagnetic wave, and because the frequencies of these oscillations in crystals are those of infrared or even visible light, the upper modes ($+$ of the $\pm$) are called *optical*. The lower modes are called *acoustic*.

Because of the forms of the dispersion, lattice vibrations are often called *phonons*, in analogy with photons, electrons, and other particles.

28. Based on the Onsager relations (Note 28), Prigogine in 1945 said that dissipation is mimimized in steady state. His proof is controversial but his result is used in biophysics. Look up the Prigogine theorem.

Look up Ilya Prigogine 1917–2003. How does thermodynamics far from equilibrium (i.e., not just linear thermodynamics) relate to chaos theory? How do dissipative structures relate to self-organization?

29. Examples of complementary pairs for Note 28 include, as well as coordinates x, y, .. and forces X, Y, .., from Note 26, also the complementary variables in the thermostatic equations of state in Note 20, Part II:

extensive	intensive
V	P
S	T
N	μ
q	$\mathcal{E}$

and so are charge q and potential difference $\mathcal{E}$, also shown above.

Here "extensive" indicates that if the amount substance is increased, the extensive variable increases proportionately. "Intensive" variables are independent of the amount of substance. (So a coordinate, by analogy, would be intensive and the corresponding force extensive.) What is the significance of the autocorrelation of $\dot{V}$ or $\dot{S}$ or $\dot{N}$? Does Kubo-Nyquist apply? Is it useful?

30. **Chemical kinetics and differential equations.** Chemical reactions generally wind up in equilibrium but may start far from equilibrium. The mathematics to explore how fast they go (reaction rates) brings us to differential equations (DE). These I could call "slope equations" because they involve relationships among functions and their slopes, but I'll be conventional. Discussing both chemistry and differential equations in the same Excursion brings an immediate conflict of terminology. What a mathematician calls the "order" of a differential equation is the highest degree of slope that appears. What a chemist calls the "order" of a reaction is the highest power of the function that appears.

What a mathematician calls "linear" differential equations is one of first (chemical) order, but may be of any (DE) order. Then

$$a_3 \, \text{slope}^3 y + a_2 \, \text{slope}^2 y + a_1 \, \text{slope} \, y + a_0 y = 0$$

is an example of a linear DE of third order (where $\text{slope}^2 y = \text{slope slope} \, y$, etc.), while

$$a_1 \, \text{slope} \, y + a_0 y^2 = 0$$

is a nonlinear DE of first order—but may describe a second (chemical) order reaction. I'll use mathematical terminology, and so will call

$$a_1 \, \text{slope} \, y + a_0 y^2 = 0$$

a first-order "quadratic" DE. If I use "order" in a chemical sense, I'll specify "chemical". I'll wind up largely avoiding the term "order" altogether, because the DEs describing chemical reactions that concern us here are all first order.

Solving differential equations requires familiarity with slopes beyond just the rules for finding slopes. You must guess the function that satisfies the DE. Once you have a guess you can apply the slope rules to find out if it works. So it is a good idea, when you are playing with slopes anywhere, to keep a record of any interesting ones. (This has been done for us in "tables of integrals", but collecting your own is good practice.) This Excursion will produce a few to start with.

a) Here is a start. What function is its own slope?

$$\text{slope} \, y = y$$

Try $y = x^2$ or x^n for any n or $\cos(x)$ or 2^x or e^x. Which ones don't work out? Which ones do and how can they be modified and still work out?

b) Now some chemistry. The decomposition of hydrogen iodide into, and its reconstitution from, hydrogen and iodine are gas-phase reactions, studied early [Bod99], which behave as though "elementary" (reactions that happen without intermediate steps)—even though they later turned out not to be [Lai87].

The reaction, including forward and reverse rate constants, k_1 and k_{-1}, respectively, is written

$$2\text{HI} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{H}_2 + \text{I}_2$$
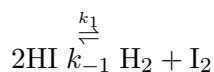
It is plausible that the rate of reaction depends on the concentrations of the reagents, written [HI], [H_2] and [I_2] respectively: since two molecules of HI must collide to cause the forward

reaction, and one molecule of H_2 must collide with one of I_2 to cause the reverse reaction, the number of collisions must depend on the density of molecules present. In fact, it is plausible that this dependence must be quadratic: we can quadruple the rate of the forward reaction by doubling the concentration [HI]; we can also quadruple the rate of the reverse reaction by quadrupling, say, $[H_2]$ while leaving $[I_2]$ fixed.

Convince yourself of this, say, by adapting the collision simulatior of Notes 12 and 13. Note that it takes binary (2-molecular) chemical reactions without intermediate steps to infer this quadratic dependence.

So we have

$$\text{rate of forward reaction} \propto [\text{HI}]^2$$
$$\text{rate of reverse reaction} \propto [\text{H}_2][\text{I}_2]$$

c) Consider the *molecular extent* $\xi(t)$ of the forward reaction to be the number of reacting collisions (not every collision produces a chemical reaction, although collision is required for reaction) as a function of time. Thus the number of molecules, #HI, $\#H_2$ and $\#I_2$ respectively, change with time as follows in the formal notation.

$$
\begin{array}{llllll}
\# \text{ HI} & \rightarrow & \# \text{ HI} -2\xi & \text{or} & \#\text{HI}(t) & = & \#\text{HI}(0) -2\xi(t) \\
\# \text{ H}_2 & \rightarrow & \# \text{ H}_2 +\xi & & \#\text{H}_2(t) & = & \#\text{H}_2(0) + \xi(t) \\
\# \text{ I}_2 & \rightarrow & \# \text{ I}_2 +\xi & & \#\text{I}_2(t) & = & \#\text{I}_2(0) + \xi(t)
\end{array}
$$

(Think of a single reacting collision, for which $\xi = 1$.)

Divide everything by the volume V, assumed constant in time, to get this in concentrations (where $x = \xi/V$).

$$
\begin{array}{rcl}
[\text{HI}] & = & [\text{HI}]_0 - 2x \\
[\text{H}_2] & = & [\text{H}_2]_0 + x \\
[\text{I}_2] & = & [\text{I}_2]_0 + x
\end{array}
$$

Now we can write the rate equation for the forward reaction by defining a suitable meaning for the forward rate constant k_1

$$\dot{x} = \text{slope}_t[\text{H}_2] = k_1[\text{HI}]^2 = k_1([\text{HI}]_0 - 2x)^2$$

and $\text{slope}_t[\text{I}_2] = \dot{x}$ while $\text{slope}_t[\text{HI}] = -2\dot{x}$.

Since x now just means the change in concentration of H_2 (or I_2), it can go both ways, and we can extend the equation to include the reverse reaction

$$\dot{x} = \text{slope}_t[\text{H}_2] = k_1[\text{HI}]^2 - k_{-1}[\text{H}_2][\text{I}_2] = k_1([\text{HI}]_0 - 2x)^2 - k_{-1}([\text{H}_2]_0 + x)(([\text{I}_2]_0 + x))$$

and, again, $\text{slope}_t[\text{I}_2] = \dot{x}$ while $\text{slope}_t[\text{HI}] = -2x$, where $\dot{x} = \text{slope}_t x$ is a conventional abbreviation for slope with respect to time.

This is a differential equation. The leap from discrete molecules to continuous math should not bother us if we see the differential equations as an approximation, in the limit of the very large number of molecules usually involved in macroscopic chemistry.

Of course, there is a slope we'll need to know before we can solve the differential equation.

d) Show that

$$\text{slope}_t \frac{1}{2d} \ln \frac{u - d}{u + d} = \frac{\dot{u}}{u^2 - d^2}$$

where d is constant, $u(t)$ is a function of t (time) and, as above, $\dot{u} = \text{slope}_t u$.

(Use $\text{slope}_x \ln x = 1/x$ and $\text{slope}_x z(y) = \text{slope}_x y \, \text{slope}_y z(y)$.)

Then show that, if

$$a = \frac{\dot{u}}{u^2 - d^2}$$

then

$$at = \frac{1}{2d} \ln(\frac{u - d}{u + d}\frac{u_0 + d}{u_0 - d})$$

where $u_0 = u(0)$ and the fraction involving it is the constant of integration that ensures $at = 0$ when $t = 0$.

e) Now solve the differential equation describing the decomposition of HI with $[\text{HI}]_0 = r_0$, $[\text{H}_2]_0 = 0 = [\text{I}_2]_0$ and $x_0 = x(0) = 0$.

(We'll call this the "forward" reaction even though it goes both ways, because it starts with zero concentration of the "products" H_2 and I_2 and some initial concentration r_0 of the "reagents".)

$$
\begin{aligned}
\dot{x} &= k_1(r_0 - 2x)^2 - k_{-1}x \\
&= ax^2 + bx + c \\
&= a((x + \frac{b}{2a})^2 - (\frac{b}{2a})^2 + \frac{c}{a}) \\
\dot{u} &= a(u^2 - d^2)
\end{aligned}
$$

where I've introduced some intermediate symbols a, b, c and u, and you can show

$$
\begin{aligned}
u &= x - \frac{2x_e^2}{4x_e - r_0} \\
d &= x_e\frac{2x_e - r_0}{4x_e - r_0}
\end{aligned}
$$

if you use the equilibrium condition

$$0 = \dot{x} = k_1(r_0 - 2x_e)^2 - k_{-1}x_e$$

for the equilibrium value x_e of x, to find k_{-1} in terms of k_1.

The d I've written above could alternatively have a negative sign: does it make a difference? So the expression for a will involve k_1 and the result of part (d) above becomes

$$k_1t = \frac{x_e}{2x_e(2x_e - r_0)} \ln \frac{r_0(x - x_e)}{x(4x_e - r_0) - x_er_0}$$

Compare this with [Lai87, p.30] noting my slightly different starting point.

f) The result of (e) may be used to determine k_1 from experimental measurement. This was famously done for this HI reaction by Max Bodenstein in the 1890s—the first quntification of the kinetics of a purely gas-phase reaction. His paper [Bod99] needs more analysis than I have given it, but Giunta [Giu03] has put some of his data on the Web, in particular the observation that at $443°\text{C}$, 22% of the HI is decomposed at equilibrium. Giunta's quotations for the rate constants k_1 and k_{-1} are in "arbitrary units" (taken from [Bod99, pp.306, 312]) so we must calculte them for ourselves.

Also on the Web is a high school chemistry text showing a plot of the HI concentration against time [Roe91, p.113]. It's obviously drawn by hand but we can pretend that it gives experimental results. The forward reaction starts with an HI concentration of $r_0 = 2$ moles/litre and measurements by ruler on the computer screen give the following

time(min.)	20	40	60	80	("equilibrium")
[HI] mol/l.	1.75	1.67	1.6	1.56	

This data is said to be for $445°\text{C}$ so you should compare the equilibrium concentration given with the 22% mentioned above. And you should show that it gives the following values for x

time(min.)	20	40	60
x	0.125	0.167	0.2

(even though I am giving them far too much precision for ruler measurements of a small graph on a computer screen).

Now plug these numbers, and x_e, into the result of (e)—write a small program!—and show that they give three differing values for k_1: 0.0020, 0.0016, 0.0017 respectively for an average of $k_1 = 0.0017$. Compare this with Bodenstein's value for $716°$K.

g) Now that we know k_1 we can rearrange the result of (e) to show the time dependence of the decomposition reaction.

$$ x = \frac{x_e}{4x_e - r_0}\left(2x_e + (2x_e - r_0)\frac{1+f}{1-f}\right) $$

where

$$ f = \frac{4x_e - r_0}{r_0}e^{2r_0(2x_e-r_0)k_1 t} $$

Show that the following limits come out of this

$$ f \rightarrow \begin{cases} 0 & t \rightarrow \infty \\ (4x_e - r_0)/r_0 & t \rightarrow 0 \\ -\infty & t \rightarrow -\infty \end{cases} $$

$$ x \rightarrow \begin{cases} x_e & t \rightarrow \infty \\ 0 & t \rightarrow 0 \\ x_e r_0/(4x_e - r_0) & t \rightarrow -\infty \end{cases} $$

(It might be easier to work with dat, which has the opposite sign from t, rather than t in checking these limiting cases.)

Check my results for f and x and write a program to plot them. Note that $x_e = 0.22$ for this data: why?

h) Repeat the approach of parts (e), (f) and (g) for the "reverse reaction", the formation of HI, using

$$ \dot{x} = k_{-1}(r_0 - x)^2 - k_1(2x)^2 $$

using $r_0 = [HI]_0 = 0$, $[H_2]_0 = r_0 = [I_2]_0$, $x_0 = 0$ again, and, from Roebuck,

time(min.)	20	40	60
x	0.44	0.66	0.73

Start with $r_0 = 1$: what must x_e be?

Find k_{-1} and compare with [Whi72], then find the time variation of $x(t)$, check the limiting cases and plot.

Here's my result—still using the faulty "experimental" data—for both reactions at $445°$C. I've given the six "experimental" points to show the effect of taking the averages. And I've misleadingly used one-way arrows for the reactions in the legend.

concentrations of HI
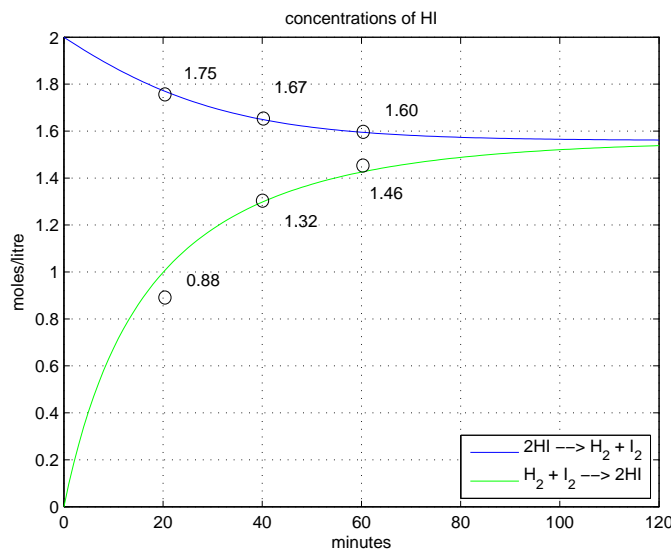
i) I've mentioned the unit "mole" in (f). This converts numbers of molecules to the macroscopic measure of mass, grams: one mole of ^{12}C (pure carbon-12) masses 12 grams, and one mole of anything massses the mean molecular weight of that anything. The number of molecules to do this conversion turns out to be "Avogadro's number", 6.02×10^{23} (see Note 25). This number is close to a yotta (10^{24}) and you can show that a concentration of 1 molecule/cubic nanometer is also a concentration of 1 yotta-molecule/litre. So if you want the exact equivalence to be in molecules/nm^3 you should use another unit, the "moly" (yotta-molecules), for quantities of molecules large enough to interest a chemist (and for differential equations to apply to, since it seems strange to use differential equations to describe small collections of molecules).

Show that 1 moly = 1.66 moles. Should the unit of mass be redefined?

j) The slope you worked out in part (d) enables us to solve any second-order differential equation. Here is another example, involving "autocatalysis". It is an example with fictitious chemical species, A and X. X arises chemically from A but it catalyzes the reaction producing itself. If we suppose that the reverse reaction rate is negligible compared with the forward, we can write the forward reaction only

$$\text{A} \rightarrow \text{BX}$$
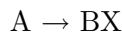
and the differential equation

$$[\dot{\text{X}}] = k_1[\text{A}][\text{X}]$$

or, with $[\text{A}] = [\text{A}]_0 - x$, $[\text{X}] = [\text{X}]_0 + x$

$$\dot{x} = k_1([\text{A}]_0 - x)([\text{X}]_0 + x)$$

Show that

$$-k_1 t = \frac{1}{[\text{A}]_0 + [\text{X}]_0} \ln\left(-\frac{x - [\text{A}]_0}{x + [\text{A}]} \frac{[\text{X}]_0}{[\text{A}]_0}\right)$$

and compare this carefully with [Lai87, p.22].

Hence show that

$$x = \frac{[\text{A}]_0[\text{X}]_0(1 - e^{-([\text{A}]_0 - [\text{X}]_0)k_1 t})}{[\text{X}]_0 + [\text{A}]_0 e^{-([\text{A}]_0 - [\text{X}]_0)k_1 t}}$$

and plot the resulting S-curve. Why does the reaction accelerate then decelerate?

autocatalytic product from A --> X for x0 = 0.01, k_1 = 0.5
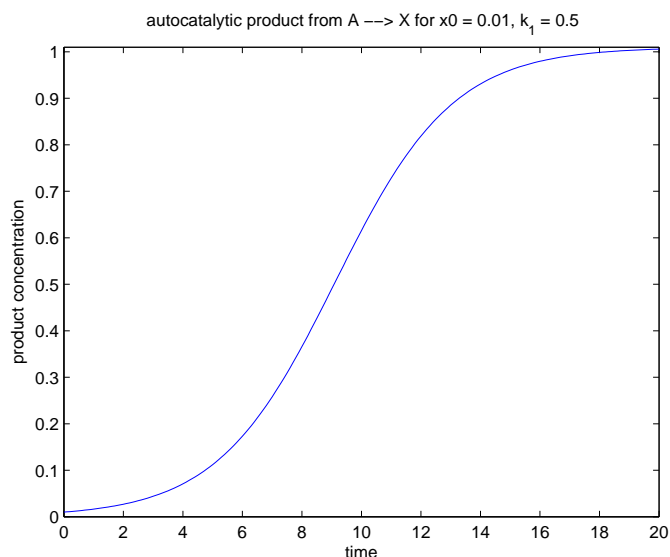
k) Fortunately, this is not all there is to chemistry. For example, the quadratic (second-order (chemical)) differential equation is an idealization based on the somewhat hopeful theory of part (b). That theory is plausible for "elementary reactions" which occur directly from the collision of reagent molecules. But many reactions are multi-step, with the steps proceeding at different rates and only the slowest being the "rate-determining" step. Indeed, even the famous HI reactions, plausibly elementary and long thought to be so, were shown in 1967 by John Sullivan to be multi-step.

The differential equation for the forward reaction only (as in (j) we can suppose the reverse rate to be negligible, or we can suppose that the product species are pumped out of the reaction chamber as fast as they are formed) is easy to solve, no matter what the (chemical) order.

Show that if

$$\frac{1}{nx^n} = \frac{1}{nx_0^n} + kt$$

then

$$\dot{x} = -kx^{n+1}$$

for any n (integer or not) except, of course, $n = 0$.

Show that if

$$x = x_0 e^{-kt}$$

then

$$\dot{x} = -kx$$

(Hence show that

$$x_0 e^{-k} = m \overset{\lim}{\to} \infty \left(\frac{1}{x_0^{1/m}} + \frac{kt}{m} \right)^{-m}$$

and furthermore

$$e^{-k} = m \overset{\lim}{\to} \infty \left(1 + \frac{kt}{m} \right)^m$$

or

$$e = m \overset{\lim}{\to} \infty \left(1 + \frac{1}{m} \right)^m$$

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You might want to write a program to plot $x_0 e^{-kt}$ and $(\frac{1}{x_0^n} + nkt)^{-\frac{1}{n}}$ to convince yourself that they agree as $n \to 0$.)

So we can solve any one-way chemical reaction of (chemical) order n

$$A \to X$$
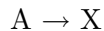
using

$$[\dot{A}] = -k_1 [A]^n$$

Chemists say the most common (chemical) orders are 1/2, 1, 2 and 3, but the (chemical) order of a reaction might be anything and experiments are needed to determine it. Stevens [Ste70] gives several examples of linear, quadratic and cubic (1st, 2nd and 3rd order (chemical), respectively) reactions in Tables 3.1, 3.2 and 3.3 both in the gas phase and in solution. We have not discussed chemistry in solution, which is more common than gas chemistry, but much the same ideas apply. Examples: linear (gas or solution) $2N_2O_5 = 4NO_2 + O_2$; quadratic (gas) $2NO_2 = 2NO + O_2$ (solution) $3KClO = 2KCl + KClO_2$; cubic (gas) $2NO + O_2 = 2NO_2$.

l) **Coupled linear first-order DEs.** (This part is purely mathematical. You may want to skip to part (n) below for chemical motivation and less intense algebra before returning to this more general discussion.)

We can solve coupled differential equations of the form

$$
\begin{aligned}
\dot{x} &= ax + cy \\
\dot{y} &= bx + fy
\end{aligned}
$$

formally by writing them in matrix form

$$
\begin{pmatrix} \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} a & c \\ b & 2\sqrt{d} - a \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}
$$

(we'll see soon that it's handier to redefine $f = 2\sqrt{d} - a$ in terms of a new symbol d) or

$$\dot{\vec{x}} = \mathcal{A}\vec{x}$$

where the vector $\vec{x} = (x, y)^{\mathrm{T}}$.

The formal solution comes from (k) above

$$\vec{x} = e^{\mathcal{A}t} \vec{x_0}$$

since matrices behave like numbers except that we must be careful not to change the order of products because matrix multiplication does not commute.

That's why I wrote the initial value $\vec{x_0} = (x_0, y_0)^{\mathrm{T}}$ *after* the $e^{\mathcal{A}t}$: we'll see that $e^{\mathcal{A}t}\vec{x_0}$ will involve products such as $\mathcal{A}\vec{x_0}t$ which we could not write $\vec{x_0}\mathcal{A}t$.

We must figure out how to calculate $e^{\mathcal{A}t}$. What we do is write it as a series

$$e^{\mathcal{A}t} = I + \mathcal{A}t + \mathcal{A}^2\frac{t^2}{2} + \mathcal{A}^3\frac{t^3}{3!} + \mathcal{A}^4\frac{t^4}{4!} + ..$$

Confirm that $\mathrm{slope}_t e^{\mathcal{A}t} = \mathcal{A}e^{\mathcal{A}t}$ as a result of this series.

But this infinite series will not help us calculate $\vec{x}(t)$. Unless $\mathcal{A}$ happened to be diagonal, e.g.,

$$\mathcal{A} = \begin{pmatrix} \lambda_1 & \\ & \lambda_2 \end{pmatrix}$$

Then

$$e^{\mathcal{A}t} = \begin{pmatrix} 1 & \\ & 1 \end{pmatrix} + \begin{pmatrix} \lambda_1 & \\ & \lambda_2 \end{pmatrix} t + \begin{pmatrix} \lambda_1^2 & \\ & \lambda_2^2 \end{pmatrix} \frac{t^2}{2} + ..$$

$$= \begin{pmatrix} 1 + \lambda_1 t + \lambda_1^2 t^2/2 + .. & \\ & 1 + \lambda_2 t + \lambda_2^2 t^2/2 + .. \end{pmatrix}$$

$$= \begin{pmatrix} e^{\lambda_1 t} & \\ & e^{\lambda_2 t} \end{pmatrix}$$

and this is just two numbers we can evaluate on a calculator or in a simple program.
So what we must do is diagonalize $\mathcal{A}$ by finding a transformation matrix S such that $S\mathcal{A}S^{-1}$ is diagonal, say

$$S\mathcal{A}S^{-1} = \begin{pmatrix} \lambda_1 & \\ & \lambda_2 \end{pmatrix}$$

Then

$$\vec{x} = S^{-1} \begin{pmatrix} e^{\lambda_1 t} & \\ & e^{\lambda_2 t} \end{pmatrix} S\vec{x}_0$$

will be a calculable solution, because

$$\begin{aligned} S\vec{x} &= Se^{\mathcal{A}t}S^{-1}S\vec{x}_0 \\ &= S(I + \mathcal{A}t + \mathcal{A}^2 t^2/2 + ..)S^{-1}S\vec{x}_0 \\ &= (I + S\mathcal{A}S^{-1}t + S\mathcal{A}S^{-1}S\mathcal{A}S^{-1}t^2/2 + ..)S\vec{x}_0 \\ &= \begin{pmatrix} e^{\lambda_1 t} & \\ & e^{\lambda_2 t} \end{pmatrix} S\vec{x}_0 \end{aligned}$$

(Note that t is a *scalar* not a vector or a matrix, so we can write it anywhere in any product, not worrying about commutativity.)

Start with S^{-1}. First, the λ_1 and λ_2 are the *eigenvalues* of $\mathcal{A}$. The Excursion *Diagonalizing matrices* of Week iv showed how to find them using *determinants*:

$$0 = \begin{vmatrix} a - \lambda_1 & c \\ b & 2\sqrt{d} - a - \lambda_1 \end{vmatrix}$$

and

$$0 = \begin{vmatrix} a - \lambda_2 & c \\ b & 2\sqrt{d} - a - \lambda_2 \end{vmatrix}$$

gives

$$\lambda_1, \lambda_2 = \frac{\text{tr}}{2} \pm \sqrt{\left(\frac{\text{tr}}{2}\right)^2 - \det}$$

where the *trace* $\text{tr} = a + (2\sqrt{d} - a) = 2\sqrt{d}$ and the determinant

$$\det = \begin{vmatrix} a & c \\ b & 2\sqrt{d} - a \end{vmatrix} = a(2\sqrt{d} - a) - bc$$

We'll need a new symbol $\epsilon = \sqrt{(\text{tr}/2)^2 - \det} = \sqrt{d - \det}$ so

$$\lambda_1, \lambda_2 = \sqrt{d} \pm \epsilon$$

and

$$bc = -(a - \sqrt{d} - \epsilon)(a - \sqrt{d} + \epsilon)$$

(Thus the matrix $\mathcal{A}$ depends on four numbers, which we can take to be a, b, tr and det—although it's useful to keep using c as well, which we can take out whenever we want by using the above relationship for bc. The reason for involving tr and det is that the eigenvalues

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depend only on tr and det.)
Now we can find S^{-1}. Show that

$$\begin{pmatrix} a & c \\ b & 2\sqrt{d} - a \end{pmatrix} \begin{pmatrix} -c \\ a - \sqrt{d} - \epsilon \end{pmatrix} = \lambda_1 \begin{pmatrix} -c \\ a - \sqrt{d} - \epsilon \end{pmatrix}$$

and

$$\begin{pmatrix} a & c \\ b & 2\sqrt{d} - a \end{pmatrix} \begin{pmatrix} -c \\ a - \sqrt{d} + \epsilon \end{pmatrix} = \lambda_2 \begin{pmatrix} -c \\ a - \sqrt{d} + \epsilon \end{pmatrix}$$

so that the two column vectors I've just invented (discovered) are the *eigenvectors* of $\mathcal{A}$ corresponding respectively to the eigenvalues λ_1 and λ_2.
We'll assemble S^{-1} from these two column vectors and normalize it so its determinant $= 1$.

$$S^{-1} = \frac{1}{\sqrt{-2c\epsilon}} \begin{pmatrix} -c & -c \\ a - \sqrt{d} - \epsilon & a - \sqrt{d} + \epsilon \end{pmatrix}$$

Its inverse is

$$S = \frac{1}{\sqrt{-2c\epsilon}} \begin{pmatrix} a - \sqrt{d} + \epsilon & c \\ -(a - \sqrt{d} - \epsilon) & -c \end{pmatrix}$$

Check that $SS^{-1} = I = S^{-1}S$.
Check that

$$S\mathcal{A}tS^{-1} = \begin{pmatrix} e^{(\sqrt{d}+\epsilon)t} & \\ & e^{(\sqrt{d}-\epsilon)t} \end{pmatrix}$$

Now the final major bit of algebra. Show that

$$
\begin{aligned}
\vec{x} &= S^{-1} \begin{pmatrix} e^{(\sqrt{d}+\epsilon)t} & \\ & e^{(\sqrt{d}-\epsilon)t} \end{pmatrix} S\vec{x_0} \\
&= \frac{e^{\sqrt{d}t}}{-2c\epsilon} \begin{pmatrix} -c(a - \sqrt{d})(e^{\epsilon t} - e^{-\epsilon t}) - c\epsilon(e^{\epsilon t} + e^{-\epsilon t}) & -c^2(e^{\epsilon t} - e^{-\epsilon t}) \\ -bc(e^{\epsilon t} - e^{-\epsilon t}) & c(a - \sqrt{d})(e^{\epsilon t} - e^{-\epsilon t}) - c\epsilon(e^{\epsilon t} + e^{-\epsilon t}) \end{pmatrix} \vec{x_0}
\end{aligned}
$$

As a reward for all this math we should try to see how this complicated expression behaves with time t.
First show that when $t = 0$, $\vec{x} = \vec{x_0}$ as it should. You can also explore the limits as $t \to \infty$ and $t \to -\infty$.
Next use ϵ to generate some special cases. Remember $\epsilon = \sqrt{d - \det}$ and so can be "real" or "imaginary". First try $\epsilon \to 0$. Because $e^{\epsilon t} \approx 1 + \epsilon t$ and $e^{-\epsilon t} \approx 1 - \epsilon t$ with the approximation getting better the smaller ϵ is,

$$\vec{x} \xrightarrow{\epsilon \to 0} e^{\sqrt{d}t} \begin{pmatrix} 1 + (a - \sqrt{d})t & ct \\ bt & 1 - (a - \sqrt{d})t \end{pmatrix} \vec{x_0}$$

So the behaviour with time for this case is a superexponential growth proportional to $te^{\sqrt{d}t}$.
We'll revisit this result.
Second suppose that ϵ is imaginary, $\epsilon = i\delta$ with real $\delta = \sqrt{\det - d}$. Then we get oscillations

$$\vec{x} \xrightarrow{\epsilon = i\delta} \frac{e^{\sqrt{d}t}}{\delta} \begin{pmatrix} (a - \sqrt{d})\sin(\delta t) + \delta\cos(\delta t) & c\sin(\delta t) \\ b\sin(\delta t) & -(a - \sqrt{d})\sin(\delta t) + \delta\cos(\delta t) \end{pmatrix} \vec{x_0}$$

When $d = 0$ (corresponding to tr $= 0$) it is a pure oscillation, neither growing nor shrinking with time. If the trace is negative (so $\sqrt{d} = $ tr$/2$ is negative) the oscillations will damp down
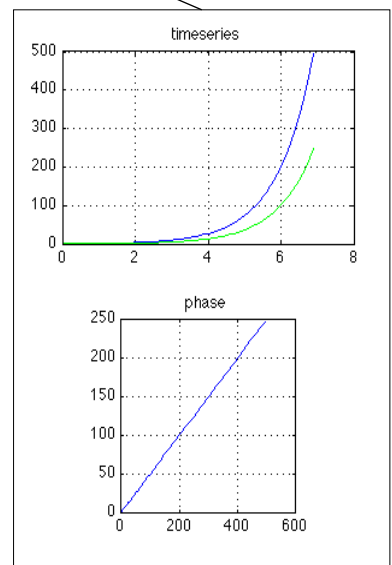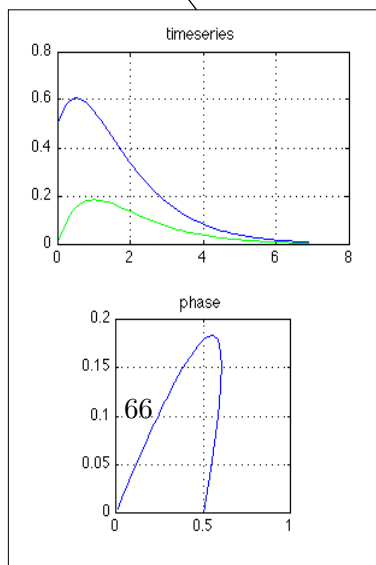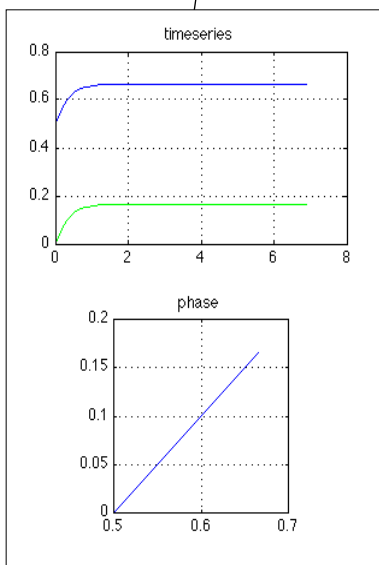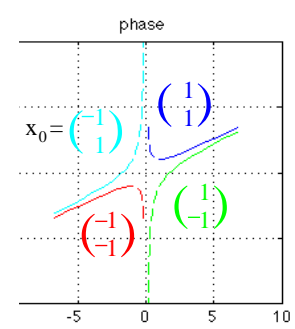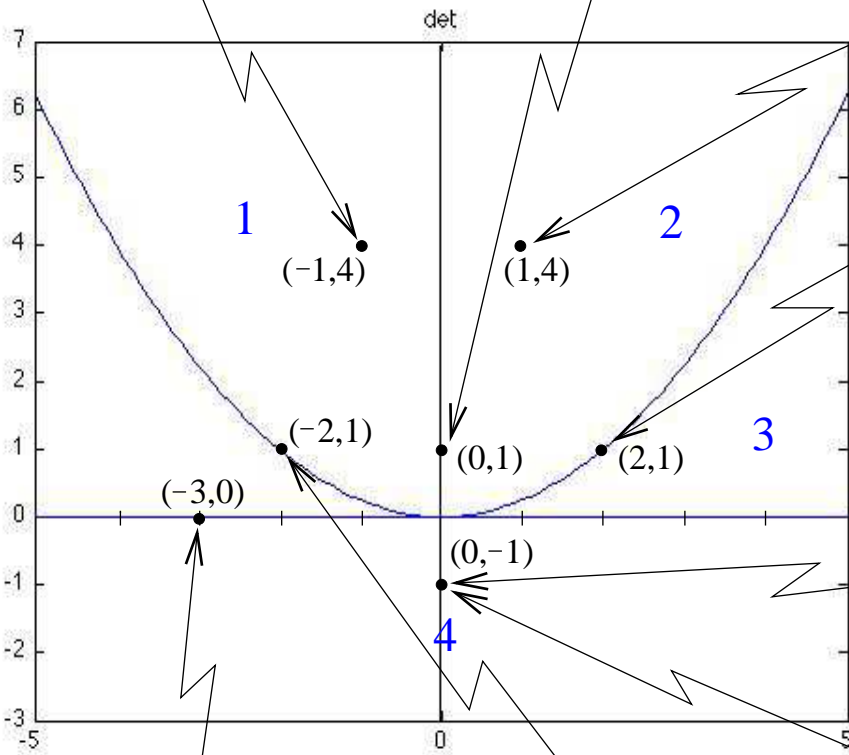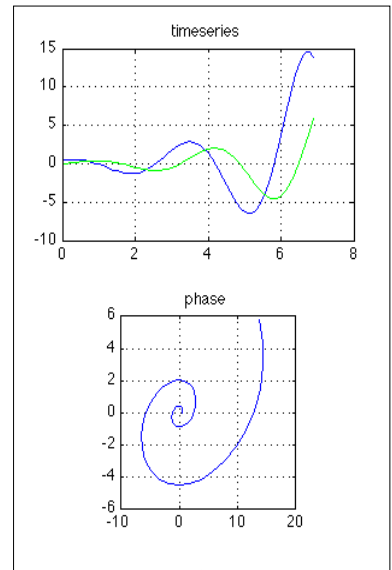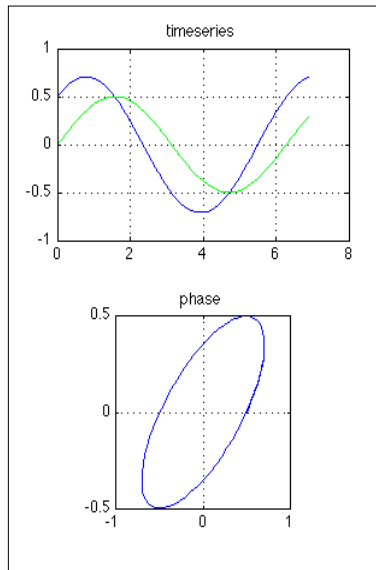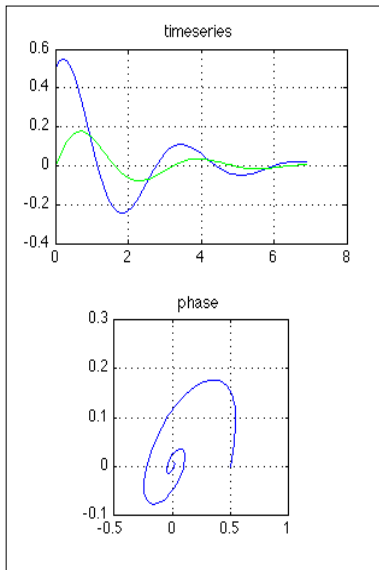
to zero after enough time has elapsed. But if $\sqrt{d} > 0$ it will blow up.

Third, suppose that det $= 0$ so $\epsilon = \sqrt{d}$. Then

$$\vec{x}\,\epsilon \stackrel{=}{=} \sqrt{\delta}\, \frac{1}{2\sqrt{d}} \begin{pmatrix} a(e^{2\sqrt{d}t-1}) + 2\sqrt{d} & c(e^{2\sqrt{d}t-1}) \\ b(e^{2\sqrt{d}t-1}) & 2\sqrt{d} - a(e^{2\sqrt{d}t-1}) \end{pmatrix} \vec{x_0}$$

It's better to make a picture. These various spacial cases delineate changes in behaviour at the lines $0 = \epsilon = \sqrt{(\text{tr}/2)^2 - \det}$ and det $= 0$. So we'll make a two-dimensional map for this four-parameter $(a, b, \text{tr}, \det)$ set of equations, based on tr and det.

The three special lines are the tr-axis (det $= 0$), the det-axis (tr $= 0$) and the parabola det $= (\text{tr}/2)^2$. These divide the space into six regions, but two pairs of regions show essentially the same behaviour.

Here is the map, with illustrative behaviours at seven sample points on and off the boundary lines. I've shown both time behaviour and phase diagrams in six of the cases, and in two cases (4-colour plots to the right of the map) I've let time run both forwards and backwards.

timeseries

phase

timeseries

phase

timeseries

phase

det

1
(−1,4)

2
(1,4)

(−2,1)
(0,1)
(2,1)

3

(−3,0)

(0,−1)

4

tr

phase

$x_0 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

$\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$\begin{pmatrix} -1 \\ -1 \end{pmatrix}$

phase

$x_0 = \begin{pmatrix} -1 \\ 1 \end{pmatrix}$ $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$\begin{pmatrix} -1 \\ -1 \end{pmatrix}$

timeseries

phase

timeseries

phase

66

timeseries

phase
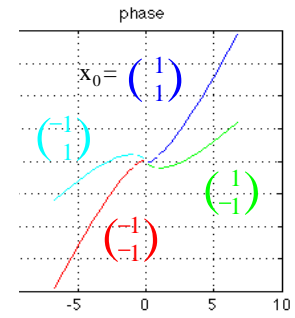
Note the shrinking and expanding spirals in regions 1 and 2, respectively, and the unchanging oscillation on the boundary $\mathrm{tr} = 0$. Note the non-oscillatory damping or expansion in regions 3 and 4, with region 4 showing saddle-point behaviour if we run time in both directions. Finally note the convergence to two different values for x and y (the components of $\vec{x}$) on the line $\det = 0$.

Show how the linear differential equation of any order, given at the beginning of this Excursion, can be expressed as a linear first-order coupled DE—which can then be solved by the method if this part (l). Hint: define $v = \mathrm{slope}\ y$ and $u = \mathrm{slope}\ v$, etc.

m) I can make an important mathematical point from part (l) even though it continues the mathematical digression. Skip on if you think you're not interested.

The case $\epsilon = 0$ in part (l) above worked out by taking a limit in the more general scenario. What if we wanted to solve it directly? Then we have the matrix

$$\mathcal{A} = \begin{pmatrix} a & c \\ b & 2\sqrt{d} - a \end{pmatrix}$$

with $d = \det$ (which is a good reason for calling it d).

So both eigenvalues $\lambda_1 = \lambda_2 = \sqrt{d}$ are the same and the matrix *may not be diagonalizable.* We may be stuck with "Jordan normal form"

$$\begin{pmatrix} \sqrt{d} & 1 \\ 0 & \sqrt{d} \end{pmatrix}$$

which has the two (same) eigenvalues on the diagonal, and a 1 just above the diagonal. Furthermore, the transformation matrix we called S^{-1} is *singular*—it has no inverse—because it necessarily has two columns the same.

How do we get Jordan normal form?

It makes sense to put for one column of S^{-1} what we had before. For the other, though, we'll just have to put some other vector which is not proportional to the first column. To save nitty-gritty, I'm not going to write this second column $(x, y)^{\mathrm{T}}$ and impose constraints of independence from the first column. I've found that $(0, y)^{\mathrm{T}}$ is good enough so we'll work with that. So

$$S^{-1} = \frac{1}{\sqrt{-cy}} \begin{pmatrix} -c & 0 \\ a - \sqrt{d} & y \end{pmatrix}$$

and so

$$S = \frac{1}{\sqrt{-cy}} \begin{pmatrix} y & 0 \\ -(a - \sqrt{d}) & -c \end{pmatrix}$$

Now you can show $SS^{-1} = I = S^{-1}S$ and

$$SAS^{-1} = \begin{pmatrix} \sqrt{d} & -y \\ 0 & \sqrt{d} \end{pmatrix}$$

So $y = -1$ will give us Jordan normal form and we can replace y by -1.

We continue as in part (l)

$$\begin{aligned}
\vec{x} &= S^{-1}Se^{\mathcal{A}t}S^{-1}S\vec{x}_0 \\
&= S^{-1}e^{\begin{pmatrix} \sqrt{d} & -y \\ 0 & \sqrt{d} \end{pmatrix}t}S\vec{x}_0 \\
&= S^{-1}e^{\sqrt{d}t}\begin{pmatrix} 1 & t \\ & 1 \end{pmatrix}S\vec{x}_0 \\
&= e^{\sqrt{d}t}\begin{pmatrix} 1 + (a - \sqrt{d})t & ct \\ bt & 1 - (a - \sqrt{d})t \end{pmatrix}S\vec{x}_0
\end{aligned}$$

This is the same result we got for $\epsilon \to 0$ in (l).

You'll have to use the series expansion of e^{At} to show the connection between the second and third lines above.

n) The only case of direct chemical interest in the whole machinery of part (l) above is the case of det $= 0$. This is because otherwise the null space of the matrix $\mathcal{A}$ is trivially $\vec{x} = 0$ if det $\mathcal{A} \neq 0$

$$\mathcal{A}\vec{x} = 0 \quad \text{requires} \quad \vec{x} = 0$$

Excursion *Null spaces and stoichiometry* of Week 8 shows that chemistry needs a nontrivial null space.

So linear (first-order (chemical)) reactions cannot oscillate.

But there *are* oscillating chemical reactions. The first attempt to make a theory which predicts this was by the chemist Alfred James Lotka in 1920. He did not postulate a particular reaction but only the formal equations

$$\text{A} + \text{X} \to 2\text{X}$$
$$\text{X} + \text{Y} \to 2\text{Y}$$
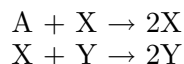
with the mixed (chemical) order rate equations

$$[\dot{\text{X}}] = k_1[\text{A}][\text{X}] - k_2[\text{X}][\text{Y}]$$
$$\left[\dot{\text{Y}}\right] = k_2[\text{X}][\text{Y}] - k_3[\text{Y}]$$

These are coupled nonlinear differential equations and are normally solved by resorting to numerical computation—i.e., on a computer.

But before we do that, let's see if we can find a special case which is linear, since (from part (l)) we already know how to solve it.

All of the chemistry we've been doing in this Excursion so far is *far from equilibrium.* I am in fact violating the title of this Note, namely linear thermodynamics. The regime is linear only close to equilibrium. We've gone all the way to equilibrium to determine x_e in part (e) as one of the experimental parameters. But now we want to work in the linear regime *near* equilibrium.

Since Lotka's equation does not describe any actual chemical reaction, we might as well generalize it into the form it is most commonly known in today (for ecology: Lotka applied it in 1925 to predator-prey populations and Vito Volterra investigated it independently in 1926 applied to fish catches; so it is known as the Lotka-Volterra equation).

$$\dot{x} = x(a - by)$$
$$\dot{y} = -y(c - dx)$$

(The chemical species A, above, is assumed to have a fixed concentration, so $k_1[\text{A}]$ becomes the constant a: A is to be supplied continuously to drive the "reaction". The translation of constants b, c and d is straightforward, but note b and d need not be the same. Show that, at equilibrium,

$$(x_e, y_e) = \left(\frac{c}{d}, \frac{a}{b}\right)$$

Near equilibrium let's invent (small) variables ξ, η

$$x = \frac{c}{d} + \xi$$
$$y = \frac{a}{b} + \eta$$

So, supposing $c/d + \xi$ is negligibly different from c/d and similarly for $a/b + \eta$,

$$\dot{\xi} = \dot{x} = x(a - by) = \left(\frac{c}{d} + \xi\right)\left(a - b(\frac{a}{b} + \eta)\right)$$

$$\approx \quad \frac{c}{d}(-b\eta)$$

$$= \quad \frac{-bc}{d}\eta$$

$$\dot{\eta} \quad = \quad \dot{y} = -y\left(c - dx\right) = -\left(\frac{a}{b} + \eta\right)\left(c - d(\frac{c}{d} + \xi)\right)$$

$$\approx \quad -\frac{a}{b}(-d\xi)$$

$$= \quad \frac{ad}{b}\xi$$

This is just the coupled linear first-order differential equation

$$\begin{pmatrix} \dot{\xi} \\ \dot{\eta} \end{pmatrix} = \begin{pmatrix} & -\frac{bc}{d} \\ \frac{ad}{b} & \end{pmatrix} \begin{pmatrix} \xi \\ \eta \end{pmatrix}$$

and has the formal solution

$$\begin{pmatrix} \xi \\ \eta \end{pmatrix} = e^{\begin{pmatrix} & -\frac{bc}{d} \\ \frac{ad}{b} & \end{pmatrix} t} \begin{pmatrix} \xi_0 \\ \eta_0 \end{pmatrix}$$

We don't need to use the eigenvalue approach (of our work in part (l) above) to solve the special case. Use the series expansions

$$e^x \quad = \quad 1 + x + \frac{x^2}{2} + \frac{x^3}{3!} + \frac{x^4}{4!} + ..$$

$$\cos x \quad = \quad 1 \quad - \frac{x^2}{2} \quad + \frac{x^4}{4!} + ..$$

$$\sin x \quad = \quad + x \quad - \frac{x^3}{3} \quad + ...$$

to show that the formal solution becomes

$$\begin{pmatrix} \xi \\ \eta \end{pmatrix} = \begin{pmatrix} \cos(\sqrt{ac}\,t) & -\frac{b}{d}\sqrt{\frac{c}{a}}\sin(\sqrt{ac}\,t) \\ -\frac{d}{b}\sqrt{\frac{a}{c}}\sin(\sqrt{ac}\,t) & \cos(\sqrt{ac}\,t) \end{pmatrix} \begin{pmatrix} \xi_0 \\ \eta_0 \end{pmatrix}$$

In the special case $d^2 a = b^2 c$ the matrix is a pure rotation and the values of ξ and η oscillate in time. The phase relationship between the two will give a perfect circle.

o) As a matter of fact, before we go on to the numerical solution, we can get an exact result for the phase relationship between x and y in the full Lotka-Volterra equation far from equilibrium—even if this doesn't give us the time behaviour of x or y.

Here's the approach followed by Murray [Mur02, pp.80ff.]. Change variables to $u = xd/c$ and $v = yb/a$ (so $(u, v) = (1, 1)$ at equilibrium). We'll find slope$_u v$ and from that y as a function of x giving the contours in the phase space of y vs. x.

(Well, it's a little tricky. We've seen that x and y describe a circle in the linear, near-equilibrium case: y is not an explicit function of x, nor x of y—they are implicit functions of each other, with each contour characterized by a constant, as in

$$\text{const.} = f(x, y)$$

.. unless we know them both as interrelated explicit functions of the time parameter t, and we're assuming in this case that we don't know this.)

First. let's explore the contour

$$\text{const.} = \alpha u + v - \ln(u^\alpha v)$$

to find what $\text{slope}_u v$ is for this. Call $\text{slope}_u v = q$ wherever it appears

$$\begin{aligned}
0 &= \text{slope}_u(\alpha u + v - \ln(u^\alpha v)) \\
&= \alpha + q - \frac{1}{u^\alpha v}(\alpha u^{\alpha-1} v + u^\alpha q)
\end{aligned}$$

So you can show

$$\text{slope}_u v = q = -\alpha \frac{u}{v}\frac{u-1}{v-1}$$

Is this the $\text{slope}_u v$ we get from the Lotka-Volterra equation?
Well, we know

$$\begin{aligned}
\text{slope}_t x &= x(a - by) \\
\text{slope}_t y &= -y(c - dx) \\
\text{slope}_t y &= \text{slope}_t x\ \text{slope}_x y
\end{aligned}$$

so

$$\begin{aligned}
\frac{a}{b}\frac{d}{c}\text{slope}_u v &= \text{slope}_x y \\
&= -\frac{y(c - dx)}{x(a - by)} \\
&= -\frac{(a/b)v(c - cu)}{(c/d)u(a - av)} \\
\text{slope}_u v &= -\frac{cv(1 - u)}{au(1 - v)}
\end{aligned}$$

which is the q above, if $\alpha = c/a$.
So

$$\alpha u + v - \ln(u^\alpha v) = \text{const.}$$

is the implicit equation for the contours.
Converting back to x and y

$$\frac{xd + yb}{a} - \ln\left(\left(x\frac{d}{a}\right)^{\frac{c}{a}} y\frac{b}{a}\right) = \text{const}$$

is the contour equation.
The smallest such constant occurs at equilibrium,

$$(x, y) = (\frac{c}{d}, \frac{a}{b}) \quad \text{or} \quad (u, v) = (1, 1)$$

and is $1 + c/a$.
p) It's good to have these exact results under our belt so that we can check the numerical calculations. But now let's find the time dependence of x and y in the Lotka-Volterra equation. It's going to be deceptively easy.
To compute

$$\begin{aligned}
\dot{x} &= x(a - by) \\
\dot{y} &= -y(c - dx)
\end{aligned}$$

we just replace the slopes by their approximate definition

$$
\begin{aligned}
\frac{x(t + \Delta t) - x(t)}{\Delta t} &= x(t)(a - by(t)) \\
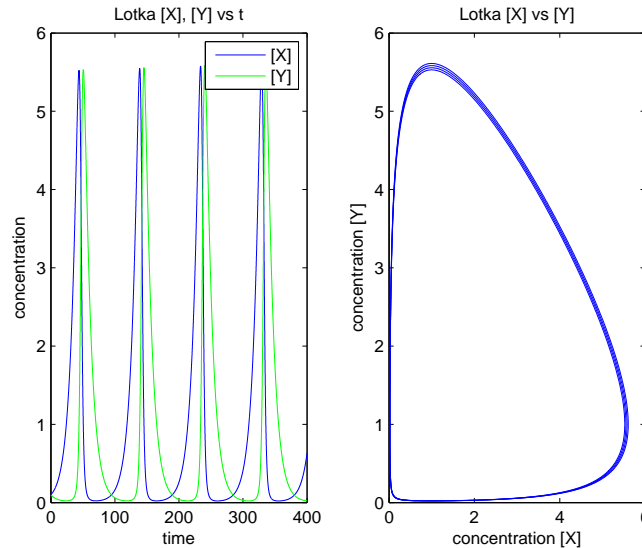\frac{y(t + \Delta t) - y(t)}{\Delta t} &= -y(t)(c - dx(t))
\end{aligned}
$$

or

$$
\begin{aligned}
x(t + \Delta t) &= x(t) + x(t)(a - by(t))\Delta t \\
y(t + \Delta t) &= y(t) - y(t)(c - dx(t))\Delta t
\end{aligned}
$$

Then we pick a small enough Δt and iterate, starting at given values for $x(0)$ and $y(0)$.
Here is a result for the original Lotka equation

$$
\begin{aligned}
[\dot{X}] &= a[X] - b[X][Y] \\
[\dot{Y}] &= b[X][Y] - c[Y]
\end{aligned}
$$

with $(a, b, c, [X_0], [Y_0]) = (0.1, 0.1, 0.1, 0.1, 0.1)$ and running from $t = 0$ to 400 with $\Delta t = 0.01$.

You can see that the phase contour is a little fuzzy. This is because Δt should be even smaller, but one must compromise between accuracy and running time.
The equilibrium value for the parameters a, b and c is $([X],[Y]) = (1,1)$. Running with $([X]_0,[Y]_0) = (0.9,0.9)$ produces pretty sinusoidal time plots and a pretty circular phase plot.

• • • • •

Numerical differential equation solving gets much more elaborate than this. In principle, any desired accuracy can be achieved by making Δt small enough. But in practice there is a speed tradeoff.
So, many improvements have been devised. The method I've used is called "Euler's method".
One improvement observes that Euler's method evaluates the functions $x(t)$ and $y(t)$ only at the *start* of each Δt-wide interval. It would be better to find the functions at the *middle* of the interval, because then the approximate slope would be closer to the true slope over the whole interval. This is one of the "Runge-Kutta" improvements.
Another improvement uses $x(t + \Delta t)$ and $y(t + \Delta t)$ on the right as well as on the left of the

$=$ assignment, and so must solve *implicit* equations in $x(t + \Delta t)$ and $y(t + \Delta t)$, using, say, Newton's method (see Excursion *Newton's method 1* in Part I).

Fancier methods note that the resulting curves may be very smooth and easy to calculate in some places but very wiggly in others: they *adapt* the step size Δt to be relaxed where the calculation is easy and can be done quickly with satisfactory accuracy, but to be very picky where the result is wiggly and hard to pin down.

Write the Euler's method program to solve Lotka-Volterra and explore different parameter values and starting points as well as step sizes. Build in Murray's exact solution for the phase relationship (part (o)) as a check on accuracy. Compare near-equilibrium results with the perfect waves and circles of part (n).

q) The history of oscillating chemical reactions is not simple. Superficially the chronology is [FB85]

1910 A J Lotka introduces his equation for a hypothetical reaction. The equation is subsequently (1925) taken up in predator-prey population dynamics.

1921 W C Bray observes an oscillation of iodine concentration in a reaction involving hydrogen peroxide. In 1931 he is joined by H A Liebhafsky investigating the Bray-Liebhafsky oscillation.

1951 B P Belousov observes striking oscillations, both temporal and spatial, in the relative concentrations of the Ce^{4+} and the Ce^{3+} ions in a complex reaction involving bromine and citric acid. He can publish only in 1958 and then only obscurely (even in Russia). In 1961 his work is taken up by A M Zhabotinskii, who introduces malonic acid instead of citric, and publishes in 1964.

1971 P Glansdorff and I Prigogine publish the theory of the Brusselator

$$\begin{aligned}
A &\rightarrow X \\
2X + Y &\rightarrow 3X \\
B + X &\rightarrow Y + D \\
X &\rightarrow E
\end{aligned}$$
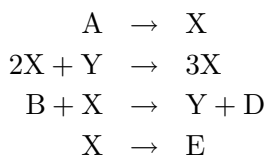
another hypothetical reaction with rate equation

$$\begin{aligned}
[\dot{X}] &= k_1[A] + k_2([X]^3 - [X]^2[Y]) - k_3[B][X] - k_4[X] \\
[\dot{Y}] &= k_2[X]^2[Y] + k_3[B][X]
\end{aligned}$$

(see how the (chemical) orders follow the stoichiometry: this is frequently supposed but not necessarily true).

1972 R J Field, E Körös and R M Noyes abstract the Oregonator model from the Belousov-Zhabotinskii (BZ) reaction:

$$\begin{aligned}
A + Y &\rightarrow X \\
X + Y &\rightarrow P \\
B + Z &\rightarrow 2X + [Z] \\
2X &\rightarrow Q \\
Z &\rightarrow fY
\end{aligned}$$
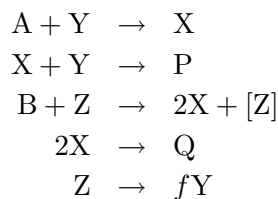
(at last a theory for an actual reaction) with rate equations

$$\begin{aligned}
[\dot{X}] &= k_1[A][Y] - k_2[X][Y] + k_3[B][X] - 2k_4[X]^2 \\
[\dot{Y}] &= -k_1[A][Y] - k_2[X][Y] + fk_5[Z] \\
[\dot{Z}] &= k_5[B][X] - k_3[Z]
\end{aligned}$$

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1973 High school teachers T S Briggs and W C Rauscher make an oscillator with KIO_3, $HClO_4$, $MnSO_4$ and malonic acid.

But the intellectual sequence did not follow the chronology, with workers unfamiliar with earlier work or prejudiced against it (notably believing that the second law of thermodynamics prohibits oscillations which prevent the reaction settling monotonically to equilibrium, as in parts (h) and (j) above).

Using Euler's method you should be able to plot the time dependence and phase relationship for [X] and [Y] for the Brusselator. You should be able to make it converge to a fixed point or to enter an oscillatory cycle. You'll need some extra study to choose the parameter values. These two plots both start at $(x, y) = (1, 0)$.
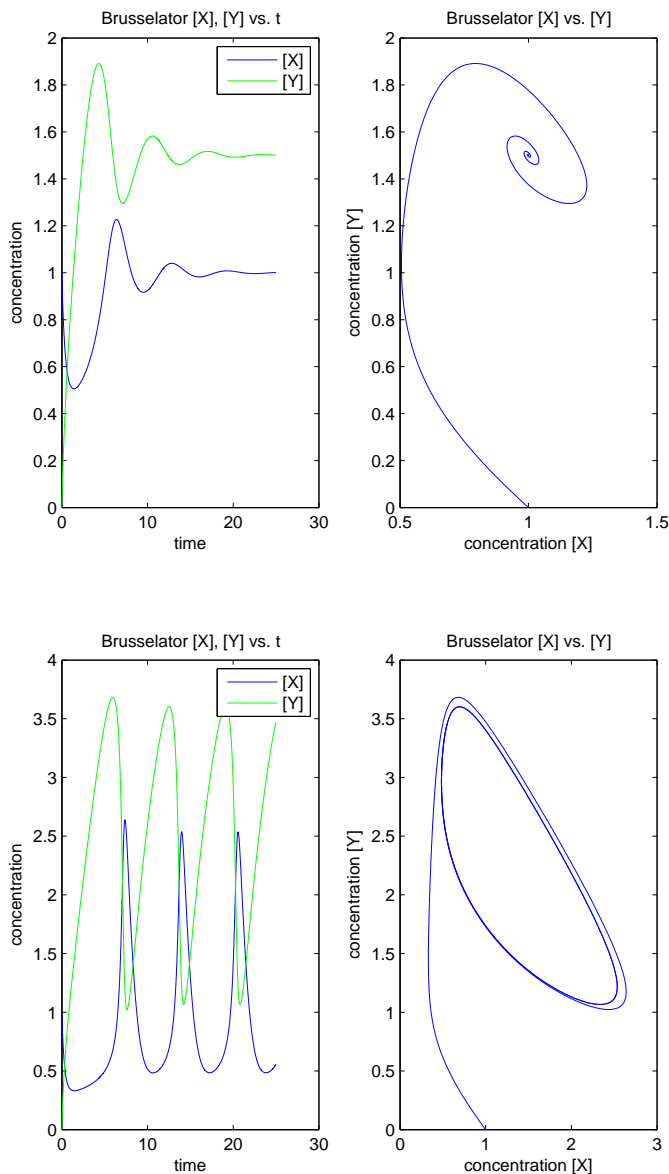

Both the fixed point and the final cycle are called "attractors" since they are what the differential equation is drawn to.

The three-dimensional Oregonator can also be plotted. Instead, let's follow the precedent

that chemical kinetics leads into other fields and look at Saltzmann's equations for *convection* as simplified by the meteorologist Edward Norton Lorenz [Lor63]

$$\begin{array}{rcrcrcr}
\dot{X} & = & & - & sX & + & sY \\
\dot{Y} & = & -XZ & + & rX & - & Y \\
\dot{Z} & = & XY & & & - & bZ
\end{array}$$

Here are the timeseries and phase space plots for the first 1000 iterations ($t = 0:10$) with $s = 10$, $b = 8/3$ and $r = 28$, starting at $(X, Y, Z) = (0, 1, 0)$.
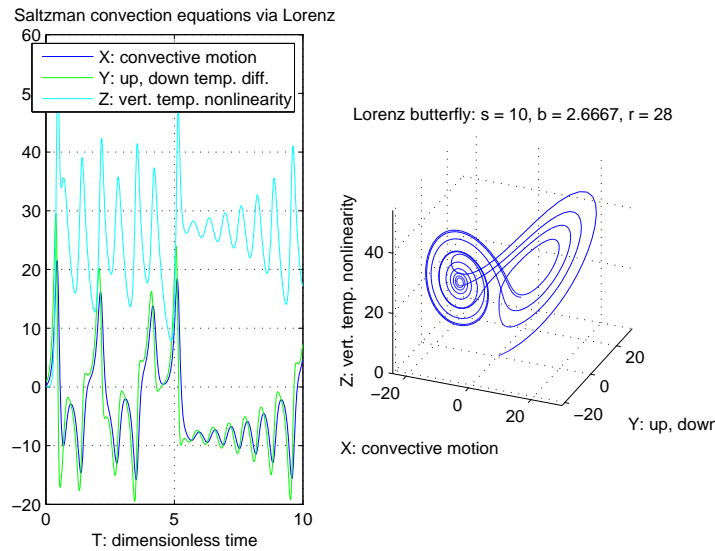
The attractor of this differential equation is strange. You can see that it is undecided between two apparent cycles, but switches back and forth. Further study shows that the path in phase space never repeats itself: this "strange attractor" was the first inkling of the existence of *chaos*. Gleick [Gle88] gives an accessible discussion.

r) Having mentioned chaos, we should look at one more differential equation

$$\text{slope}_t x = (r - 1)x - rx^2$$

Show that

$$x = d\left(1 + \frac{1 + f}{1 - f}\right)$$

where

$$f = \frac{x_0 - 2d}{x_0}e^{-2drt}$$

and

$$d = \frac{r - 1}{2r}$$

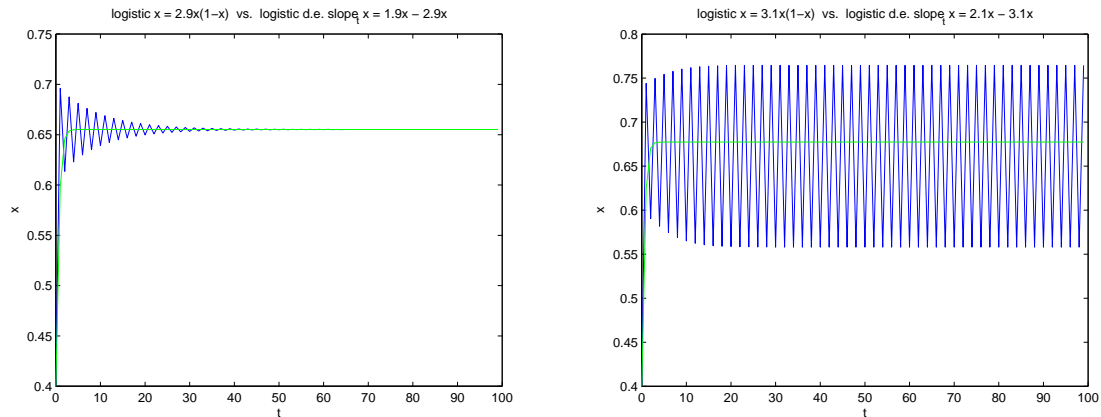We can also solve this numerically with Euler's method

$$x(t + \Delta t) = x(t) + ((r - 1)x(t) - rx(t)^2)\Delta t$$

but a remarkable thing happens when $\Delta t = 1$

$$x(t + 1) = rx(t)(1 - x(t))$$

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Plot $x(1-x)$ for $0 \leq x \leq 1$ and show that if $0 \leq r \leq 2$ the iteration will converge to 0. (There is one exception: what is it?)

Write a program to calculate i) the iteration and ii) the solved differential equation. Here are two runs

The green is the solved DE; the blue plot is the iteration.

Notice that the iteration settles down to i) a single value and ii) two different values between which it oscillates. What happens at $r = 3.5$? 3.6? 3.7?

Here is a synopsis of the final values of the iterated equation as r increases from 0 to 4.3
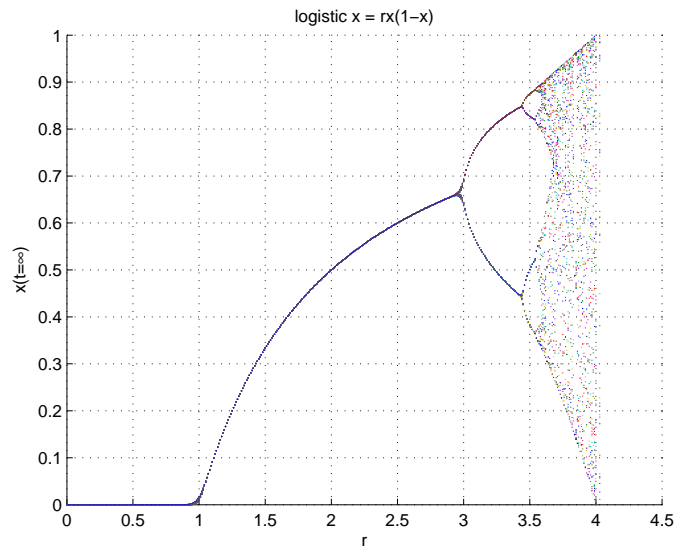
It shows the terminal values starting at 0 then increasing as r rises from 2 to 3 then doubling in number. Then doubling again, and again, ... until the results suddenly become chaotic. Deeper explorations in the chaotic region reveals microscopic versions of the entire diagram repeating itself. See [Gle88] for pointers to the literature.

The iterations—which may be considered a very crude approximation to the differential equation—is much more interesting than the differential equation. So the latter may be considered, indeed, to be a failed approximation to the iteration.

31. **Chemistry in the language of physics.** a) In the thermodynamic equation of state in Note 20, we had terms involving $\mu \Delta N$ (or $N \Delta \mu$, depending on which variant of energy is

most useful in a given situation). With chemical reactions there are multiple species, so this term must become the sum

$$\sum_j \mu_j \Delta N_j$$

over all the different species, j.

But in a chemical reaction all the ΔN_j are related, by the *extent* ξ of the reaction

$$\Delta N_j = \nu_j \Delta\xi$$

where ν_j is the stoichiometric coefficient for the jth species in this reaction.

Thus, for $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$,

$$\Delta N_{\text{HI}} = -2\Delta\xi$$
$$\Delta N_{\text{H}_2} = \Delta N_{\text{I}_2} = \Delta\xi$$

(see part (c) of the previous Excursion: why did I change ξ to $\Delta\xi$?)

So it would seem possible to express the "forces" μ_j as a single effective "force" driving the reaction. This force is called the *affinity* $\mathcal{A}$, defined

$$\mathcal{A} = -\sum \nu_j \mu_j$$

(Note the minus sign: this will give $\mathcal{A}$ and $\text{slope}_t\xi$ the same sign—the latter is the chemical reaction rate, which should be in the same direction as the "force" causing it.)

From this

$$\sum \mu_j \Delta N_j = \sum \mu_j \nu_j \Delta\xi = -\mathcal{A}\Delta\xi$$

For a chemical reaction, the multiple terms $\mu_j \Delta N_j$ can be replaced by a single term $-\mathcal{A}\Delta\xi$. ("Affinity" was formulated by De Donder: look up Théophile Ernest De Donder, 1872–1957.)

We can calculate the extent and the affinity for a reaction such as $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$.

The extent (per litre) is just x in part (c) of the previous Excursion. In that Excursion we wrote and solved the differential equations for x in the HI reactions.

The affinity is defined in terms of the chemical potentials μ_j, and these are related to the concentrations in Note 26

$$\mu - \mu_0 = k_B T \ln \frac{c}{c_0}$$

Since there is an arbitrary baseline for any potential such as μ, we can set $\mu_0 = 0$. And let's take the *reference concentration* c_0 to be c_e, the concentration at equilibrium.

Thus, at equilibrium

$$\mu_e = k_B T \ln \frac{c_e}{c_e} = 0$$

So

$$\mathcal{A}_e = -\sum \nu_j \mu_{ej} = 0$$

(Note that, if we changed every potential by the same base amount μ_b, the equilibrium affinity is still zero

$$\mathcal{A}_e = -\sum \nu_j (\mu_{ej} + \mu_b) = -\sum \nu_j \mu_b = 0$$

because $\sum \nu_j = 0$ for any reaction, by the sign convention for stoichiometry.)

Rerun the differential equation of the previous Excursion with $k_1 = 0.000025$ moly/l-sec (or molec/nm^3-sec) to show that the concentrations are (moly/l or molec/nm^3)

time(sec.)	0	1600	3200	4800	equil.
[HI]]	2	1.747	1.627	1.582	1.56
$[\text{H}_2] = [\text{I}_2]$	0	0.127	0.187	0.209	0.22

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Thus at $T = 443°C$ (716.15°K) with Boltzmann's constant $k_B = 0.0862$ meV/K° (milli-electron Volt), the chemical potentials are

time(sec.)	0	1600	3200	4800	equil.
$\mu_{[HI]}$	15.33	6.99	2.60	0.88	0
$\mu_{[H_2]} = \mu_{[I_2]}$	$-\infty$	-34.15	-10.21	-3.22	0

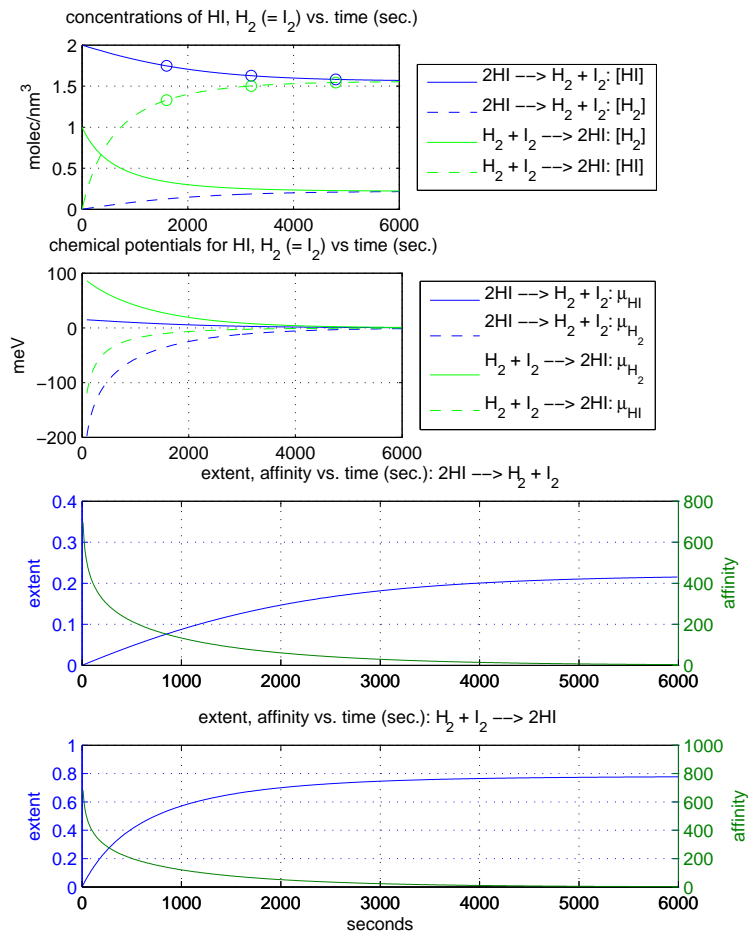This will make the affinity infinite when the reaction starts with no products, and zero at equilibrium.

time(sec.)	0	1600	3200	4800	equil.
$\mathcal{A}$	∞	82.3	25.6	8.2	0
ξ	0	0.127	0.187	0.209	0.22

(I've added the "extent" ξ, actually the extent per liter—or per molecule—as a reference.)
Check these and show for the reverse reaction ($k_{-1} = 0.0014$ moly/l-sec.)

time(sec.)	0	1600	3200	4800	equil.
$[H_2]=[I_2]$	1	0.335	0.249	0.228	0.22
$[HI]$	0	1.330	1.503	1.544	1.56
$\mu_{[H_2]} = \mu_{[I_2]}$	95.42	25.99	7.57	2.16	0
$\mu_{[HI]}$	$-\infty$	-9.86	-2.31	-0.62	0
$\mathcal{A}$	∞	71.7	19.8	5.6	0
ξ	0	0.665	0.751	0.772	0.78

(Note that to go from k_1, k_{-1} in mole/l-min to moly/l-sec or molec/nm^3-sec, just divide by 100.)

Write a program to extend the above results beyond the five sample times. You should get this plot.

concentrations of HI, H_2 (= I_2) vs. time (sec.)

chemical potentials for HI, H_2 (= I_2) vs time (sec.)

extent, affinity vs. time (sec.): $2HI \longrightarrow H_2 + I_2$

extent, affinity vs. time (sec.): $H_2 + I_2 \longrightarrow 2HI$

where in the top two plots the reactants are solid lines and the products dashed lines; HI is blue and H_2 (or I_2) green.

The upshot of this part (a) of this Excursion, is that there is a "force" driving chemical reactions. This force is the affinity, $\mathcal{A}$. What is the dissipation due to this force (Note 26)?

b) The energies above (for chemical potential μ and affinity $\mathcal{A}$) are all in meV, milli-electron-Volts. These are typical *thermal* energies, as we know, but not *chemical* energies, which are of the order of eV, electron-Volts. In fact, expressing the free energy change or the enthalpy change as $\mathcal{A}\Delta\xi$ tells us nothing about the energies resulting from the reaction or required to make it go, only about the energies affecting the rate of the reaction.

Bodenstein's data for the HI reactions can tell us about one important aspect of the chemical energies, namely how hard the molecules must be knocked together to make the reaction go at all. This is called the *activation energy* E_a.

To figure out what E_a is, we need to know how the reaction constants k_1 or k_{-1} depend on the temperature. Since these constants reflect the probability that a collision becomes a reaction, their temperature dependence must be given by the Boltzmann distribution (Notes 14 and 17, Part II).

$$k = Ae^{-E_a/(k_B T)}$$

for some constant of proportionality A.

Let's see if we can use Bodenstein's data to calculate E_a and A. Here it is [Whi72, p.202]
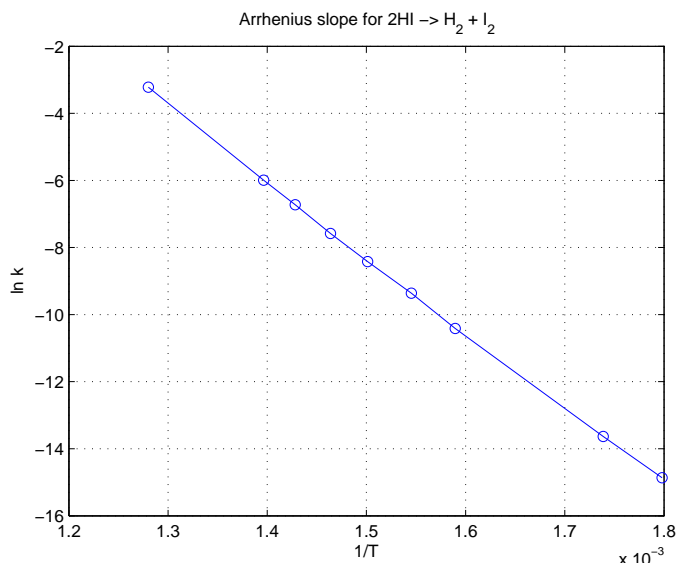
(ks in mole/l-sec).[4]

T(°C)	508	443	427	410	393	374	356	302	283
k_1	4.0E−2	2.5E−3	1.2E−3	5.1E−4	2.2E−4	8.6E−5	3.0E−5	1.2E−6	3.5E−7
k_{-1}	1.3	1.4E−1	6.4E−2	2.5E−2	1.4E−2	5.2E−3	2.5E−3	1.3E−4	4.4E−5

Here's a trick: try plotting $\ln k$ versus $1/T$: show that this should be a linear relationship

$$\ln k = \ln A - \frac{E_a}{k_B}\frac{1}{T}$$

Thus the slope of the line is $-E_a/k_B$, and its y-intercept is ("$1/T = 0$") $\ln A$.
Here is the plot for k_1, the "forward reaction" $2HI \rightarrow H_2 + I_2$.

The line is pretty straight. Calculate that its slope is $-2.25E4$ and its y-intercept is 25.5. Show that this gives

$$
\begin{aligned}
E_a &= 1.94\text{eV (per molecule)} \\
&= 1.87E5 \text{ Joules/mole} \\
&= 44.7\text{Kcal/mole} \\
A &= 1.19E11
\end{aligned}
$$

I've converted E_a to chemists' units, Kcal/mole, via joules/mole: roughly 1 eV/molec $= 10^5$ J/mole $= 24$ Kcal/mole.
A of course is the value for k when $t = \infty$.
Note that the activation energy is measured (per molecule) in electron Volts: 2 eV is well above typical thermal energies. The energy yield of "exothermic" reactions and the input to "endothermic" reactions are of similarly large magnitudes.

32. Any part of the Preliminary Notes that needs working through.

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[4]I confess to some numerical confusion here. Bodenstein, e.g. [Bod99, p.308], clearly shows reaction times in the order of minutes or hours, and my calculations in part (f) of the previous Excursion, based on [Roe91, p.113] are consistent with this. But here I've used [Whi72, p.202] who uses units of seconds not minutes. I leave this to the chemists to sort out.

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