Velocity Autocorrelation Function

Consider $F^s(\vec{q},t)$ without drift, $v_\alpha = \langle \Delta \dot{R}_\alpha(t)\rangle = 0$

$\forall \alpha = 1,2,3$

and for isotropic systems, i.e., $F^s(\vec{q},t) = F^s(q,t)$
for $q = |\vec{q}|$

long-wavelength (= small-q) expansion of $F^s(q,t)$

$$\boxed{F^s(q,t) = 1 - q_\alpha q_\beta \langle \Delta R_\alpha(t)\, \Delta R_\beta(t)\rangle + O(q^4)}$$

$$\langle \Delta R_\alpha(t) \Delta R_\beta(t)\rangle = \delta_{\alpha\beta} \frac{1}{d}\, \delta r^2(t)$$

$$\delta r^2(t) = \langle [\Delta R(t)]^2 \rangle \,, \quad \delta r^2(t=0) = 0$$

mean-squared displacement (MSD)

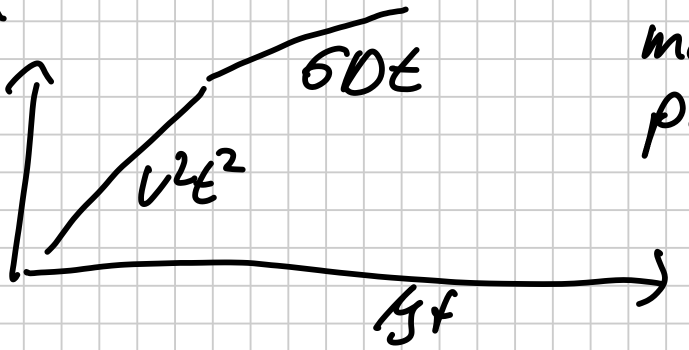
$$\hookrightarrow \boxed{F^s(q,t) = 1 - \frac{q^2}{2d}\, \delta r^2(t) + O(q^2)}$$

$$\delta r^2(t-t') = \langle [\vec{R}(t) - \vec{R}(t')]^2 \rangle \to 2dD|t-t'|$$

upon increments becoming uncorrelated random walk (i.e. diffusion)

e.g. for Brownian particle in dilute suspension

$\hookrightarrow \delta r^2(t)$



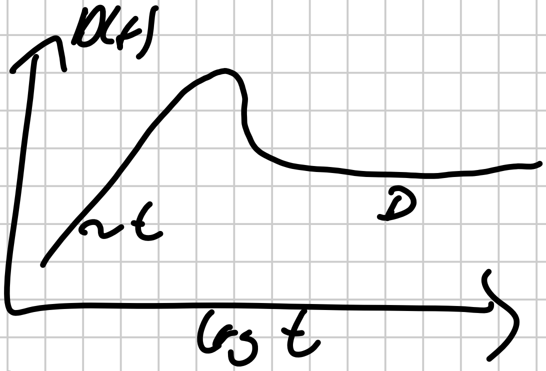
measurable in particle tracking

diffusion coefficient from MSD

$$\boxed{D = \frac{1}{2d}\lim_{t\to\infty} \delta r^2(t)/t = \frac{1}{2d}\lim_{t\to\infty}\partial_t\, \delta r^2(t)}$$

derivative defines time-dependent diffusion coefficient

$$\boxed{D(t) = \frac{1}{2d}\,\partial_t\, \delta r^2(t)}$$



$$D(t) = \frac{1}{d}\langle \Delta \vec{R}(t)\cdot \underbrace{\Delta\dot{\vec{R}}(t)}_{=V^s}\rangle \qquad D(t=0)=0$$

$$\frac{d^2}{dt^2}\,\delta r^2(t-t') = -\frac{d}{dt}\frac{d}{dt'}\,\delta r^2(t-t') = 2\langle \dot{\vec{R}}(t)\,\dot{\vec{R}}(t')\rangle$$

Def: Velocity Autocorrelation Function (VACF)

$$\boxed{\begin{aligned} Z(t) &:= \frac{1}{2d}\,\partial_t^2\, \delta r^2(t) = \partial_t\, D(t) \\ Z(t) &= \frac{1}{d}\langle \vec{v}^s(t)\cdot\vec{v}^s(0)\rangle, \quad \vec{v}^s(t) = \dot{\vec{R}}^s(t) \end{aligned}}$$

Long-time diffusion coefficient

$$D = D(t\to\infty) = \int_0^\infty dt'\, Z(t'),$$

Green-Kubo relation: transport coefficient from correlation function

MSD from VACF

$$\delta r^2(t) = 2d\int_0^t dt'\, D(t') = \text{integration by parts} \ldots$$

$$= 2d\left\{t' D(t')\Big|_0^t - \int_0^t dt'\, t'\, \dot D(t')\right\} =$$

$$= 2d\left\{t\, D(t) - \int_0^t dt'\, t'\, Z(t')\right\}$$

$$\boxed{\delta r^2(t) = 2d\int_0^t dt'\,(t-t')\,Z(t')}$$

dynamic structure factor

$$\hat F^s(q,z) = i\int_0^\infty dt\, e^{izt}\, F^s(q,t) = i\int_0^\infty dt\, e^{izt}\left[1-\frac{q^2}{2d}\delta r^2(t)\right]$$

$$= -\frac{1}{z} - i\frac{q^2}{2d}\int_0^\infty dt\, e^{izt}\,\delta r^2(t)$$

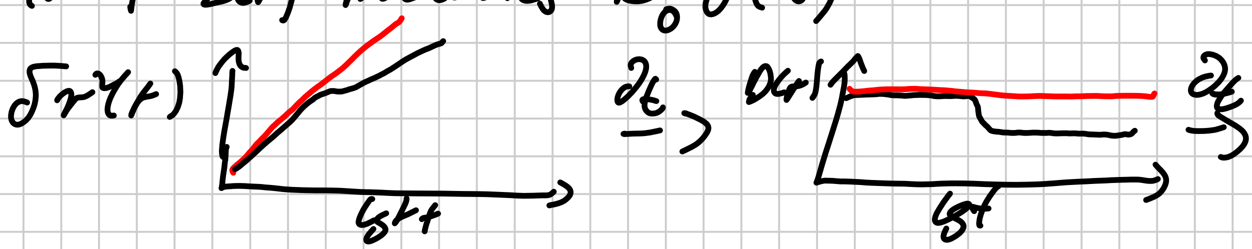
again integration by parts for integral involving $\delta r^2(t)$

$$i\int_0^\infty dt\, e^{izt}\,\delta r^2(t) = i\Big\{\underbrace{\frac{1}{iz}\delta r^2(t)\, e^{izt}\Big|_0^t}_{=0} - \frac{1}{iz}\int_0^t dt\, e^{izt}\,\partial_t\delta r^2(t)\Big\} =$$

$$-\frac{1}{z}\int_0^t dt\, e^{izt}\,\partial_t\delta r^2(t) = -\frac{1}{z}\Big\{\underbrace{\frac{1}{iz}(\partial_t r^2(t))\, e^{izt}\Big|_0^t}_{=0} - \frac{1}{iz}\int_0^t dt\, e^{izt}\,\partial_t^2\delta r^2(t)\Big\} =$$

$$= -\frac{i}{z^2}\int_0^\infty dt\, e^{izt}\, 2d\, Z(t) = -\frac{1}{z^2}\, 2d\, \hat Z(z)$$

derivation above for newtonian dynamics, for Brownian dynamics, $\partial_t\delta r^2(t)\big|_{t=0} = 2dD_0$, VACF $Z(t)$ includes $D_0\,\delta(t)$



VACF decays instantly

hence
$$\boxed{\hat{F}^s(q,z) = -\frac{1}{z} - \frac{q^2}{z^2}\hat{Z}(z) + O(q^2) \text{ with } \hat{Z}(z) = \lim_{q\to 0}\hat{D}(q,z)}$$

Limits and (failed) expansions

hydrodynamic limit $\quad iD = \lim_{z\to 0}\hat{Z}(z)$

↳ $\hat{F}^s(q,z) = \frac{-1}{z+iq^2D}$

generalized hydrodynamics
$$\boxed{\hat{F}^s(q,z) = \frac{-1}{z+q^2\hat{Z}(z)}}$$

expansions

① in q, $\quad \hat{D}(q,z) = \hat{Z}(z) + q^2\hat{Z}_2(z) + \dots$

↳ non-analytic in q for $z=0$

① in z, $\quad \hat{D}(q,z) = D(q,z=0) + z\,\hat{D}'(q,z=0) + \dots$

↳ non-analytic in z for $q=0$

③ in n, for Newtonian dynamics non-analytic in density n

alternative to expansion: additional MZ step for $Z(t)$:

$$\boxed{\begin{aligned}&\hat{Z}(z) = \frac{-k_B T}{z + \hat{\zeta}(z)} \\ &\dot{Z}(t) + \int_0^t dt'\, Z(t')\,\zeta(t-t')\end{aligned}}$$

retarded friction $\zeta(t)$ and subsequent simple model for friction: e.g., $\zeta(t) = \zeta\,\delta(t)$

$$\hat{\zeta}(z) = i\zeta$$

$$\boxed{\hat{Z}(z) = \frac{-k_B T}{z + i\zeta}}\ , \quad \dot{Z}(t) + \zeta Z(t) = 0$$

↳ exponential decay $\boxed{Z(t) = k_B T\, e^{-t/\tau}}$

with relaxation time $\tau = 1/\zeta$

hence, the time-dependent diffusion

$$D(t) = \int_0^t dt'\, Z(t') = \frac{k_B T}{\zeta}\left(1 - e^{-t/\tau}\right)$$

for $t \to \infty$, $D(t) \to \boxed{D = \frac{k_B T}{\zeta}}$ Stokes Einstein relation

SE-like relations: transport coefficient (describing fluctuations) related to friction (dissipation) defines temperature

example of fluctuation-dissipation relation (FDR)

for Stokes friction $\zeta = 6\pi\eta r$ of particle of radius r in fluid of viscosity η

$$\boxed{D = \frac{k_B T}{6\pi\eta r}}$$

approach to long-time diffusion $6Dt$ as

$$\delta r^2(t) = 2d\int_0^t dt'\, D(t')$$

$$\boxed{\delta r^2(t) = 2dD\left[t + \tau\left(e^{-t/\tau}-1\right)\right]}$$

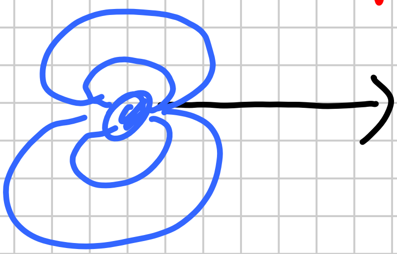
$\delta r^2(t\to\infty) = 2dDt$ but constant offset $-2dD\tau$

nice consistent result: diffusion is approached <u>exponentially</u> fast

HOWEVER: (numerical) experiments find

$$\boxed{\begin{aligned} Z(t) &\sim t^{-3/2} \quad \text{for } t\to\infty,\ d=3 \\ Z(t) &\sim t^{-1} \quad \text{for } t\to\infty,\ d=2 \end{aligned}}$$

algebraic long-time tails due to persistent correlations from slow diffusion of momentum



hydrodynamic backflow distributes initial momentum ($v(0)$) into region of size $L(t)$ that grows only via diffusion

$L(t) \sim \sqrt{t} \rightarrow$ 3d: $V(t) \sim L(t)^3 = t^{3/2}$

2d: $V(t) \sim L(t)^2 = t^1$

with τ_f for vortex diffusion

3D : $\delta r^2(t) = 6Dt\left[1 - 2\sqrt{\tau_f/t}\right]$

2D : D does not exist