Solutions to Mid-Term Exam

1. Given that

$$f(t) = f_0(t) - i\lambda \int_0^t dt'\, e^{-i(t-t')\mathcal{L}_0}\, \mathcal{L}_1(t') f(t')$$

$$\therefore\ \dot{f}(t) = \dot{f}_0(t) - i\lambda \mathcal{L}_1(t) f(t) + i\mathcal{L}_0\, i\lambda \int_0^t dt'\, e^{-i(t-t')\mathcal{L}_0}\, \mathcal{L}_1(t') f(t')$$

$$= \dot{f}_0(t) - i\lambda \mathcal{L}_1(t) f(t) + i\mathcal{L}_0 \left(f_0(t) - f(t) \right)$$

$$= \dot{f}_0(t) - i\left(\mathcal{L}_0 + \lambda \mathcal{L}_1(t)\right) f(t) - \dot{f}_0(t)$$

$$= -i\mathcal{L} f(t)$$

which is the Liouville eqn. for the phase space density.

Similarly, given that

$$A(t) = A_0(t) + i\lambda \int_0^t dt'\, e^{i(t-t')\mathcal{L}_0}\, \mathcal{L}_1(t') A(t')$$

$$\therefore\ \dot{A}(t) = \dot{A}_0(t) + i\lambda \mathcal{L}_1(t) A(t) + i\mathcal{L}_0\, i\lambda \int_0^t dt'\, e^{i(t-t')\mathcal{L}_0}\, \mathcal{L}_1(t') A(t')$$

$$= \dot{A}_0(t) + i\lambda \mathcal{L}_1(t) A(t) + i\mathcal{L}_0 \left(A(t) - A_0(t) \right)$$

$$= \dot{A}_0(t) + i\left(\mathcal{L}_0 + \lambda \mathcal{L}_1(t)\right) A(t) - \dot{A}_0(t)$$

$$= i\mathcal{L} A(t)$$

which is the Liouville eqn. for a dynamical variable.

2. The Hamiltonian of the system is

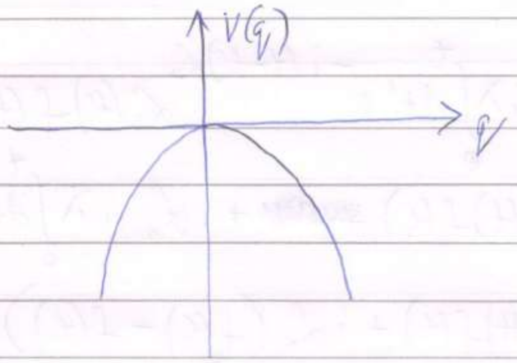
$$H = \frac{1}{2m} p^2 - \frac{k}{2} q^2$$

Its potential energy, $V(q)$, is

$$V(q) = -\frac{k}{2} q^2$$

which is an inverted parabola

a) So as a function of q, $V(q)$ looks like this

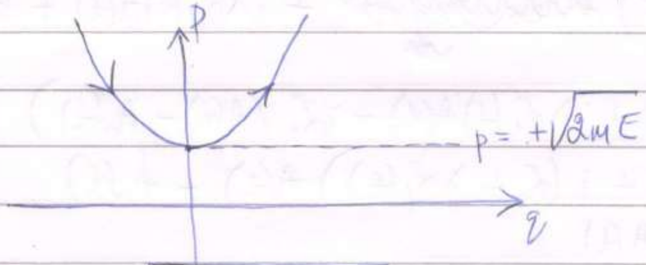


b) (i) Total energy $E > 0$

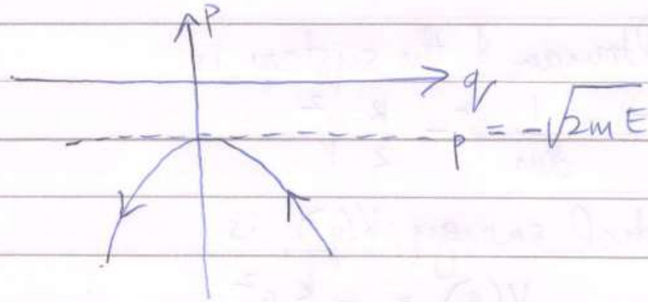
$$\frac{p^2}{2m} - \frac{k}{2}q^2 = E \quad \text{or}$$

$$\therefore \ p = \pm\sqrt{2m\left(E + \frac{k}{2}q^2\right)}$$

Consider $p = +\sqrt{2m(E+kq^2/2)}$. The variation of p with q is



Similarly for $p = -\sqrt{2m(E+kq^2/2)}$

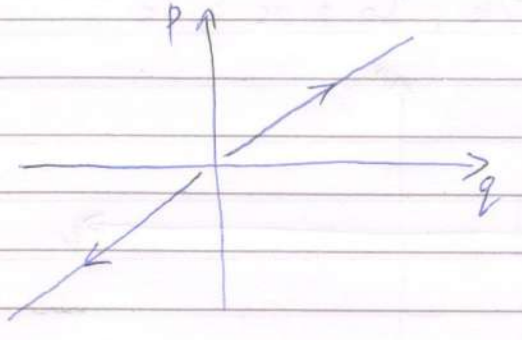


(ii) Total $E = 0$

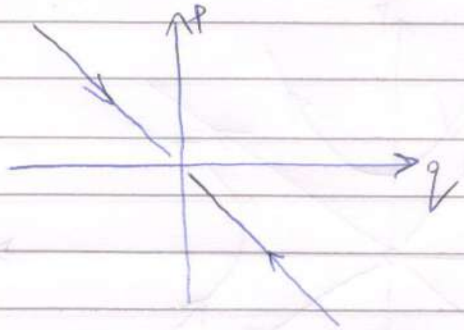
$$\therefore \ \frac{p^2}{2m} = \frac{kq^2}{2} \quad \text{or} \quad p = \pm\sqrt{mk}\, q$$

P.T.O.

Consider $p = +\sqrt{mk}\, q$. This is the equation of a straight line with positive slope, so variation of p with q is

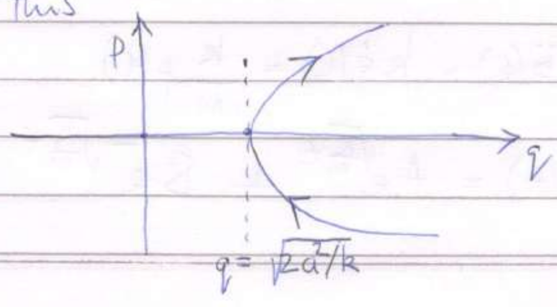


Notice that the trajectories do not actually meet at $p = q = 0$, since phase space trajectories cannot intersect. (The origin is a special trajectory)
Similarly, for $p = -\sqrt{mk}\, q$,



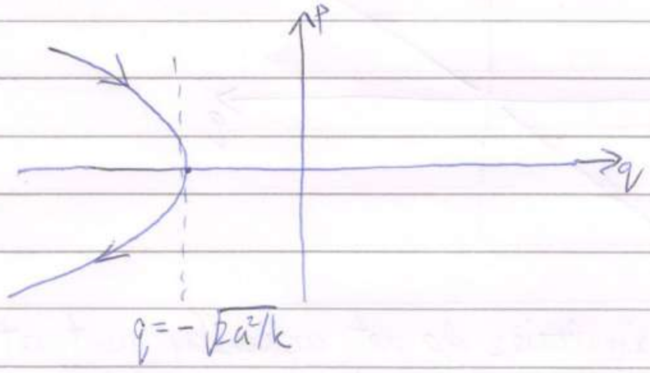
(iii) Total $E < 0$. Let $E = -a^2$, with 'a' real
Then
$$p = \pm\sqrt{2m\left(\frac{k}{2}q^2 - a^2\right)}$$

Consider $p = +\sqrt{2m\left(\frac{k}{2}q^2 - a^2\right)}$. For $q > 0$, q cannot be less than $\sqrt{2a^2/k}$.
$\therefore$ p vs q looks like this

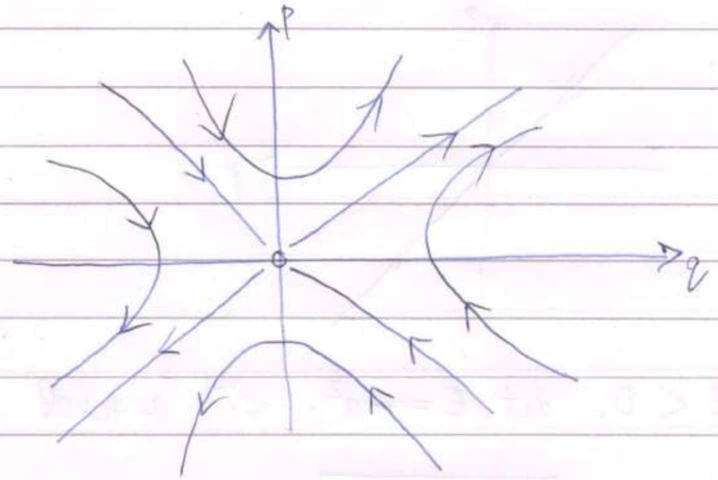


P.T.O.

Similarly for $p = -\sqrt{2m\left(\frac{kq^2}{2} - a^2\right)}$, when $q < 0$, q cannot be greater than $-\sqrt{2a^2/k}$. So p vs q is



So putting all the curves together, we have



(c) From the given Hamiltonian

$$\dot{p} = kq \quad \text{and} \quad \dot{q} = \frac{p}{m}$$

$$\therefore \ddot{p}(t) = k\dot{q}(t) = \frac{k}{m}p(t)$$

$$\therefore p(t) = Ae^{\sqrt{\frac{k}{m}}t} + Be^{-\sqrt{\frac{k}{m}}t}$$

Assuming $p(0)$ and $\dot{p}(0)$ are known, can solve for A and B.

$$A = \frac{1}{2}\sqrt{\frac{m}{k}}\,\dot{p}(0) + \frac{1}{2}p(0)$$

$$B = \frac{p(0)}{2} - \frac{1}{2}\sqrt{\frac{m}{k}}\,\dot{p}(0)$$

$$\therefore\ p(t) = \left(\frac{1}{2}\sqrt{\frac{m}{k}}\,\dot{p}(0) + \frac{1}{2}p(0)\right)e^{\sqrt{\frac{k}{m}}t} + \left(\frac{p(0)}{2} - \frac{1}{2}\sqrt{\frac{m}{k}}\,\dot{p}(0)\right)e^{-\sqrt{\frac{k}{m}}t}$$

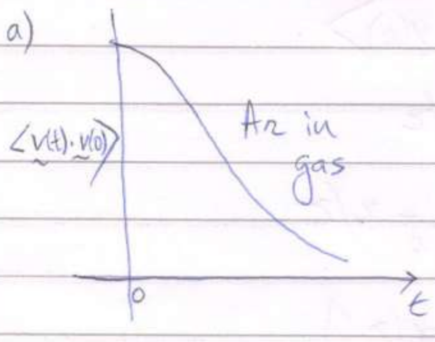
$$\therefore\ \langle p(t)p\rangle = \frac{1}{2}\langle p^2\rangle e^{\sqrt{k/m}\,t} + \frac{1}{2}\langle p^2\rangle e^{-\sqrt{k/m}\,t}$$

$$= \cancel{\tfrac{1}{4}}\langle p^2\rangle \cosh\sqrt{\frac{k}{m}}\,t$$

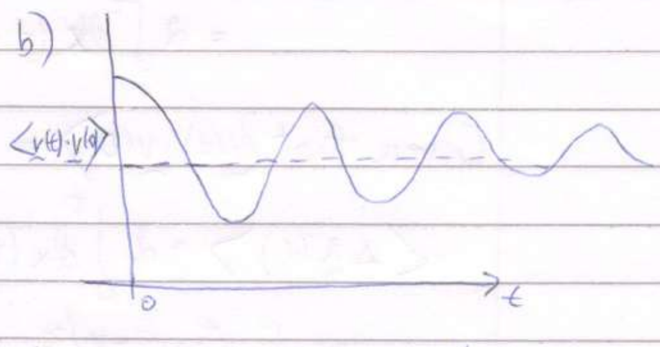
$$\text{or } \frac{\langle p(t)p\rangle}{\langle p^2\rangle} = \cosh\sqrt{\frac{k}{m}}\,t \equiv \bar{C}(t)$$

Graphically,

3 a)



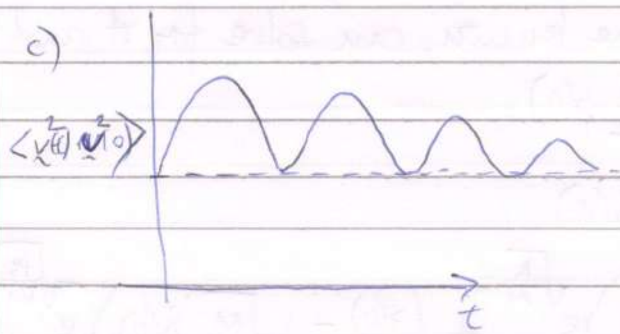
b)



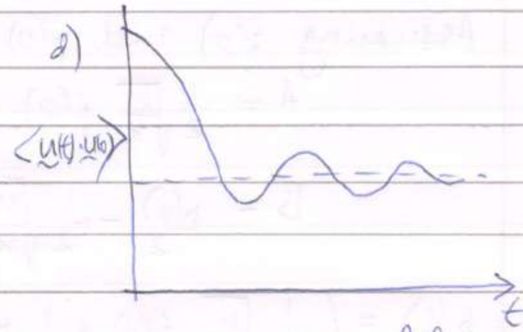
(Similar to the Q=0 oscillator model discussed in class)

P.T.O.

c)



d)



(like Q=0 oscillator model, but there are additional rotations, so decorrelation is faster)

In all these functions, the characteristic timescales are roughly determined by the mean collision time, and are in the picosecond to nanosecond regime.

4 a)

$$\Delta \underset{\sim}{r}(t) = \underset{\sim}{r}(t) - \underset{\sim}{r}(0) = \int_0^t dt' \, \underset{\sim}{v}(t')$$

$$\therefore \langle \Delta \underset{\sim}{r}^2(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle \underset{\sim}{v}(t_1) \cdot \underset{\sim}{v}(t_2) \rangle$$

$$= 2\int_0^t dt_1 \int_0^{t_1} dx \langle \underset{\sim}{v}(x) \cdot \underset{\sim}{v}(0) \rangle$$

$$= 2\int_0^t dx \, (t - x) \langle \underset{\sim}{v}(x) \cdot \underset{\sim}{v}(0) \rangle$$

Given that $\langle \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(0) \rangle = \langle \underset{\sim}{v}^2 \rangle e^{-t/\tau}$

$$\langle \Delta \underset{\sim}{r}^2(t) \rangle = 2\int_0^t dx \, (t-x) \langle \underset{\sim}{v}^2 \rangle e^{-x/\tau}$$

$$= 2\langle \underset{\sim}{v}^2 \rangle \left[t\int_0^t dx \, e^{-x/\tau} - \int_0^t dx \, x \, e^{-x/\tau} \right]$$

$$= 2\langle \underset{\sim}{v}^2 \rangle \left[t \frac{1}{(-1/\tau)} \left(e^{-t/\tau} - 1 \right) - \frac{1}{(-1/\tau)} \left\{ t e^{-t/\tau} - \frac{1}{(-1/\tau)} \left(e^{-t/\tau} - 1 \right) \right\} \right]$$

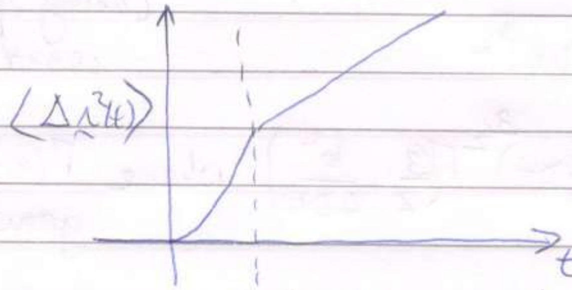
i.e. $$\langle \Delta \underset{\sim}{r}^2(t)\rangle = 2\langle \underset{\sim}{v}^2\rangle t\tau\left[1+\frac{\tau}{t}\left(e^{-t/\tau}-1\right)\right] \quad \ldots (1)$$

As $t\to\infty$, $\langle \Delta \underset{\sim}{r}^2(t)\rangle \sim t$, while as $t\to 0$

$$\langle \Delta \underset{\sim}{r}^2(t)\rangle \xrightarrow{t\to 0} 2t\tau\langle \underset{\sim}{v}^2\rangle\left[1+\frac{1}{t/\tau}\left(1-\frac{t}{\tau}+\frac{1}{2}\left(\frac{t}{\tau}\right)^2-\cdots-1\right)\right]$$

$$= \langle \underset{\sim}{v}^2\rangle t^2 + \cdots$$

Therefore, as a function of t, $\langle \Delta \underset{\sim}{r}^2(t)\rangle$ behaves as



$t \simeq \tau$ (crossover from ballistic to diffusive motion)

b) Since $\langle \Delta \underset{\sim}{r}^2(t)\rangle = 6Dt$, from Eq (1)

$$D = \lim_{t\to\infty}\frac{1}{3}\langle \underset{\sim}{v}^2\rangle\tau\left[1+\frac{1}{t/\tau}\left(e^{-t/\tau}-1\right)\right] = \frac{k_BT\tau}{m}$$ (using equipartition of energy)

For $D \simeq 10^{-5}\ cm^2\ s^{-1}$ and m corresponding to mass of a water molecule, with $T \equiv 300K$,

$$\tau \simeq 6.5\times 10^{-10}\ s = 650\ ps$$

c) The diffusion eqn. is given by

$$\frac{\partial G(\underset{\sim}{r},t)}{\partial t} = D\nabla_{\underset{\sim}{r}}^2 G(\underset{\sim}{r},t) \quad \ldots (2)$$

where $G(\underset{\sim}{r},t)$ can be interpreted as the probability, or fraction, of particles at $\underset{\sim}{r}$ at time t.

The solution of Eq (2) is (for $\underset{\sim}{r}_0 \neq \underset{\sim}{0}$)

$$G(\underset{\sim}{r},t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{(\underset{\sim}{r}-\underset{\sim}{r}_0)^2}{4Dt}\right)$$

The fraction of particles with $|\underset{\sim}{r}| > b$, where b is some number is

$$4\pi \int_b^\infty dr\, r^2 \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$ (using spherical polar coordinates)

$$= \frac{4\pi}{(4\pi Dt)^{3/2}} \cdot \frac{1}{2} (4Dt)^{3/2} \Gamma\left(\frac{3}{2}, \frac{b^2}{4Dt}\right)$$ where $\Gamma(a,B)$ is the incomplete gamma function

So for $b = 5$ Å, $D = 10^{-5}\ cm^2 s^{-1}$ and $t = 5\,ps$,

$$\text{Fraction} = \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, 12.5\right)$$

5. Given $H = \sum_{i=1}^{N} \sum_{\alpha} \left[\frac{1}{2m} p_{i\alpha}^2 + \frac{k}{2} r_{i\alpha}^2\right]$

From Hamilton's equations

$$\dot{p}_{i\alpha} = -k r_{i\alpha} \quad \text{and} \quad \dot{r}_{i\alpha} = \frac{1}{m} p_{i\alpha}$$

$$\therefore \ddot{r}_{i\alpha}(t) = -\frac{k}{m} r_{i\alpha} \Rightarrow r_{i\alpha}(t) = \frac{1}{\sqrt{mk}} p_{i\alpha}(0) \sin\sqrt{\frac{k}{m}}t + r_{i\alpha}(0)\cos\sqrt{\frac{k}{m}}t$$

$$\therefore \dot{r}_{i\alpha}(t) = \frac{1}{m} p_{i\alpha}(0) \cos\sqrt{\frac{k}{m}}t - \sqrt{\frac{k}{m}}\, r_{i\alpha}(0) \sin\sqrt{\frac{k}{m}}t$$

$$\therefore \dot{r}_{i\alpha}^2(t) = \frac{1}{m^2} p_{i\alpha}^2(0) \cos^2\sqrt{\frac{k}{m}}t + \frac{k}{m} r_{i\alpha}^2(0) \sin^2\sqrt{\frac{k}{m}}t - \frac{1}{m}\sqrt{\frac{k}{m}}\, p_{\alpha}(0) r_{i\alpha}(0) \sin 2\sqrt{\frac{k}{m}}t$$

$$\therefore \left\langle KE_{system}(t) \right\rangle = \frac{1}{2m} \cos^2\sqrt{\frac{k}{m}}t \sum_{i=1}^{N}\sum_{\alpha} \langle p_{i\alpha}^2(0) \rangle + \frac{k}{2}\sin^2\sqrt{\frac{k}{m}}t \sum_{i=1}^{N}\sum_{\alpha} \langle r_{i\alpha}^2(0) \rangle$$

The initial distribution is

$$P = C e^{-\sum_{i=1}^{N}(a \underset{\sim}{p}_i^2 + b \underset{\sim}{r}_i^2)}$$

$$\therefore \langle p_{i\alpha}^2 \rangle = C\left(\prod_{i=1}^{N}\int d\underset{\sim}{p}_i \int d\underset{\sim}{r}_i\right) p_{i\alpha}^2 \, e^{-\sum_{i=1}^{N}(a \underset{\sim}{p}_i^2 + b \underset{\sim}{r}_i^2)}$$

$$= C\int dp_{i\alpha}\, p_{i\alpha}^2 e^{-a p_{i\alpha}^2}\left(\prod_{\beta\neq\alpha}\int dp_{i\beta}\, e^{-a p_{i\beta}^2}\right)\left(\prod_{j\neq i}^{N}\prod_{\alpha}\int dp_{j\alpha}\, e^{-a p_{j\alpha}^2}\right) \cdot \left(\prod_{i=1}^{N}\prod_{\alpha}\int dr_{i\alpha}\, e^{-b r_{i\alpha}^2}\right)$$

$$= C\,\frac{1}{2a}\sqrt{\frac{\pi}{a}}\left(\sqrt{\frac{\pi}{a}}\right)^2\left(\frac{\pi}{a}\right)^{\frac{3}{2}(N-1)}\left(\frac{\pi}{b}\right)^{3N/2} = \frac{C}{2a}\left(\frac{\pi^2}{ab}\right)^{3N/2}$$

Similarly

$$\langle r_{i\alpha}^2 \rangle = \frac{C}{2b}\left(\frac{\pi^2}{ab}\right)^{3N/2}$$

$$\therefore \left\langle KE_{system}(t)\right\rangle = \frac{3N}{2m}\cos^2\sqrt{\frac{k}{m}}t \cdot \frac{C}{2a}\left(\frac{\pi^2}{ab}\right)^{3N/2} + \frac{3Nk}{2}\sin^2\sqrt{\frac{k}{m}}t \cdot \frac{C}{2b}\left(\frac{\pi^2}{ab}\right)^{3N/2}$$

$$= \frac{3N}{2}\,C\left(\frac{\pi^2}{ab}\right)^{3N/2}\left[\frac{1}{2ma}\cos^2\sqrt{\frac{k}{m}}t + \frac{k}{2b}\sin^2\sqrt{\frac{k}{m}}t\right]$$

6. Given $C(t) = \langle v_z(t)\, v_z(0) \rangle$

Taylor expanding $C(t)$,

$$C(t) \simeq C(0) + \frac{t^2}{2!}\ddot{C}(0) + O(t^3)$$

(There is no odd term, since $C(t)$ is even in time)

Now $C(t) = \int d\Gamma\, f_0\, v_z^* \, e^{it\mathcal{L}}\, v_z$

$\therefore\ \ddot{C}(t) = \int d\Gamma\, f_0\, v_z^*\, i\mathcal{L}\, i\mathcal{L}\, v_z(t) = \int d\Gamma\, f_0\, v_z^*\, i\mathcal{L}\, \dot{v}_z(t)$

$= i\langle v_z | \mathcal{L}\, \dot{v}_z(t)\rangle = i\langle \mathcal{L} v_z | \dot{v}_z(t)\rangle$ (Hermiticity of $\mathcal{L}$)

$= -\langle i\mathcal{L} v_z | \dot{v}_z(t)\rangle = -\langle \dot{v}_z | \dot{v}_z(t)\rangle$

$\therefore\ \ddot{C}(0) = -\langle \dot{v}_z | \dot{v}_z\rangle$

But $\dot{v}_z = \frac{F_z}{m}$, where F_z is the force along z

$\therefore\ \ddot{C}(0) = -\frac{1}{m^2}\langle F_z | F_z\rangle = -\frac{1}{m^2}\left\langle\left(\frac{\partial U}{\partial z}\right)^2\right\rangle$, where U is the energy

$\left\langle\left(\frac{\partial U}{\partial z}\right)^2\right\rangle = \mathcal{N}\int d\Gamma\, e^{-\beta U}\left(\frac{\partial U}{\partial z}\right)^2$, where $\mathcal{N}$ is a normalization

and we're assuming particle is in a reservoir of temperature T.

$\left\langle\left(\frac{\partial U}{\partial z}\right)^2\right\rangle = -\frac{\mathcal{N}}{\beta}\int d\Gamma\left(\frac{\partial e^{-\beta U}}{\partial z}\right)\frac{\partial U}{\partial z}$

$= -\frac{\mathcal{N}}{\beta}\left[e^{-\beta U}\frac{\partial U}{\partial z}\Big|_S - \int d\Gamma\, e^{-\beta U}\frac{\partial^2 U}{\partial z^2}\right] = +\frac{1}{\beta}\left\langle\frac{\partial^2 U}{\partial z^2}\right\rangle$

$\therefore\ C(t) \simeq \langle v_z^2\rangle - \frac{t^2}{2m^2}k_BT\left\langle\frac{\partial^2 U}{\partial z^2}\right\rangle = \frac{k_BT}{m} - \frac{t^2}{2m^2}k_BT\left\langle\frac{\partial^2 U}{\partial z^2}\right\rangle$

$\simeq \cancel{\exp}\ \frac{k_BT}{m}\exp\left(-\frac{t^2}{2m}\left\langle\frac{\partial^2 U}{\partial z^2}\right\rangle\right)$