Nonequilibrium and Transport Phenomena: Summary

- **Boltzmann equation**: The full phase space distribution for a Hamiltonian system, \( \varphi(\varphi, t) \), where \( \varphi = \{ (q, \dot{q}), (p, \dot{p}) \} \), satisfies \( \dot{\varphi} + \varphi \cdot \nabla \varphi = 0 \). This is not true, however, for the one-particle distribution \( f(q, p, t) \). Rather, \( f \) is related to two-, three-, and higher order particle number distributions in a chain of integrodifferential equations known as the BBGKY hierarchy. We can lump our ignorance of these other terms into a collision integral and write

\[
\frac{\partial f}{\partial t} = -\dot{r} \cdot \frac{\partial f}{\partial r} - \dot{p} \cdot \frac{\partial f}{\partial p} + \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}.
\]

In the absence of collisions, the distribution evolves solely due to the streaming term with \( \dot{r} = p/m \) and \( \dot{p} = -\nabla U_{\text{ext}} \). If \( \dot{p} = F_{\text{ext}} \) is constant, we have the general solution

\[
f(r, p, t) = \varphi \left( r - \frac{pt}{m} + \frac{F_{\text{ext}} t^2}{2m}, p - \frac{F_{\text{ext}} t}{m} \right),
\]

valid for any initial condition \( f(r, p, t = 0) = \varphi(r, p) \). We write the convective derivative as \( \frac{\partial}{\partial t} = \frac{\partial}{\partial r} \cdot \dot{r} + \frac{\partial}{\partial p} \cdot \dot{p} \). Then the Boltzmann equation may be written \( \frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \).

- **Collisions**: We are concerned with two types of collision processes: single-particle scattering, due to a local potential, and two-particle scattering, due to interparticle forces. Let \( \Gamma \) denote the set of single particle kinematic variables, e.g., \( \Gamma = (p_x, p_y, p_z) \) for point particles and \( \Gamma = (p, L) \) for diatomic molecules. Then

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d\Gamma' \left\{ w(\Gamma | \Gamma') f(r, \Gamma'; t) - w(\Gamma' | \Gamma) f(r, \Gamma; t) \right\}
\]

for single particle scattering, and

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \left\{ w(\Gamma_1 \Gamma_1' | \Gamma' \Gamma_1') f_2(r, \Gamma', \Gamma_1; t) - w(\Gamma' \Gamma_1' | \Gamma \Gamma_1) f_2(r, \Gamma, \Gamma_1; t) \right\}
\approx \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \left\{ w(\Gamma_1 \Gamma_1' | \Gamma' \Gamma_1') f(r, \Gamma'; t) f(r, \Gamma_1; t) - w(\Gamma' \Gamma_1' | \Gamma \Gamma_1) f(r, \Gamma; t) f(r, \Gamma_1; t) \right\}.
\]

for two-body scattering, where \( f_2 \) is the two-body distribution, and where the approximation \( f_2(r, \Gamma'; \Gamma', \Gamma'; t) \approx f(r, \Gamma; t) f(\Gamma'; t) \) in the second line closes the equation. A quantity \( A(r, \Gamma) \) which is preserved by the dynamics between collisions then satisfies

\[
\frac{dA}{dt} = \frac{d}{dt} \int d^4r \int d\Gamma A(r, \Gamma) f(r, \Gamma, t) = \int d^4r \int d\Gamma A(r, \Gamma) \frac{\partial f}{\partial t} \Bigl|_{\text{coll}}.
\]

Quantities which are conserved by collisions satisfy \( \dot{A} = 0 \) and are called collisional invariants. Examples include \( A = 1 \) (particle number), \( A = p \) (linear momentum, if translational invariance applies), and \( A = \varepsilon_p \) (energy).
\begin{itemize}
  \item **Time reversal, parity, and detailed balance:** With $\Gamma = (p, L)$, we define the actions of time reversal and parity as

  \[ \Gamma^T = (-p, -L), \quad \Gamma^p = (-p, L), \quad \Gamma^C = (p, -L), \]

  where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w(\Gamma_1' \Gamma_1 | \Gamma_1') = w(\Gamma_1' \Gamma_{1T} | \Gamma^T_{1T} \Gamma_{1T}^T)$. Under conditions of detailed balance, this leads to $f^0(\Gamma) f^0(\Gamma_1) = f^0(\Gamma_{1T}) f^0(\Gamma_{1T}^T)$, where $f^0$ is the equilibrium distribution. For systems with both $P$ and $T$ symmetries, $w(\Gamma_1' \Gamma_1 | \Gamma_1') = w(\Gamma_{1C} \Gamma_{1C}^C | \Gamma^C_{1T} \Gamma^C_{1T}^T)$, whence $w(p', p'_1 | p, p_1) = w(p, p_1 | p', p'_1)$ for point particles.

  \item **Boltzmann’s H-theorem:** Let $h(r, t) = \int d\Gamma f(r, \Gamma, t) \ln f(r, \Gamma, t)$. Invoking the Boltzmann equation, it can be shown that $\frac{\partial h}{\partial t} \leq 0$, which means $\frac{\partial H}{\partial t} \leq 0$, where $H(t) = \int d\Gamma h(r, t)$ is Boltzmann’s H-function. $h(r, t)$ is everywhere decreasing or constant, due to collisions.

  \item **Weakly inhomogeneous gas:** Under equilibrium conditions, $f^0$ can be a function only of collisional invariants, and takes the Gibbs form $f^0(\Gamma, p) = C e^{(\mu + \vec{v} \cdot \varepsilon_f - \varepsilon_f)/k_B T}$. Assume now that $\mu, \vec{V}$, and $T$ are all weakly dependent on $r$ and $t$. $f^0$ then describes a local equilibrium and as such is annihilated by the collision term in the Boltzmann equation, but not by the streaming term. Accordingly, we seek a solution $f = f^0 + \delta f$. A lengthy derivation results in

  \[ \left\{ \frac{\varepsilon_f - h}{T} \vec{v} \cdot \vec{\nabla} T + m v_{\alpha} v_{\beta} Q_{\alpha \beta} - \frac{\varepsilon_f - h + T c_p}{c_V/k_B} \vec{\nabla} \cdot \vec{V} - \vec{F}_{ext} \cdot \vec{v} \right\} \frac{\partial f^0}{\partial t} + \frac{\partial \delta f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{coll}, \]

  where $\vec{v} = \frac{\partial \varepsilon_f}{\partial p}$ is the particle velocity, $h$ is the enthalpy per particle, $Q_{\alpha \beta} = \frac{1}{2} \left( \frac{\partial v_{\alpha}}{\partial x_{\beta}} + \frac{\partial v_{\beta}}{\partial x_{\alpha}} \right)$, and $\vec{F}_{ext}$ is an external force. For an ideal gas, $h = c_p T$. The RHS is to be evaluated to first order in $\delta f$. The simplest model for the collision integral is the relaxation time approximation, where $\left( \frac{\partial f}{\partial t} \right)_{coll} = -\frac{\delta f}{\tau}$. Note that this form does not preserve any collisional invariants. The scattering time is obtained from the relation $n\vec{v}_{rel} \sigma \tau = 1$, where $\sigma$ is the two particle total scattering cross section and $\vec{v}_{rel}$ is the average relative speed of a pair of particles. This says that there is on average one collision within a tube of cross sectional area $\sigma$ and length $\vec{v}_{rel} \tau$. For the Maxwellian distribution, $\vec{v}_{rel} = \sqrt{2} \vec{v} = \sqrt{\frac{16 k_B T}{\pi m}}$, so $\tau(T) \propto T^{-1/2}$. The mean free path is defined as $\ell = \vec{\tau} = \frac{1}{\sqrt{2 n \sigma}}$.

  \item **Transport coefficients:** Assuming $F_{ext}^\alpha = Q_{\alpha \beta} = 0$ and steady state, Eq. 8 yields

  \[ \delta f = -\frac{\tau (\varepsilon - c_p T)}{k_B T^2} (\vec{v} \cdot \vec{\nabla} T) f^0. \]

  The energy current is given by

  \[ j^\alpha_\varepsilon = \int \! d\Gamma \varepsilon_f v^\alpha \delta f = -\frac{n \tau}{k_B T^2} \left( v^\alpha v^\beta \varepsilon_f (\varepsilon_f - c_p T) \right) \frac{\partial T}{\partial x_{\beta}}. \]
\end{itemize}
For a monatomic gas, one finds $\kappa^{\alpha\beta} = \kappa\delta^{\alpha\beta}$ with $\kappa(T) = \frac{2}{3} n \ell \bar{v} c_p \propto T^{1/2}$. A similar result follows by considering any intensive quantity $\phi$ which is spatially dependent through the temperature $T(r)$. The $\phi$-current across the surface $z = 0$ is

$$j_\phi = n \bar{v} \int d^3v P(v) v_z \phi(z - \ell \cos \theta) + n \bar{v} \int d^3v P(v) v_z \phi(z + \ell \cos \theta) = -\frac{1}{3} n \bar{v} \ell \frac{\partial \phi}{\partial z} \bar{z}.$$ 

Thus, $j_\phi = -K \nabla T$, with $K = \frac{1}{3} n \ell \bar{v} \frac{\partial \phi}{\partial z}$ the associated transport coefficient. If $\phi = \langle \varepsilon \rangle$, then $\frac{\partial \phi}{\partial \varepsilon} = c_p$, yielding $\kappa = \frac{1}{3} n \ell \bar{v} c_p$. If $\phi = \langle p_z \rangle$, then $j_{p_z}^z = \Pi_z = -\frac{1}{3} n m \bar{v} \frac{\partial \psi}{\partial z}$, where $\eta$ is the shear viscosity. Using the Boltzmann equation in the relaxation time approximation, one obtains $\eta = \frac{1}{3} n m \bar{v}$. From $\kappa$ and $\eta$, we can form a dimensionless quantity $Pr = \eta c_p / m \kappa$, known as the Prandtl number. Within the relaxation time approximation, $Pr = 1$. Most monatomic gases have $Pr \approx \frac{2}{3}$.

- **Linearized Boltzmann equation**: To go beyond the phenomenological relaxation time approximation, one must grapple with the collision integral,

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3p_1 \int d^3p_1' \int d^3p_1'' w(p', p_1' | p, p_1) \left\{ f(p') f(p_1') - f(p) f(p_1) \right\},$$

which is a nonlinear functional of the distribution $f(p, t)$ (we suppress the $t$ index here). Writing $f(p) = f^0(p) + f^0(p) \psi(p)$, we have $\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = f^0(p) \hat{L} \psi + O(\psi^2)$, with

$$\hat{L} \psi(p) = \int d^3p_1 \int d\Omega |v - v_1| \frac{\partial \psi}{\partial \Omega} f^0(p_1) \left\{ \psi(p') + \psi(p_1') - \psi(p) - \psi(p_1) \right\}.$$ 

The linearized Boltzmann equation (LBE) then takes the form $\left( \hat{L} - \frac{\partial \psi}{\partial \Omega} \right) \psi = Y$, where

$$Y = \frac{1}{k_B T} \left\{ \frac{\varepsilon(p) - \frac{2}{3} k_B T}{k_B T} v \cdot \nabla T + m v \cdot \nabla \nabla + m v \nu \beta Q_{\alpha\beta} - \frac{k_B \varepsilon(p)}{c_v} \nabla \cdot \nabla \cdot \psi - F \cdot \psi \right\}.$$ 

for point particles. To solve the LBE, we must invert the operator $\hat{L} - \frac{\partial \psi}{\partial \Omega}$. Various useful properties follow from defining the inner product $\langle \psi_1 | \psi_2 \rangle \equiv \int d^3p f^0(p) \psi_1(p) \psi_2(p)$, such as the self-adjointness of $L$: $\langle \psi_1 | \hat{L} \psi_2 \rangle = \langle \hat{L} \psi_1 | \psi_2 \rangle$. We then have $\hat{L} \langle \phi_n \rangle = -\lambda_n \langle \phi_n \rangle$, with $\langle \phi_n | \phi_m \rangle = \delta_{nm}$ and real eigenvalues $\lambda_n$. There are five zero eigenvalues corresponding to the collisional invariants:

$$\phi_1(p) = \frac{1}{\sqrt{n}}, \quad \phi_{2,3,4}(p) = \frac{p_\alpha}{\sqrt{nmk_B T}}, \quad \phi_5(p) = \sqrt{\frac{2}{3n}} \left( \frac{\varepsilon(p) - \frac{3}{2}}{k_B T} \right).$$ 

When $Y = 0$, the formal solution to $\frac{\partial \phi}{\partial t} = \hat{L} \psi$ is $\psi(p, t) = \sum_n C_n \phi_n(p) e^{-\lambda_n t}$. Aside from the collisional invariants, all the eigenvalues $\lambda_n$ must be positive, corresponding to relaxation to the equilibrium state. One can check that the particle, energy, and heat currents are given by $j = \langle v | \psi \rangle$, $j_\varepsilon = \langle v \varepsilon | \psi \rangle$, and $j_q = \langle v (\varepsilon - \mu) | \psi \rangle$. 

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In steady state, the solution to $\hat{L}\psi = Y$ is $\psi = \hat{L}^{-1}Y$. This is valid provided $Y$ is orthogonal to each of the collisional invariants, in which case

$$\psi(p) = \sum_{n \in \text{Cl}} \lambda^{-1}_n \langle \phi_n | Y \rangle \phi_n(p).$$

Once we have $|\psi\rangle$, we may obtain the various transport coefficients by computing the requisite currents. For example, to find the thermal conductivity $\kappa$ and shear viscosity $\eta$, we have:

$$\kappa : \quad Y = \frac{1}{k_B T} \frac{\partial T}{\partial x} X_\kappa \quad \Rightarrow \quad \kappa = -\frac{\langle X_\kappa | \psi \rangle}{\partial \psi / \partial x},$$

$$\eta : \quad Y = \frac{m}{k_B T} \frac{\partial V_x}{\partial y} X_\eta \quad \Rightarrow \quad \eta = -\frac{m \langle X_\eta | \psi \rangle}{\partial V_x / \partial y}.$$ 

- **Variational approach:** The Schwarz inequality, $\langle \psi | -\hat{L} \psi \rangle \cdot \langle \phi | \hat{H} | \psi \rangle \geq \langle \phi | \hat{H} | \psi \rangle^2$, holds for the positive semidefinite operator $\hat{H} \equiv -\hat{L}$. One therefore has

$$\kappa \geq \frac{1}{k_B T^2} \frac{\langle \phi | X_\kappa \rangle^2}{\langle \phi | \hat{H} | \phi \rangle}, \quad \eta \geq \frac{m^2}{k_B T} \frac{\langle \phi | X_\eta \rangle^2}{\langle \phi | \hat{H} | \phi \rangle}.$$

Using variational functions $\phi_\kappa = (\epsilon - \frac{5}{2}k_B T)v_x$ and $\phi_\eta = v_x v_y$, one finds, after tedious calculations,

$$\kappa \geq \frac{75 k_B}{64 \sqrt{\pi} d^2} \left( \frac{k_B T}{m} \right)^{1/2}, \quad \eta \geq \frac{5 (m k_B T)^{1/2}}{16 \sqrt{\pi} d^2}.$$ 

Taking the lower limit in each case, we obtain a Prandtl number $Pr = \frac{\eta c_p}{m \kappa} = \frac{2}{3}$, which is close to what is observed for monatomic gases.

- **Quantum transport:** For quantum systems, the local equilibrium distribution is of the Bose-Einstein or Fermi-Dirac form,

$$f^0(r, \mathbf{k}, t) = \left\{ \exp \left( \frac{\epsilon(\mathbf{k}) - \mu(r, t)}{k_B T(r, t)} \right) \pm 1 \right\}^{-1},$$

with $k = p/\hbar$, and

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int \frac{d^3k_1}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \int \frac{d^3k''}{(2\pi)^3} w \left\{ f' f'_1 (1 \pm f') (1 \pm f'_1) - f f'_1 (1 \pm f) (1 \pm f'_1) \right\}$$

where $w = w(k, k', k''), f = f(k), f_1 = f(k_1), f' = f(k'),$ and $f'_1 = f(k'_1)$, and where we have assumed time-reversal and parity symmetry. The most important application is to electron transport in metals and semiconductors, in which case $f^0$ is the Fermi distribution. With $f = f^0 + \delta f$, one has, within the relaxation time approximation,

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} v \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} - v \cdot \left[ e \mathbf{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau},$$
where $\mathbf{E} = -\nabla(\phi - \mu/e) = \mathbf{E} - e^{-1} \nabla \mu$ is the gradient of the ‘electrochemical potential’ $\phi - e^{-1} \mu$. For steady state transport with $B = 0$, one has

$$j = -2e \int_{\Omega} \frac{d^3k}{(2\pi)^3} \mathbf{v} \delta f \equiv L_{11} \mathbf{E} - L_{12} \nabla T$$

$$j_q = 2 \int_{\Omega} \frac{d^3k}{(2\pi)^3} (\epsilon - \mu) \mathbf{v} \delta f \equiv L_{21} \mathbf{E} - L_{22} \nabla T$$

where $L_{11}^{\alpha \beta} = e^2 J_{0}^{\alpha \beta}$, $L_{21}^{\alpha \beta} = T L_{12}^{\alpha \beta} = -e J_{1}^{\alpha \beta}$, and $L_{22}^{\alpha \beta} = \frac{1}{T} J_{2}^{\alpha \beta}$, with

$$J_{n}^{\alpha \beta} \equiv \frac{1}{4\pi^3 \hbar} \int d\epsilon \tau(\epsilon) (\epsilon - \mu)^n \left( -\frac{\partial f_0}{\partial \epsilon} \right) \int dS_{\epsilon} v^{\alpha} v^{\beta} |\mathbf{v}| .$$

These results entail

$$\mathbf{E} = \rho j + Q \nabla T , \quad j_q = \Box j - \kappa \nabla T ,$$

or, in terms of the $J_n$,

$$\rho = \frac{1}{e^2} J_{0}^{-1} \quad , \quad Q = -\frac{1}{e T} J_{0}^{-1} J_{1} \quad , \quad \Box = -\frac{1}{e} J_{1} J_{0}^{-1} J_{1} \quad , \quad \kappa = \frac{1}{T} (J_{2} - J_{1} J_{0}^{-1} J_{1}) .$$

These results describe the following physical phenomena:

**Electrical resistance** ($\nabla T = B = 0$): An electrical current $j$ will generate an electric field $\mathbf{E} = \rho j$, where $\rho$ is the electrical resistivity.

**Peltier effect** ($\nabla T = B = 0$): An electrical current $j$ will generate an heat current $j_q = \Box j$, where $\Box$ is the Peltier coefficient.

**Thermal conduction** ($j = B = 0$): A temperature gradient $\nabla T$ gives rise to a heat current $j_q = -\kappa \nabla T$, where $\kappa$ is the thermal conductivity.

**Seebeck effect** ($j = B = 0$): A temperature gradient $\nabla T$ gives rise to an electric field $\mathbf{E} = Q \nabla T$, where $Q$ is the Seebeck coefficient.

For a parabolic band with effective electron mass $m^*$, one finds

$$\rho = \frac{m^*}{ne^2 \tau} \quad , \quad Q = -\frac{\pi^2 k_B^2 T}{2e \epsilon_F} \quad , \quad \kappa = \frac{\pi^2 n \tau k_B^2 T}{3m^*}$$

with $\Box = TQ$, where $\epsilon_F$ is the Fermi energy. The ratio $\kappa/\sigma T = \frac{\epsilon_F^2 (k_B/e)^2}{3} = 2.45 \times 10^{-8} \sqrt{2} \text{K}^{-2}$ is then predicted to be universal, a result known as the Wiedemann-Franz law. This also predicts all metals to have negative thermopower, which is not the case. In the presence of an external magnetic field $B$, additional transport effects arise:

**Hall effect** ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$): An electrical current $j = j_x \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an electric field $\mathbf{E}$. The Hall coefficient is $R_{\text{H}} = \mathbf{E}_y / j_x B_z$. 

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**Ettingshausen effect** ($\partial T/\partial x = j_y = j_{q,y} = 0$): An electrical current $j = j_x \dot{x}$ and a field $B = B_z \dot{z}$ yield a temperature gradient $\partial T/\partial y$. The Ettingshausen coefficient is $P = \partial T/\partial y / j_x B_z$.

**Nernst effect** ($j_x = j_y = \partial T/\partial y = 0$): A temperature gradient $\nabla T = \partial T/\partial x \dot{x}$ and a field $B = B_z \dot{z}$ yield an electric field $\mathcal{E}$. The Nernst coefficient is $\Lambda = \mathcal{E}_y / \partial T / \partial x B_z$.

**Righi-Leduc effect** ($j_x = j_y = \mathcal{E}_y = 0$): A temperature gradient $\nabla T = \partial T / \partial x \dot{x}$ and a field $B = B_z \dot{z}$ yield an orthogonal gradient $\partial T / \partial y$. The Righi-Leduc coefficient is $\mathcal{L} = \partial T / \partial y / \partial T / \partial x B_z$.

- **Stochastic processes**: Stochastic processes involve a random element, hence they are not wholly deterministic. The simplest example is the Langevin equation for Brownian motion, $\ddot{p} + \gamma p = F + \eta(t)$, where $p$ is a particle’s momentum, $\gamma$ a damping rate due to friction, $F$ an external force, and $\eta(t)$ a stochastic random force. We can integrate this first order equation to obtain

$$p(t) = p(0) e^{-\gamma t} + \frac{F}{\gamma} \left(1 - e^{-\gamma t}\right) + \int_0^t ds \eta(s) e^{\gamma(s-t)} .$$

We assume that the random force $\eta(t)$ has zero mean, and furthermore that

$$\langle \eta(s) \eta(s') \rangle = \phi(s - s') \approx \Gamma \delta(s - s') ,$$

in which case one finds $\langle p^2(t) \rangle = \langle p(t) \rangle^2 + \frac{F^2}{\gamma^2} (1 - e^{-2\gamma t})$. If there is no external force, we expect the particle thermalizes at long times, i.e. $\langle \frac{p^2}{2m} \rangle = \frac{1}{2} k_B T$. This fixes $\Gamma = 2\gamma m k_B T$, where $m$ is the particle’s mass. One can integrate again to find the position. At late times $t \gg \gamma^{-1}$, one finds $\langle x(t) \rangle = \text{const.} + \frac{Ft}{\gamma m}$, corresponding to a mean velocity $\langle p/m \rangle = F/\gamma$. The RMS fluctuations in position, however, grow as

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 = \frac{2k_B T t}{\gamma m} \equiv 2Dt ,$$

where $D = k_B T / \gamma m$ is the diffusion constant. Thus, after the memory of the initial conditions is lost ($t \gg \gamma^{-1}$), the mean position advances linearly in time due to the external force, and the RMS fluctuations in position also increase linearly.

- **Fokker-Planck equation**: Suppose $x(t)$ is a stochastic variable, and define

$$\delta x(t) \equiv x(t + \delta t) - x(t) .$$

Furthermore, assume $\langle \delta x(t) \rangle = F_1(x(t)) \delta t$ and $\langle [\delta x(t)]^2 \rangle = F_2(x(t)) \delta t$, but that $\langle [\delta x(t)]^n \rangle = O(\delta t^2)$ for $n > 2$. One can then show that the probability density $P(x,t) = \langle \delta(x - x(t)) \rangle$ satisfies the Fokker-Planck equation,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \left[F_1(x) P(x,t)\right] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \left[F_2(x) P(x,t)\right] .$$
For Brownian motion, $F_1(x) = F/\gamma m \equiv u$ and $F_2(x) = 2D$. The resulting Fokker-Planck equation is then $P_t = -u P_x + D P_{xx}$, where $P_t = \frac{\partial P}{\partial t}$, $P_{xx} = \frac{\partial^2 P}{\partial x^2}$, etc. The Galilean transformation $x \rightarrow x - ut$ then results in $P_t = DP_{xx}$, which is known as the diffusion equation, a general solution to which is given by $P(x, t) = \int_{-\infty}^{\infty} dx' K(x - x', t - t') P(x', t')$, where

$$K(\Delta x, \Delta t) = (4\pi D \Delta t)^{-1/2} e^{-(\Delta x)^2/4D\Delta t}$$

is the diffusion kernel. Thus, $\Delta x_{\text{RMS}} = \sqrt{2D\Delta t}$. 

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