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Time-dependent Stokes equations with random forcing on a periodic domain

(1) $$\rho \frac{\partial \underline{U}}{\partial t} + \nabla P = \mu \Delta \underline{U} + \underline{R}(\underline{x}, t)$$

(2) $$\nabla \cdot \underline{U} = 0$$

$$\underline{x} \in \Omega = [0, L)^3, \quad \text{periodic}$$

$$t \in (-\infty, \infty)$$

Solve by Fourier series

(3) $$\underline{U}(\underline{x}, t) = \sum_{\underline{k} \in \mathbb{Z}^3} \hat{\underline{U}}_{\underline{k}}(t) e^{i \frac{2\pi}{L} \underline{k} \cdot \underline{x}}$$

and similarly for all other variables.

Note that any variable has the same units as its Fourier coefficients.

The equations for the Fourier coefficients are separate ODE for each $\underline{k}$:

$$\rho \frac{d\hat{\underline{U}}_{\underline{k}}}{dt} + i\frac{2\pi}{L}\underline{k}\,\hat{P}_{\underline{k}} = -\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \mu\, \hat{\underline{U}}_{\underline{k}} + \hat{\underline{R}}_{\underline{k}} \tag{4}$$

$$i\frac{2\pi}{L}\,\underline{k}\cdot\hat{\underline{U}}_{\underline{k}} = 0 \tag{5}$$

In the special case $\underline{k} = \underline{0} = (0,0,0)$, this becomes

$$\rho \frac{d\hat{\underline{U}}_{\underline{0}}}{dt} = \hat{\underline{R}}_{\underline{0}} \tag{6}$$

Note that there is no damping in (6), so we need to set $\hat{\underline{R}}_{\underline{0}} = 0$ to keep $\hat{\underline{U}}_{\underline{0}}$ bounded. Then $\hat{\underline{U}}_{\underline{0}} =$ constant, and we may set $\hat{\underline{U}}_{\underline{0}} = 0$, which is just a choice

of reference frame. Thus, we shall exclude the term $\underline{k}=\underline{0}$ from all Fourier series.

Since $\underline{U}$, P, and $\underline{R}$ are all real, we must impose the restriction

$$\hat{\underline{U}}_{(-\underline{k})} = \overline{\hat{\underline{U}}_{(+\underline{k})}}\,, \quad \hat{P}_{(-\underline{k})} = \overline{\hat{P}_{(+\underline{k})}}, \quad \hat{\underline{R}}_{(-\underline{k})} = \overline{\hat{\underline{R}}_{(+\underline{k})}} \tag{7}$$

Thus, the Fourier series are determined once the coefficients are known for $\underline{k} \in K$, where K satisfies

$$\begin{cases} K \cap (-K) = \phi \\ K \cup (-K) \cup \{\underline{0}\} = \mathbb{Z}^3 \end{cases} \tag{8}$$

Because of (5), the velocity terms and the pressure term in (4) are orthogonal, and it follows that $\hat{\underline{U}}_{\underline{k}}$ satisfies

$$\frac{d\hat{\underline{U}}_{\underline{k}}}{dt} + \left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \frac{\mu}{\rho} \hat{\underline{U}}_{\underline{k}} = \frac{1}{\rho} P(\underline{k}) \hat{\underline{R}}_{\underline{k}} \tag{9}$$

where

$$P(\underline{k}) = I - \frac{\underline{k}\,\underline{k}^*}{\|\underline{k}\|^2} = I - \frac{\underline{k}\,\underline{k}^T}{\|\underline{k}\|^2} \tag{10}$$

which is the projection onto the plane orthogonal to $\underline{k}$. (In our notation, vectors are columns, and ^{T} denotes the transpose.)

Equation (9) can be solved for $\underline{\hat{U}}_{\underline{k}}(t)$ as follows:

$$\underline{\hat{U}}_{\underline{k}}(t) = \frac{1}{\rho}\int_{-\infty}^{t} e^{-\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \frac{\mu}{\rho}(t-t')} \mathcal{P}(\underline{k})\, \underline{\hat{R}}_{\underline{k}}(t')\, dt' \tag{11}$$

Note that in this equation there is no crosstalk between real and imaginary parts: the real part of $\underline{\hat{R}}_{\underline{k}}$ determines the real part of $\underline{\hat{U}}_{\underline{k}}$, and the imaginary part of $\underline{\hat{R}}_{\underline{k}}$ determines the imaginary part of $\underline{\hat{U}}_{\underline{k}}$.

We now make the following assumptions about the random variables $\hat{R}_{\underline{k}}(t)$:

(12) $$E\left[\hat{R}_{\underline{k}}(t)\right] = 0 \quad , \quad \underline{k} \in K$$

(13) $$E\left[\hat{R}_{\underline{k}}(t)\, \hat{R}^{*}_{\underline{k}'}(t')\right] = c(\|\underline{k}\|)\, \delta_{\underline{k},\underline{k}'}\, \delta(t-t')\, I$$

$$\underline{k}, \underline{k}' \in K$$

Here E denotes expected value, I is the 3×3 identity matrix, and $*$ denotes conjugate transpose. The function $c(\|\underline{k}\|)$ is real and remains to be determined.

From (11) & (12), it follows immediately that

(14) $$E\left[\hat{\underline{U}}_{\underline{k}}(t)\right] = 0$$

From (11) & (13) we can evaluate

(15) $$E\left[\hat{\underline{U}}_{\underline{k}}(t)\,\hat{\underline{U}}_{\underline{k}}^{*}(t)\right] =$$

$$\frac{1}{\rho^2}\int_{-\infty}^{t}\int e^{-\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2(2t-t'-t'')}$$

$$P(\underline{k})\,E\left[\hat{\underline{R}}_{\underline{k}}(t')\,\hat{\underline{R}}_{\underline{k}}^{*}(t'')\right]P(\underline{k})\,dt'dt'' =$$

$$\frac{c(\|\underline{k}\|)}{\rho^2}\int_{-\infty}^{t} e^{-\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2 2(t-t')}\,dt'\;P(\underline{k}) =$$

$$\frac{c(\|\underline{k}\|)}{\rho^2\,\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\,2}\,P(\underline{k})$$

We can use (15) to evaluate the expected value of the kinetic energy (which is an infinite sum, but we will be interested in the individual terms). The first step is to rewrite (3) as follows

$$\underline{U}(\underline{x},t) = \sum_{\underline{k}\in K}\left(\hat{\underline{U}}_{\underline{k}}(t)\, e^{i\frac{2\pi}{L}\underline{k}\cdot\underline{x}} + \overline{\hat{\underline{U}}_{\underline{k}}(t)}\, e^{-i\frac{2\pi}{L}\underline{k}\cdot\underline{x}}\right) \tag{16}$$

Then

$$\|\underline{U}(\underline{x},t)\|^2 = \underline{U}(\underline{x},t)\cdot\underline{U}(\underline{x},t) = \tag{17}$$

$$\sum_{\underline{k},\underline{k}'\in K}\Big(\hat{\underline{U}}_{\underline{k}}(t)\cdot\hat{\underline{U}}_{\underline{k}'}(t)\, e^{i\frac{2\pi}{L}(\underline{k}+\underline{k}')\cdot\underline{x}}$$

$$\overline{\hat{\underline{U}}_{\underline{k}}(t)\cdot\hat{\underline{U}}_{\underline{k}'}(t)}\, e^{i\frac{2\pi}{L}(\underline{k}-\underline{k}')\cdot\underline{x}}$$

$$+\,\overline{\hat{\underline{U}}_{\underline{k}}(t)}\cdot\hat{\underline{U}}_{\underline{k}'}(t)\, e^{-i\frac{2\pi}{L}(\underline{k}-\underline{k}')\cdot\underline{x}}$$

$$+\,\overline{\hat{\underline{U}}_{\underline{k}}(t)\cdot\hat{\underline{U}}_{\underline{k}'}(t)}\, e^{-i\frac{2\pi}{L}(\underline{k}+\underline{k}')\cdot\underline{x}}\Big)$$

Note that $\underline{k}+\underline{k}'$ is always nonzero when $\underline{k}$ and $\underline{k}'$ are both in K. Therefore

$$\int_\Omega e^{\pm i\left(\frac{2\pi}{L}\right)\left(\underline{k}+\underline{k}'\right)\cdot\underline{x}}\, d\underline{x} = 0, \qquad \underline{k},\underline{k}' \in K \tag{18}$$

On the other hand

$$\int_\Omega e^{\pm i\frac{2\pi}{L}\left(\underline{k}-\underline{k}'\right)\cdot\underline{x}}\, d\underline{x} = L^3 \delta_{\underline{k},\underline{k}'}, \qquad \underline{k},\underline{k}' \in K \tag{19}$$

Therefore

$$\frac{1}{2}\rho\int_\Omega \|\underline{U}(\underline{x},t)\|^2 d\underline{x} = \frac{1}{2}\rho\sum_{\underline{k}\in K} 2\,\hat{\underline{U}}^*_{\underline{k}}(t)\,\hat{\underline{U}}_{\underline{k}}(t)\,L^3 \tag{20}$$

$$= \rho L^3 \sum_{\underline{k}\in K} \operatorname{trace}\left(\hat{\underline{U}}^*_{\underline{k}}(t)\,\hat{\underline{U}}_{\underline{k}}(t)\right)$$

$$= \rho L^3 \sum_{\underline{k} \in K} \text{trace}\left(\hat{\underline{U}}_{\underline{k}}(t)\, \hat{\underline{U}}_{\underline{k}}^{*}(t)\right)$$

and then we have

(21) $$E\left[\frac{1}{2}\rho \int_{\Omega} \|\underline{U}(\underline{x},t)\|^2 d\underline{x}\right] =$$

$$\rho L^3 \sum_{\underline{k} \in K} \text{trace}\; E\left[\hat{\underline{U}}_{\underline{k}}(t)\, \hat{\underline{U}}_{\underline{k}}^{*}(t)\right] =$$

$$\rho L^3 \sum_{\underline{k} \in K} \frac{c(\|\underline{k}\|)}{\rho^2 \frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \cancel{2}} \cancel{\text{trace}\, P(\underline{k})} =$$

$$\sum_{\underline{k} \in K} \frac{L^3 c(\|\underline{k}\|)}{\mu\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2}$$

Note the cancellation of ρ.

Now there are 4 real degrees of freedom associated with each $\underline{k} \in K$, since

$$\underline{\hat{U}}_k = \hat{U}_{k1}\, \underline{a}_1(\underline{k}) + \hat{U}_{k2}\, \underline{a}_2(\underline{k}) \tag{22}$$

where $\underline{a}_1(\underline{k})$ and $\underline{a}_2(\underline{k})$ are orthonormal and orthogonal to $\underline{k}$, and since each of the amplitudes $\hat{U}_{k1}$ and $\hat{U}_{k2}$ has independent real and imaginary parts. Since each real degree of freedom has an expected energy of $\frac{1}{2} k_B T$ (where k_B is Boltzmann's constant, and T is the absolute temperature, the expected kinetic energy contributed by each $\underline{k} \in K$ should be $2 k_B T$.

Therefore, we should set

$$\frac{L^3 c(\|\underline{k}\|)}{\mu\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2} = 2k_B T \tag{23}$$

and it follows that

$$c(\|\underline{k}\|) = \frac{2k_B T \mu \left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2}{L^3} \tag{24}$$

Checking units:

$$c(\|\underline{k}\|) \sim \frac{\text{force} \cdot \text{length} \; \frac{\text{mass}}{\text{length}^3} \; \frac{\text{length}^2}{\text{time}} \; \frac{1}{\text{length}^2}}{\text{length}^3}$$

$$= \left(\frac{\text{force}}{\text{length}^3}\right)^2 \text{time}$$

and this is correct, since R has units of force/length^3 and $\delta(t)$ has units of 1/time, see (13).

Numerical method and details of implementation

Finite Fourier series:

Choose n odd, and let $N = n^3$ (also odd)

Let $\mathbb{Z}_n$ be the set of integers within the interval $(-\frac{n}{2}, \frac{n}{2})$, that is

(25) $$\mathbb{Z}_n = \left\{ -\frac{n-1}{2}, \cdots, 0, \cdots \frac{n-1}{2} \right\}$$

Note that

(26) $$|\mathbb{Z}_n| = n \quad , \quad |\mathbb{Z}_n^3| = n^3 = N$$

Let

(27) $$K_n = K \cap \mathbb{Z}_n^3$$

Then

(28) $$\begin{cases} K_n \cap (-K_n) = \phi \\ K_n \cup (-K_n) \cup \{0\} = \mathbb{Z}_n^3 \end{cases}$$

and

(29) $$|K_n| = \frac{N-1}{2}$$

Explicit definition of K_n:

(30) $$K_n = K_n^{(1)} \cup K_n^{(2)} \cup K_n^{(3)}$$

where

(31) $$K_n^{(1)} = \{ \underline{k} \in \mathbb{Z}_n^3 : k_1 > 0 \}$$

(32) $$K_n^{(2)} = \{ \underline{k} \in \mathbb{Z}_n^3 : k_1 = 0 \ \& \ k_2 > 0 \}$$

(33) $$K_n^{(3)} = \{ \underline{k} \in \mathbb{Z}_n^3 : k_1 = k_2 = 0 \ \& \ k_3 > 0 \}$$

It is obvious that $K^{(i)} \cap K^{(j)} = 0$ for $i \neq j$,

and we also have

(34) $$|K_n^{(1)}| = \left(\frac{n-1}{2}\right) n^2$$

(35) $$|K_n^{(2)}| = \left(\frac{n-1}{2}\right) n$$

(36) $$|K_n^3| = \left(\frac{n-1}{2}\right)$$

and therefore

$$|K_n| = \frac{n-1}{2}(n^2+n+1) = \frac{n^3-1}{2} = \frac{N-1}{2} \tag{37}$$

as required

Since change of sign is a 1-1 map on $\mathbb{Z}_n^3$, the sets $-K^{(i)}$ are pairwise disjoint and

$$|-K_n^{(i)}| = |K_n^{(i)}| \tag{38}$$

It follows that

$$-K_n = (-K_n^{(1)}) \cup (-K_n^{(2)}) \cup (-K_n^{(3)}) \tag{39}$$

Moreover it is easy to check that

$$\underline{k} \in -K_n^{(i)} \Rightarrow \left(\underline{k} \notin K^{(j)}, j = 1,2,3\right) \Leftrightarrow \underline{k} \notin K \tag{40}$$

Thus

$$K_n \cap -K_n = \phi \tag{41}$$

and by the pigeonhole principle (i.e., by counting elements)

$$K_n \cup -K_n \cup \{\underline{0}\} = \mathbb{Z}_n^3 \tag{42}$$

The following code constructs a matrix k such that $k(:,j)$ is the j^{th} member of K_n. This only needs to be run once, during initialization.

```
k = zeros(3, (N-1)/2)
nn = (n-1)/2
j = 0
for k1 = 1:nn
    for k2 = -nn:nn
        for k3 = -nn:nn
            j = j + 1
            k(:,j) = [k1; k2; k3]
        end
    end
end
for k2 = 1:nn
    for k3 = -nn:nn
        j = j + 1
        k(:,j) = [0; k2; k3]
    end
end
for k3 = 1:nn
    j = j + 1
    k(:,j) = [0; 0; k3]
end
```

~~k8g = sum(k.^2,1);~~

Still during initialization, we can evaluate

```
ksq = sum(k.^2, 1)
c = (2*kB*T*mu*(2*pi/L).^2/L.^3)*ksq
s = sqrt(c/2)*sqrt(1/dt)
```

Here s contains scale factors that will be applied as follows whenever new $\hat{R}_k$ are needed:

```
Rhat1 = randn(3,(N-1)/2).*[s;s;s]
Rhat2 = randn(3,(N-1)/2).*[s;s;s]
Rhat = Rhat1 + 1i*Rhat2
```

(Note that "1i" is the recommended Matlab notation for $\sqrt{-1}$.)

In the formula for s, dt is the time step.

The complex vectors $\underline{\hat{U}}_{\underline{k}}$, $\underline{k} \in K_n$ will be stored in an array Uhat with 3 rows and $(N-1)/2$ columns, like the array k constructed above, and the columns of these two arrays will correspond so that Uhat(:,j) is the complex vector Fourier coefficient with real vector label $k(:,j)$.

The following function uses Uhat and k to evaluate the fluid velocity at a arbitrary point $\underline{x}$. Note that $\underline{x}$ can be anywhere in $\mathbb{R}^3$, since the velocity field is periodic.

```
function U = vel(x, k, Uhat, L)
kx = x(1)*k(1,:) + x(2)*k(2,:) + x(3)*k(3,:)
cs = exp(1i*(2*pi/L)*kx)
U = 2*real(sum(Uhat.*[cs;cs;cs], 2))

% input x is 3x1 or 1x3
% output U is 3x1
```

The above function is an implementation of equation (16), but with K replaced by the finite set K_n.

We need a timestepping scheme to update $\hat{\underline{U}}_{\underline{k}}(t) \to \hat{\underline{U}}_{\underline{k}}(t+\Delta t)$. The ODE for $\hat{\underline{U}}_{\underline{k}}$ is equation (9), and the backward-Euler method for this ODE is

$$\frac{\hat{\underline{U}}_{\underline{k}}(t+\Delta t) - \hat{\underline{U}}_{\underline{k}}(t)}{\Delta t} + \frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \hat{\underline{U}}_{\underline{k}}(t+\Delta t) = \frac{1}{\rho} \mathcal{P}(\underline{k}) \hat{\underline{R}}_{\underline{k}}(t) \tag{43}$$

The solution of (43) for $\hat{\underline{U}}_{\underline{k}}(t+\Delta t)$ is as follows:

$$\hat{\underline{U}}_{\underline{k}}(t+\Delta t) = \frac{\hat{\underline{U}}_{\underline{k}}(t) + \frac{\Delta t}{\rho} \mathcal{P}(\underline{k}) \hat{\underline{R}}_{\underline{k}}(t)}{1 + \frac{\Delta t}{\rho} \mu \left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2} \tag{44}$$

The choice of the backward-Euler method makes the scheme be well behaved regardless of the values of Δt and ρ.

In the limit $\rho \to 0$, we get a stochastic simulation of the time-independent Stokes equations.

For the implementation of (44), the following steps can be done during initialization

```
D = 1+(dt/rho)*mu*((2*pi/L).^2) * ksq
knrm = sqrt(ksq)
kk = k./[knrm; knrm; knrm]
```

Then, at each time step, with Rhat constructed as described previously, the update of Uhat can be done as follows:

```
kR = sum(kk.*Rhat, 1)
PR = Rhat - kk.*[kR; kR; kR]
Uhat = (Uhat + (dt/rho)*PR)./[D; D; D]
```

An alternative to (44) is to apply the projection operator at the end of each time step

$$\underline{\hat{U}}_{\underline{k}}(t+\Delta t) = \mathcal{P}(\underline{k})\left(\frac{\underline{\hat{U}}_{\underline{k}}(t) + \frac{\Delta t}{\rho}\underline{\hat{R}}_{\underline{k}}(t)}{1 + \frac{\Delta t}{\rho}\mu\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2}\right) \tag{45}$$

Equations (44) & (45) are equivalent if $\underline{k} \cdot \hat{\underline{U}}_{\underline{k}} = 0$, as it should be, but (45) is better if there is any numerical error that makes $\underline{k} \cdot \hat{\underline{U}}_{\underline{k}}$ be nonzero, or if an initial condition is specified in which $\underline{k} \cdot \hat{\underline{U}}_{\underline{k}}$ is nonzero. The implementation of (45) needs the same initialization and the same random Rhat, but then proceeds as follows:

```
Uh = (Uhat + (dt/rho)*Rhat)./[D; D; D]
kUh = sum(kk.*Uh, 1)
Uhat = Uh - kk.*[kUh; kUh; kUh]
```

Finally, to track the motion of a particle in the random velocity field $\underline{U}(\underline{x}, t)$ we can just use Euler's method

$$\frac{\underline{X}(t+\Delta t) - \underline{X}(t)}{\Delta t} = \underline{U}(\underline{X}(t), t) \tag{46}$$

implemented by calling the function vel defined above:

```
X = X + dt * vel(X, k, Uhat, L)
```

Here X needs to be 3×1, since the output of vel is 3×1.

The particle with random position $\underline{X}(t)$ will have an effective radius that should be some constant times L/n. To determine the effective radius, do multiple runs and plot the mean of $\|\underline{X}(t)\|^2$. This can be used as Einstein did to find the diffusion coefficient, and then through the Einstein relation and the Stokes drag formula to find the radius of the particle.

Note that each computation of $\underline{X}(t)$ should start after a warm-up interval

during which the fluid has had time to equilibrate to the specified temperature T. This can be checked by monitoring the total kinetic energy.

Appendix A: Effect of the backward-Euler time-discretization on the energy spectrum.

The difference equation (43) can be solved in the same manner as the differential equation (9). First, we rewrite (43) as

$$r_{\underline{k}} \hat{\underline{U}}_{\underline{k}}^{(m+1)} - \hat{\underline{U}}_{\underline{k}}^{(m)} = \frac{\Delta t}{\rho} \mathcal{P}(\underline{k}) \hat{\underline{R}}_{\underline{k}}^{(m)} \tag{A1}$$

where

$$r_{\underline{k}} = 1 + \frac{\Delta t}{\rho} \mu \left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 > 1 \tag{A2}$$

Here m is the time-step index, that is, $t^{(m)} = m\Delta t$, and $\hat{\underline{U}}_{\underline{k}}^{(m)} = \hat{\underline{U}}_{\underline{k}}(m\Delta t)$.

Now we multiply both sides of (A1) by the "integrating factor" $r_{\underline{k}}^{m}$, with the result

$$r_{\underline{k}}^{m+1}\hat{U}_{\underline{k}}^{(m+1)} - r_{\underline{k}}^{m}\hat{U}_{\underline{k}}^{(m)} = \frac{\Delta t}{\rho} r_{\underline{k}}^{m} P(\underline{k}) \hat{R}_{\underline{k}}^{(m)} \tag{A3}$$

For any $m_0 \le m$, repeated application of (A3) gives

$$r_{\underline{k}}^{m+1}\hat{U}_{\underline{k}}^{(m+1)} - r_{\underline{k}}^{m_0}\hat{U}_{\underline{k}}^{(m_0)} = \frac{\Delta t}{\rho} \sum_{m'=m_0}^{m} r_{\underline{k}}^{m'} P(\underline{k}) \hat{R}_{\underline{k}}^{(m')} \tag{A4}$$

Now let $m_0 \to -\infty$. Assuming that $\hat{U}_{\underline{k}}$ is bounded (and lowering m by 1), we get

(A5) $$r_{\underline{k}}^{m}\,\hat{\underline{U}}_{\underline{k}}^{(m)} = \frac{\Delta t}{\rho}\sum_{m'=-\infty}^{m-1} r_{\underline{k}}^{m'}\,\mathcal{P}(\underline{k})\,\hat{\underline{R}}_{\underline{k}}^{(m')}$$

or

(A6) $$\hat{\underline{U}}_{\underline{k}}^{(m)} = \frac{\Delta t}{\rho}\sum_{m'=-\infty}^{m-1} r_{\underline{k}}^{-(m-m')}\,\mathcal{P}(\underline{k})\,\hat{\underline{R}}_{\underline{k}}^{(m')}$$

which is a discretization of equation (11).

Now we can proceed exactly as we did in equation (15):

(A7) $$E\left[\hat{U}_{\underline{k}}^{(m)}\left(\hat{U}_{\underline{k}}^{(m)}\right)^*\right] =$$

$$\left(\frac{\Delta t}{\rho}\right)^2 \sum_{m'=-\infty}^{m-1} \sum_{m''=-\infty}^{m-1} r_{\underline{k}}^{-(2m-m'-m'')}$$

$$\mathcal{P}(\underline{k})\, E\left[\hat{R}_{\underline{k}}^{(m')}\left(\hat{R}_{\underline{k}}^{(m'')}\right)^*\right] \mathcal{P}(\underline{k})$$

Here we must use the discretization of (13), which is

(A8) $$E\left[\hat{R}_{\underline{k}}^{(m)}\left(\hat{R}_{\underline{k}'}^{*}\right)^{(m')}\right] =$$

$$C(\|\underline{k}\|)\, \delta_{\underline{k},\underline{k}'} \left(\frac{\delta_{m,m'}}{\Delta t}\right) I$$

Thus (A7) becomes

(A9) $$E\left[\hat{U}_{\underline{k}}^{(m)}\left(\hat{U}_{\underline{k}}^{(m)}\right)^*\right] = \frac{c(\|\underline{k}\|)}{\rho^2}\Delta t\left(\sum_{m'=-\infty}^{m-1} r_{\underline{k}}^{-(2(m-m'))}\right)\mathcal{P}(\underline{k})$$

The sum in the above formula is a geometric series with initial term $r_{\underline{k}}^{-2}$ and ratio $r_{\underline{k}}^{-2}$.

It is therefore equal to

(A10) $$\frac{r_{\underline{k}}^{-2}}{1 - r_{\underline{k}}^{-2}} = \frac{1}{r_{\underline{k}}^2 - 1}$$

$$= \frac{1}{\left(1 + \frac{\Delta t}{\rho}\mu\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\right)^2 - 1}$$

$$= \frac{1}{\frac{\Delta t}{\rho}\mu\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2 \left(2 + \frac{\Delta t}{\rho}\mu\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2\right)}$$

and (A9) becomes

(A11) $$E\left[\hat{\underline{U}}_{\underline{k}}^{(m)} \left(\hat{\underline{U}}_{\underline{k}}^{(m)}\right)^*\right] =$$

$$\frac{c(\|\underline{k}\|)\, P(\underline{k})}{\rho^2 \left(\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2\right)\left(2 + (\Delta t)\,\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2 \|\underline{k}\|^2\right)}$$

Proceeding now as in equation (21), we have

(A12) $$E\left[\frac{1}{2}\rho\int_{\Omega}\|\underline{U}(\underline{x},t)\|^2 d\underline{x}\right] =$$

$$\rho L^3 \sum_{\underline{k}\in K_n} \text{trace}\, E\left[\hat{\underline{U}}_{\underline{k}}^{(m)}\left(\hat{\underline{U}}_{\underline{k}}^{(m)}\right)^{*}\right] =$$

$$\rho L^3 \sum_{\underline{k}\in K_n} \frac{c(\|k\|)\,\text{trace}\left(\mathcal{P}(\underline{k})\right)}{\rho^2 \frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\left(2+(\Delta t)\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\right)} =$$

$$\sum_{\underline{k}\in K_n} \frac{L^3\, c(\|\underline{k}\|)}{\mu\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\left(1+\frac{\Delta t}{2}\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2\right)} =$$

$$\sum_{\underline{k}\in K_n} \frac{2k_B T}{1+\frac{\Delta t}{2}\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2}$$

In the last step of (A12), we have made use of equation (23) for $c(\|k\|)$.

Equation (A12) reveals exactly what the effect of the backward-Euler discretization is on the distribution of energy among the various modes. In the limit $\Delta t \to 0$, we recover the result of classical statistical mechanics that each degree of freedom has mean kinetic energy $\frac{1}{2} k_B T$. (Recall that there are 4 degrees of freedom associated with each $\underline{k} \in K_n$.) For any fixed Δt, there is a reduction in the mean kinetic energy of all modes. The reduction

depends on $\|\underline{k}\|^2$ and is negligible when

$$\frac{\Delta t}{2}\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2 \ll 1 \tag{A13}$$

Equation (A12) can also be used to evaluate the mean squared displacement of a particle in the fluid over one time step. Since $E[\|\underline{U}(\underline{x},t)\|^2]$ is independent of $\underline{x}$ and t, equation (A12) can be rewritten as follows

$$\frac{1}{2}\rho L^3 E[\|\underline{U}(\underline{x},t)\|^2] \tag{A14}$$

$$= \sum_{\underline{k}\in K_n} \frac{2k_BT}{1+\frac{\Delta t}{2}\frac{\mu}{\rho}\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2}$$

Therefore,

(A15) $$E\left[\|\underline{U}(\underline{x},t)\Delta t\|^2\right] =$$

$$\frac{1}{L^3}\sum_{\underline{k}\in K_n}\frac{4k_BT(\Delta t)^2}{\rho+\frac{\Delta t}{2}\mu\left(\frac{2\pi}{L}\right)^2\|\underline{k}\|^2}$$

This is $O((\Delta t)^2)$, which shows that we cannot evaluate a diffusion coefficient by looking at the displacement over a single time step when $\rho > 0$. Note however, that by taking the limit $\rho \to 0$, we get a result that is $O(\Delta t)$:

(A16) $$\lim_{\Delta t \to 0} E\left[\|\underline{U}(\underline{x}, t)\,\Delta t\|^2\right] =$$

$$\frac{8 k_B T \Delta t}{L^3 \mu \left(\frac{2\pi}{L}\right)^2} \sum_{\underline{k} \in K_n} \frac{1}{\|\underline{k}\|^2}$$

The large-n behavior of (A15) and (A16) can be found in the following way.

First we note that

(A17) $$\sum_{\underline{k} \in K_n} = \frac{1}{2} \sum_{\underline{k} \in \mathbb{Z}_n^3 - \{0\}}$$

Next we replace the sums by integrals over $\left(-\frac{n}{2}, \frac{n}{2}\right)^3$, and finally, we make the change of variables in

these integrals

(A18) $$\underline{k} = n\underline{\theta}\,, \quad dk_1 dk_2 dk_3 = n^3 d\theta_1 d\theta_2 d\theta_3$$

so that the domain becomes

(A19) $$\underline{\theta} \in \left(-\tfrac{1}{2}, \tfrac{1}{2}\right)^3$$

In this way, we get the following layer-n results:

(A20) $$E\left[\left\| \underline{U}(\underline{x}, t)\Delta t \right\|^2\right] \sim$$

$$\frac{1}{(L/n)^3} \iiint_{-1/2}^{1/2} \frac{2k_B T (\Delta t)^2 \, d\theta_1 d\theta_2 d\theta_3}{\rho + \frac{\Delta t}{2}\mu\left(\frac{2\pi}{L/n}\right)^2 \|\underline{\theta}\|^2}$$

(A21) $$\lim_{\rho \to 0} E\left[\left\| \underline{U}(\underline{x}, t)\Delta t \right\|^2\right] \sim$$

$$\frac{4k_B T \Delta t}{(L/n)\mu\pi} \frac{1}{4\pi} \iiint_{-1/2}^{1/2} \frac{d\theta_1 d\theta_2 d\theta_3}{\|\underline{\theta}\|^2}$$

Let

$$\alpha = \frac{1}{4\pi} \int_{-1/2}^{1/2} \iiint \frac{d\theta_1 d\theta_2 d\theta_3}{\|\underline{\theta}\|^2} \tag{A22}$$

This integral is finite, despite the singularity at the origin, as is easily seen by using spherical polar coordinates in the neighborhood of the origin. Moreover, we can use spherical polar coordinates to derive lower and upper bounds on α by integration over the largest ball that fits within $\left(-\frac{1}{2}, \frac{1}{2}\right)^3$ and over the smallest ball that contains $\left(-\frac{1}{2}, \frac{1}{2}\right)^3$. The radii of these balls are $\frac{1}{2}$ and $\sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} = \frac{\sqrt{3}}{2}$. Also,

(A23) $$\frac{1}{4\pi}\iiint_{\|\underline{\theta}\|<r} \frac{d\theta_1 d\theta_2 d\theta_3}{\|\underline{\theta}\|^2} = \frac{1}{4\pi}\int_0^r \frac{4\pi\|\underline{\theta}\|^2 d\|\underline{\theta}\|}{\|\underline{\theta}\|^2} = r$$

so we may conclude that

(A24) $$\frac{1}{2} < \alpha < \frac{\sqrt{3}}{2}$$

According to Matlab's integrate3 routine $\alpha \approx 0.61$. (To get this result it is necessary to put the singularity of the integrand on the boundary of the domain by writing $\alpha = \frac{8}{4\pi}\iiint_0^{1/2} \frac{d\theta_1 d\theta_2 d\theta_3}{\|\underline{\theta}\|^2}$.)

Equation (A21) implies a diffusion constant D given by

$$6D = \frac{4\alpha k_B T}{(L/n)\mu\pi} \tag{A25}$$

and therefore, by the Einstein relation, a drag coefficient

$$\gamma = \frac{k_B T}{D} = \frac{6\mu\pi(L/n)}{4\alpha} \tag{A26}$$

From this we see that the effective radius of our "point" particle is

$$\frac{(L/n)}{4\alpha} \approx \frac{L/n}{2.44} \tag{A27}$$

and the effective diameter is $\approx \frac{L/n}{1.22}$, not far from L/n.

Appendix B: Brownian motion, Einstein, and Avagadro's number

In the 19th Century, it was widely believed that matter consists of discrete molecules, but the actual number of molecules in any particular mass of any particular kind of matter was completely unknown. To deal with this situation, chemists use a unit of molecular number called the mole, which is the number of atoms in a sample of Carbon-12 that weighs 12 grams.

When the ideal gas law is expresed in terms of moles, it reads

(B1) $$PV = nRT$$

where P = pressure, V = volume, T = absolute temperature, n = number of moles, and R is called the gas constant. This is an empirical law, and the constant R can be experimentally determined.

The ideal gas law can also be theoretically derived from kinetic theory of statistical mechanics, and the theoretical version of the ideal gas law is

(B2) $PV = Nk_B T$

Here N is the number of molecules, and k_B is Boltzmann's constant. The variables P, V, T have the same meanings as in (B1). The theoretical derivation of (B2) does not give a value to the constant k_B. One can set $k_B = 1$, and that defines a temperature scale, but it is then unknown how that natural unit of temperature is related to a practical unit like ^oK.

The number of molecules in a mole is called Avagadro's number, and is denoted N_A. By comparison of (B1) and (B2), we see that

$$N_A = \frac{N}{n} = \frac{R}{k_B} \tag{B3}$$

Since R is experimentally determined, any method that determines k_B can be used to infer Avagadro's number. Albert Einstein had the amazing insight that Brownian motion could be used in this way.

Brownian motion

Microscopic particles suspended in water undergo random motion that we now know is the result of collisions with water molecules. This was first seen (or first reported) by Brown, who was looking at pollen grains. Quantitative measurement of Brownian motion shows that mean squared displacement grows linearly with time. This suggests that an ensemble of Brownian particles would be governed by the diffusion equation, and it provides a way

to determine the diffusion coefficient D.
Consider the initial-value problem

$$\frac{\partial \rho}{\partial t} = D\Delta\rho \,, \quad \rho(\underline{x},0) = \delta(\underline{x}) \tag{B4}$$

where $\rho(\underline{x},t)$ is the probability density function for the random variable $\underline{X}(t)$, and we are given that $\underline{X}(0) = \underline{0}$. Here $\underline{x} \in \mathbb{R}^3$. The solution of (B4) is Gaussian, and has rapid decay as $\|\underline{x}\| \to \infty$, so we can integrate by parts freely without worrying about boundary terms at ∞. This makes it easy to evaluate the expected value of $\|\underline{X}(t)\|^2$:

(B5) $$\frac{d}{dt}E\left[\|\underline{X}(t)\|^2\right] = \frac{d}{dt}\int_{\mathbb{R}^3} \|\underline{x}\|^2 \rho(\underline{x},t)\, d\underline{x}$$

$$= \int_{\mathbb{R}^3} \|\underline{x}\|^2 \frac{\partial \rho}{\partial t}(\underline{x},t)\, d\underline{x} = D\int_{\mathbb{R}^3} \|\underline{x}\|^2 (\Delta\rho)(\underline{x},t)\, d\underline{x}$$

$$= D\int_{\mathbb{R}^3} \Delta(\|\underline{x}\|^2)\, \rho(\underline{x},t)\, d\underline{x}$$

$$= 6D\int_{\mathbb{R}^3} \rho(\underline{x},t)\, d\underline{x} = 6D$$

Then, since $E\left[\|\underline{X}(0)\|^2\right] = 0$, we have

(B6) $$E\left[\|\underline{X}(t)\|^2\right] = 6Dt$$

Einstein relation

It turns out that there is a simple relationship between D, γ, and $k_B T$, where γ is a drag coefficient defined below. This was discovered by Einstein. The derivation we give here is not exactly the same as Einstein's but it involves the same ideas.

Imagine that a particle undergoes Brownian motion with diffusion coefficient D in a fluid with viscosity μ is also subject to a deterministic force that can be derived from a potential energy $\phi(x)$, so that

the force on the particle when it is at position $\underline{x}$ is $-(\nabla\phi)(\underline{x})$.

If viscosity is dominant over inertia, and if the particle is spherical, such a force produces a drift velocity

(B7) $$\underline{v}_{drift} = -\frac{1}{f}\nabla\phi$$

which biases the random walk of the Brownian particle. The constant f is the <u>drag coefficient</u>, and $1/f$ is the <u>mobility</u> of the particle. The drag coefficient for a spherical particle is given by a formula derived by Stokes:

(B8) $$f = 6\pi\mu r$$

where μ is the fluid viscosity, and r is the radius of the particle.

The probability density function $\rho(\underline{x}, t)$ for an ensemble of such particles satisfies the drift-diffusion equation

(B9) $$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{F} = 0$$

where

(B10) $$\underline{F} = -D\nabla\rho - \frac{1}{f}(\nabla\phi)\rho$$

In this formula for the flux, $\underline{F}$, $-D\nabla\rho$ is the diffusion flux and $-\frac{1}{f}(\nabla\phi)\rho = v_{drift}\rho$ is the drift flux.

Now consider the special case in which our system is in a state of thermodynamic equilibrium. In such a state, the principle of detailed balance tells us that $\underline{F} = 0$. Note that this is a stronger condition than $\frac{\partial f}{\partial t} = 0$, which only implies that $\nabla \cdot \underline{F} = 0$. Moreover, an important remark is that in this application of the principle of detailed balance, we are regarding drift-diffusion as a single process, not as two separate processes. The justification for this is that the drag

on a particle immersed in fluid to which a force B applied ultimately comes from collisions with molecules of the fluid, and this is the same process that causes Brownian motion.

With $\underline{F}=0$, we can divide by ρD in (B10) and obtain

$$\nabla\left(\log\rho + \frac{\phi}{D\mathcal{J}}\right) = 0 \tag{B11}$$

and thus implies

$$\rho(\underline{x}) = \rho(\underline{x}_0)\, e^{-\frac{\phi(\underline{x})-\phi(\underline{x}_0)}{D\mathcal{J}}} \tag{B12}$$

where $\underline{x}_0$ is any chosen reference point.

Equation (B12) looks like the Boltzmann relation that can be derived for our system from thermodynamics or statistical mechanics, and which says that at thermal equilibrium

$$\rho(\underline{x}) = \rho(\underline{x}_0)\, e^{-\frac{\phi(\underline{x})-\phi(\underline{x}_0)}{k_B T}} \tag{B13}$$

Of course, (B12) & (B13) are in agreement only if

$$D\zeta = k_B T \tag{B14}$$

and this is the Einstein relation.

Two aspects of the above reasoning deserve comment. First, although we needed to postulate a potential $\phi(\underline{x})$ in order to arrive at the result (B14), that result does not involve $\phi(\underline{x})$, and therefore it is valid for any $\phi(\underline{x})$ including the case in which there is no potential, i.e., $\phi(\underline{x}) = 0$.

Second, the result was derived by consideration of thermodynamic equilibrium, but it is a relationship among constants (if we hold T = constant), and therefore it is applicable even when the system is <u>not</u> at thermal equilibrium.

With regard to temperature dependence, note that D and f may both be functions of temperature, but $D(T)$ and $f(T)$ must satisfy $D(T)f(T) = k_B T$, where k_B is a universal constant.

Avagadro's Number

As described above, we can use measurements on Brownian motion to evaluate D, and f can be obtained for the particles undergoing Brownian motion by using the Stokes formula (B8), since the radii of the particles can be seen under the microscope, and since

the viscosity of the fluid can be measured separately in a viscometer. With D and f known, one simply multiply them to obtain $k_B T$, and with the temperature known thus determines k_B. Finally with the gas constant R independently known from experiments on gasses, we get Avagadro's number from equation (83), $N_A = R/k_B$. The (enormous) result is approximately 6×10^{23}. In this way, for the first time, the actual mass of any molecule can be

derived from its "molecular weight".
For example, H_2 has a molecular
weight of 2, so the mass of an H_2
molecule is $2/N_A$ grams.
Molecules are really, really small!