Phy 504 hw 3 solution

March 12, 2013

1 The Boltzmann Transport Equation

1. $\left[\frac{\partial f}{\partial t}\right]_{coll}$ obeys Boltzmann approximation: $F_{12}(\vec{r},\vec{p}_1,\vec{p}_2,t) \approx f_1(\vec{r},\vec{p}_1,t)\cdot f_2(\vec{r},\vec{p}_2,t)$. Therefore,

$$\left[\frac{\partial f}{\partial t}\right]_{coll} = \int d^3p_2 d\Omega|\vec{v}_1 - \vec{v}_2|\left(\frac{d\sigma}{d\Omega}\right)(f_1'f_2' - f_1f_2) \tag{1}$$

Consider the conservation $X(r,p_1) + X(r,p_2) = X(r,p_1') + X(r,p_2')$, as well as the identity $\delta^4(p_f - p_i) = \delta^4(p_i - p_f)$ and $|T_{fi}|^2 = |T_{if}|^2$, one can get the collision term as

$$\left[\frac{\partial f_1}{\partial_5}\right]_{coll} = \int d^3p_2 d^3p_1' d^3p_2' \delta^4(p_1' + p_2' - p1 - p2)|T_{fi}|^2(f_2'f_1' - f_2f_1) \tag{2}$$

The conservation requires $X(r,p_1) + X(r,p_2) = X(r,p_1') + X(r,p_2')$ we have

$$\begin{aligned}\int d^3p_1 X(r,p_1)\left[\frac{\partial f_1}{\partial_5}\right]_{coll} &= \int d^3p_1 d^3p_2 d^3p_1' d^3p_2'[X(r,p_1') + X(r,p_2') - X(r,p_2)] \\ &\quad \times \delta^4(p_1' + p_2' - p_1 - p_2)|T_{fi}|^2(f_2'f_1 - f_2f_1)\end{aligned} \tag{3}$$

Apply the i and f exchange for the first term in the bracket and apply i and f, 1 and 2 for the second term, apply 1 and 2 for the third term, then the integral becomes $-3\int d^3p_1 X(r,p_1)\left[\frac{\partial f_1}{\partial_5}\right]_{coll}$. This means

$$\int d^3p_1 X(r,p)\left[\frac{\partial f_1}{\partial_5}\right]_{coll} = 0 \tag{4}$$

2. Use the Boltzmann Transport Equation for the result above

$$\int d^3p_1 X(r,p)\left[\frac{\partial f_1}{\partial_5}\right]_{coll} = \int d^3p X(r,p)\left(\frac{\partial}{\partial t} + \frac{p}{m}\cdot\nabla_r + F\cdot\nabla_p\right) f \tag{5}$$

Do some transformations

$$\begin{aligned}\int d^3p X(r,p)\frac{p}{m}\cdot\nabla_r f &= \int d^3p\left[\frac{\partial}{\partial r}\cdot(Xvf) - \frac{\partial X}{\partial r}\cdot vf\right] \\ &= \frac{\partial}{\partial r}\cdot\langle nXv\rangle - n\langle\frac{\partial X}{\partial r}\cdot v\rangle\end{aligned} \tag{6}$$

and

$$\begin{aligned}\int d^3p X(r,p)F\cdot\nabla_p f &= -\int d^3p\frac{\partial}{\partial p}\cdot(XF)f \\ &= -\frac{n}{m}\langle\frac{\partial X}{\partial v}\cdot F\rangle - \frac{n}{m}\langle X\frac{\partial}{\partial v}\cdot F\rangle\end{aligned} \tag{7}$$

Therefore, we can finally get the conservation theorem

$$\frac{\partial}{\partial t}\langle nX\rangle+\frac{\partial}{\partial r}\cdot\langle nvX\rangle-n\langle v\cdot\frac{\partial X}{\partial r}\rangle-\frac{n}{m}\langle F\cdot\frac{\partial X}{\partial v}\rangle-\frac{n}{m}\langle X\frac{\partial}{\partial v}\cdot F\rangle=0 \tag{8}$$

3. The value of X can take mass m or momentum mv or energy $\frac{1}{2}mv^2$
The Mass: $X=m$ one can get $\partial X/\partial\vec{r}=0$ and $\partial X/\partial v=0$.

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial r}\cdot(\rho u)-\frac{\rho}{m}\langle\frac{\partial}{\partial v}\cdot F\rangle=0 \tag{9}$$

so

$$\frac{\partial}{\partial t}\rho(\vec{r},t)+\nabla\cdot\vec{u}=\langle n\frac{\partial}{\partial v_i}F_i\rangle \tag{10}$$

The momentum: $X=mv_i$: The conservation theorem is

$$\begin{aligned}&\frac{\partial}{\partial t}\langle\rho v_i\rangle+\frac{\partial}{\partial r}\cdot\langle\rho\vec{v}v_i\rangle-\frac{\rho}{m}\langle F_i\rangle-\frac{\rho}{m}\langle v_i\frac{\partial}{\partial\vec{v}}\cdot\vec{F}\rangle\\ =&\rho\frac{\partial u_i}{\partial t}+\frac{\partial\rho}{\partial t}u_i+\frac{\partial}{\partial r_j}\cdot\langle\rho v_jv_i\rangle-\frac{\rho}{m}\langle F_i\rangle-\frac{\rho}{m}\langle v_i\frac{\partial}{\partial\vec{v}}\cdot\vec{F}\rangle\\ =&0\end{aligned} \tag{11}$$

This can be simplified using

$$\begin{aligned}\frac{P_{ij}}{\rho}&=\langle(v_i-u_i)(v_j-u_j)\rangle\\ &=\langle v_iv_j\rangle-u_iu_j\end{aligned} \tag{12}$$

With the conservation theorem of mass, the momentum conservation can be finally reduced to

$$\rho\frac{\partial u_i}{\partial t}+\rho\frac{\partial u_i}{\partial r_j}u_j+\frac{\partial P_{ij}}{\partial r_j}=\langle nF_i\rangle+\langle n(v_i-u_i)\frac{\partial}{\partial v_j}F_j\rangle \tag{13}$$

The Energy: $X=\frac{1}{2}m(\vec{v}-\vec{u})^2$: The conservation theorem is

$$\frac{\partial(nE)}{\partial t}+\frac{1}{2}m\frac{\partial}{\partial\vec{r}}\cdot\langle n\vec{v}(\vec{v}-\vec{u})^2\rangle-\frac{1}{2}\rho\langle\cdot\frac{\partial}{\partial\vec{r}}(\vec{v}-\vec{u})^2\rangle-\frac{1}{2}n\langle\vec{F}\cdot\frac{\partial}{\partial\vec{v}}(\vec{v}-\vec{u})^2\rangle-\frac{1}{2}\langle(\vec{v}-\vec{u})^2\frac{\partial}{\partial\vec{v}}\cdot F\rangle \tag{14}$$

where $E(r,t)=\frac{1}{2}m\langle(\vec{v}-\vec{u})^2\rangle$
Define the velocity strain tensor

$$\Lambda_{ij}=\frac{1}{2}m\left(\frac{\partial u_i}{\partial r_j}+\frac{\partial u_j}{\partial r_i}\right) \tag{15}$$

After simplification, one can get

$$\frac{\partial\theta}{\partial t}+\vec{u}\cdot\nabla_r\theta+\frac{2}{3n}\nabla_r\cdot\vec{q}+\frac{2}{3n}P_{ij}\Lambda_{ij}=\frac{1}{3}\langle(\vec{v}-\vec{u})^2\frac{\partial}{\partial\vec{v}}\cdot\vec{F}\rangle-\frac{\theta}{mn}\langle n\frac{\partial}{\partial\vec{v}}\cdot\vec{F}\rangle \tag{16}$$

4. Consider $f(\vec{r},\vec{p},t)$ is a Maxwell-Boltzmann distribution in the form of

$$f(\vec{r},\vec{p},t)=\frac{n}{(2\pi m\theta)^{3/2}}\exp\left[-\frac{(\vec{p}-m\vec{u})^2}{2m\theta}\right] \tag{17}$$

The pressure tensor becomes

$$
\begin{aligned}
P_{ij} &= \rho\langle(v_i - u_i)(v_j - u_j)\rangle \\
&= \frac{\rho}{nm^2}\int d^3\vec{p}(p_i - mu_i)(p_j - mu_j)f(r,p,t) \\
&= \delta_{ij}\frac{1}{m}\int d^3\vec{p}(p_i - mu_i)^2 f(r,p,t) \\
&= \delta_{ij}n\theta
\end{aligned} \tag{18}
$$

while the heat flux $\vec{q} = 0$ because of oddity. The conservation theorems become

$$
\begin{aligned}
&\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{u}) = 0 \\
&\rho(\frac{\partial u_i}{\partial t} + u_j\frac{\partial u_i}{\partial r_j}) + \frac{\partial(n\theta)}{\partial r_i} - F_i = 0 \\
&\frac{\partial\theta}{\partial t} + \vec{u}\cdot\nabla\theta + \frac{2}{3}\theta\nabla\cdot\vec{u} = 0
\end{aligned} \tag{19}
$$

2 Random Walks and Diffusion

1, The Langevin equation describing the overdamped motion of a random walker reads

$$\frac{d\vec{r}}{dt} = \vec{\eta}(t) \tag{20}$$

Integrating it over a time step τ, the change of position is

$$\vec{r}(t+\tau) - \vec{r}(t) = \tau\vec{\eta}(t) \tag{21}$$

Then at each time step, the displacement of the random walker is given by the random displacement $\tau\vec{\eta}(t)$. That means each direction for the hop is equally likely. The hop does not depend on the history. So we conclude that the integral of Langevin equation leads to the rules required for a random walk.

2, In d dimension, the probability of moving along $a\hat{e}_\mu$ is $1/(2d)$ because every dimension has two directions, the probability of finding the random walker at r in N time steps is in the recursive relation

$$P(r,0,N) = \sum_{d=\pm a\hat{e}_\mu} P(r-d,0,N-1)\frac{1}{2d} \tag{22}$$

The initial condition is $P(r,0,0) = \delta_{r,0}$

3, From the recursion relation

$$P(r,0,t+\tau) = \sum_{d=\pm a\hat{e}_\mu} P(r-d,0,N-1)\frac{1}{2d}$$

This can be written in the form of

$$\frac{P(r,0,t+\tau) - P(r,0,t)}{\tau} = \frac{a^2}{2d\tau}\sum_\mu \frac{P(r+a\hat{e}_\mu,0,\tau) - P(r,0,t) + P(r+a\hat{e}_\mu,\tau)}{a^2} \tag{23}$$

In the continuum limit, we take $a \to 0$ and $\tau \to 0$, then

$$\frac{\partial P(r,0,t)}{\partial t} = \frac{a^2}{2d\tau}\nabla^2 P(r,0,t) \tag{24}$$

The coefficient is so called the diffusion constant $D = \frac{a^2}{2d\tau}$

4, The equation in 3 is solvable by Fourier Transforamtion, let

$$\tilde{P} = \int dk e^{-ikx} P(x,t) \tag{25}$$

we get

$$\frac{\partial}{\partial t}\tilde{P} = -Dk^2\tilde{P} \tag{26}$$

That has the solution

$$\tilde{P}(u,t) = e^{-Dk^2 t} \tag{27}$$

By inverse Fourier transformation

$$P(x,t) = (4\pi Dt)^{-d/2} e^{-x^2/(4Dt)} \tag{28}$$

For $P(\vec{r},0,N)$ where $N = t/\tau$

$$P(\vec{r},0,N) = (4\pi DN\tau)^{-d/2} e^{-r^2/(4DN\tau)} \tag{29}$$

$P(x,t)$ here is defined as the first passage time. The total probability for the walker to reach $\vec{r}$ after at most time t is

$$\begin{aligned} & 1 - \prod_0^\tau (1 - P(r,t)) \\ =& 1 - \exp(\int_0^\tau \ln(1 - P(t))dt \\ \approx& 1 - \exp\left(-\int_0^\tau \frac{\exp(-r^2/(4Dt))}{(4\pi Dt)^{d/2}} dt\right) \end{aligned} \tag{30}$$

5, Take the previously equation and set $r = 0$ and the integration is from $\tau \to \tau'$. For $d = 2$ The probability reduces to

$$P(0,\tau') = 1 - \exp\left(-\frac{\ln\frac{\tau'}{\tau}}{4\pi D}\right) \tag{31}$$

This result is quite understandable because if $\tau = 0$, we can 100% certain that the walker reaches origin because it starts from the origin!

3 Langevin Equation in a Force Field

1, There are several ways to prove, one of which is here:

The particle has equation of motion

$$m\ddot{x} = \eta(x,t) - \gamma\dot{x} + F(x) \tag{32}$$

Assume that the system is overdamped so

$$\dot{x} = \frac{\eta}{\gamma} + \frac{F}{\gamma} \tag{33}$$

The probability distribution $P(x,t)$ of finding the particle at x at time t if it departed from the origin at $t = 0$ satisfies

$$P(x, t+\epsilon) = \int d^3x' P(x', t)\langle x|T_\epsilon(t)|x'\rangle \tag{34}$$

where $\langle x|T_\epsilon(t)|x'\rangle$ is the prob of the particle going from x' to x in an infinitesimal time interval ϵ. The particle goes from x' to x at time t in random force

$$x - x' = \int_t^{t+\epsilon} d\tau \eta/\gamma + \epsilon F/\gamma \tag{35}$$

Assuming that the random force is Gaussian, the prob

$$\langle x|T_\epsilon(t)|x'\rangle = \left(\frac{\gamma^2}{2\pi\Gamma\epsilon}\right) \exp\left[-\frac{\gamma^2}{2\Gamma\epsilon}\left((x - x') - \epsilon\tilde{F}(x')\right)\right] \tag{36}$$

where $\tilde{F} = F/\gamma$.

It follows that

$$P(x,t) = \int d^3x' P(x', t-\epsilon)\left(\frac{\gamma^2}{2\pi\Gamma\epsilon}\right)^{3/2} \exp\left[-\frac{\gamma^2}{2\Gamma\epsilon}(x - x' - \epsilon\tilde{F}(x'))^2\right] \tag{37}$$

Consider the substitution

$$y = x' - x + \epsilon\tilde{F}(x') \tag{38}$$

$$d^3y = d^3x'(1 + \epsilon\nabla\cdot\tilde{F}(x'))$$

$$\approx d^3x'(1 + \epsilon\nabla\cdot\tilde{F}(x)) \tag{39}$$

The equation becomes

$$P(x,t) = \int d^3y(1 - \epsilon\nabla\cdot\tilde{F}(x))P(x + y - \epsilon\tilde{F}(x'), t-\epsilon)\left(\frac{\gamma^2}{2\pi\Gamma\epsilon}\right)^{3/2} \exp\left(-\frac{\gamma^2y^2}{2\Gamma\epsilon}\right) \tag{40}$$

Expanding and keeping terms up to $O(\epsilon)$ gives

$$P(x,t) = \int d^3y(1 - \epsilon\nabla\cdot\tilde{F}(x))\left(P(x,t) - \epsilon\partial_t P - \epsilon\tilde{F}(x)\cdot\nabla P + \frac{\epsilon\Gamma}{2\gamma^2}\nabla^2 P\right) \tag{41}$$

Finally collecting the $O(\epsilon)$ terms gives

$$\partial_t P + \nabla\cdot(\tilde{F}P) = \frac{\Gamma}{2\gamma^2}\nabla^2 P \tag{42}$$

or

$$\frac{d}{dt}P = \partial_x\left(\frac{1}{2\gamma}P\partial_x U\right) + \frac{1}{2}\partial_x^2\Gamma P \tag{43}$$

2.

At equilibrium $dP/dt = 0$, on substitution we get

$$\partial_x \left(\frac{1}{\gamma} P \partial U \right) + \frac{1}{2} \partial_x^2 \Gamma P = 0 \tag{44}$$

The solution is in the form of

$$P_{eq} \propto e^{-2U/(\gamma\Gamma)} \tag{45}$$

The role of kT is played by $\frac{1}{2}\gamma\Gamma$

3. From the Fokker-Planck equation

$$\partial_t P + \nabla \cdot (\tilde{F} P) = \frac{\Gamma}{2\gamma^2} \nabla^2 P \tag{46}$$

we can write

$$\partial_t P = -\frac{\mathcal{H}}{\hbar} P \tag{47}$$

where $\mathcal{H} = -\frac{\hbar\Gamma}{2\gamma^2}\nabla^2 + \hbar(\nabla \cdot \tilde{F} + \tilde{F} \cdot \nabla)$

Express the $P(x,t)$ in terms of a path integral. Divide the time interval t into N equal parts of infinitesimal length ϵ

$$\begin{aligned} P(x,t) &= \langle x | e^{-tH\mathcal{H}/\hbar} 0 \rangle \\ &= \int \left(\prod_{i=1}^{N-1} d^3 x_i \right) \left(\prod_{i=0}^{N-1} \langle x_{i+1} | e^{-\epsilon \mathcal{H}/\hbar} | x_i \rangle \right) \end{aligned} \tag{48}$$

Then computing

$$\begin{aligned} \langle x_{i+1} | e^{-\epsilon\mathcal{H}/\hbar} | x_i \rangle &= \langle x_{i+1} 1 - \frac{\epsilon}{\hbar} \mathcal{H} + O(\epsilon^2) | x_i \rangle \\ &= \int \frac{d^3 p_i}{(2\pi\hbar)^3} \langle x_{i+1} | 1 - \frac{\epsilon}{\hbar} \mathcal{H} + O(\epsilon^2) | p_i \rangle \langle p_i | x_i \rangle \\ &= \cdots \\ &= const \times \exp \left[-\frac{\epsilon}{2} \frac{\gamma^2}{\Gamma} (\frac{1}{\gamma} \nabla U - \dot{x}_i)^2 - \frac{\epsilon}{\gamma} \nabla^2 U \right] \end{aligned} \tag{49}$$

we obtain

$$\begin{aligned} P(x,t) \propto & \int \left(\prod_{i=1}^{N-1} d^3 x_i \right) \left(\prod_{i=0}^{N-1} \exp \left[-\frac{\epsilon}{2} \frac{\gamma^2}{\Gamma} \left(\frac{1}{\gamma} \nabla U - \dot{x}_i \right)^2 - \frac{\epsilon}{\gamma} \nabla^2 U \right] \right) \\ & \int \left(\prod_{i=1}^{N-1} d^3 x_i \right) \left(\exp \sum_{i=1}^{N-1} \left[-\frac{\epsilon}{2} \frac{\gamma^2}{\Gamma} \left(\frac{1}{\gamma} \nabla U - \dot{x}_i \right)^2 - \frac{\epsilon}{\gamma} \nabla^2 U \right] \right) \\ &= \int Dx \exp \int_0^t d\tau \left[-\frac{\epsilon}{2} \frac{\gamma^2}{\Gamma} \left(\frac{1}{\gamma} \nabla U - \dot{x}_i \right)^2 - \frac{\epsilon}{\gamma} \nabla^2 U \right] \\ &= \int Dx \exp[-\frac{1}{\hbar} S(x, \dot{x})] \end{aligned} \tag{50}$$

where

$$S(x,\dot{x}) = \hbar \int_0^t d\tau \left[\frac{\gamma^2}{2\Gamma} \left(\frac{1}{\gamma} \nabla U - \dot{x} \right)^2 + \frac{1}{\gamma} \nabla^2 U \right] \tag{51}$$

is the classical action.

4.

When U_0 is small, $(\nabla U)^2 \to 0$the action becomes

$$S(x, \dot{x}) \approx \hbar \int_0^t d\tau \left[\frac{\gamma^2}{2\Gamma}\dot{x}^2 - \frac{\gamma}{\Gamma}(\nabla U)\cdot \dot{x} + \frac{1}{\gamma}\nabla^2 U \right] \tag{52}$$

and the probability distribution is

$$\begin{aligned} P(x,t) &= const \times \int Dx \exp\left(- \int d\tau \left[\frac{\gamma^2}{2\Gamma}\dot{x}^2 - \frac{\gamma}{\Gamma}(\nabla U)\cdot \dot{x} + \frac{1}{\gamma}\nabla^2 U \right] \right) \\ &\approx const \times \int Dx \exp(-\frac{\gamma^2}{2\Gamma}\int_0^t d\tau \dot{x}^2)(1 - \int_0^t d\tau[-\frac{\gamma}{\Gamma}(\nabla U)\cdot \dot{x} + \frac{1}{\gamma}\nabla^2 U]) \end{aligned} \tag{53}$$

The constant which is independent of U, can be determined by ensuring that the probability distribution sums to unity

$$\int dx P(x,t) = 1 \tag{54}$$

The difference between the true probability of distirbution $P(x,t)$ and the free walker distribution is

$$const \times \int Dx \exp \int Dx \exp(-\frac{\gamma^2}{2\Gamma}\int_0^t d\tau \dot{x}^2) \int_0^t d\tau[-\frac{\gamma}{\Gamma}(\nabla U)\cdot \dot{x} + \frac{1}{\gamma}\nabla^2 U] \tag{55}$$

Take the $U = U_0 e^{-r^2/(2\epsilon^2)}$ then

$$\langle x|e^{-tH}|0\rangle \approx \frac{1}{4U_0\epsilon^2\gamma}\frac{1}{(2\pi\Gamma)^{3/2}t^{1/2}}e^{-r^2/(2\Gamma t)}e^{-\frac{U_0}{2\gamma\Gamma}(1-e^{-r^2/(2\epsilon^2)})} \tag{56}$$

The dimensionless quantity is $U_0/(\Gamma\gamma)$

5, The total probability of being at origin is

$$\langle 0|e^{-t\tilde{H}}|0\rangle = \frac{1}{4\epsilon^2\gamma}\frac{1}{(2\pi\Gamma)^{3/2}U_0 t^{1/2}}e^{-\frac{U_0}{2\gamma\Gamma}} \tag{57}$$

This has a $t^{-1/2}$ dependence, so it is somewhat like the $d = 1$ case. The increase of U_0 enhances the exclusion and reduces the probability of returning to origin.

4 Path Integral and the Density Matrix

1, The Hamiltonian of the particle is

$$\mathcal{H} = \frac{p^2}{2m} + U(q) \tag{58}$$

To evaluate the partition function

$$\begin{aligned} Z &= tre^{-\beta\mathcal{H}} \\ &= \int d^3q \langle q|e^{-\beta\mathcal{H}}|q\rangle \end{aligned} \tag{59}$$

Divide $\beta\hbar$ into N infinitesimal parts of length ϵ, and write

$$\langle q|e^{-\beta\mathcal{H}}|q\rangle = \int \left(\prod_{i=1}^{N-1} dq_i\right)\left(\prod_{i=0}^{N-1}\langle q_{i+1}|e^{-\epsilon\mathcal{H}/\hbar}|q_i\right)$$

Computing

$$\begin{aligned}
\langle q_{i+1}|e^{-\epsilon\mathcal{H}/\hbar}|q_i\rangle &= \langle q_{i+1}|1-\frac{\epsilon}{\hbar}\mathcal{H}+O(\epsilon^2)|q_i\rangle \\
&\approx \int \frac{dp_i}{h^3}\langle q_{i+1}|1-\frac{\epsilon}{\hbar}\left[\frac{p^2}{2m}+U(q)\right]|p_i\rangle\langle p_i|q_i\rangle \\
&= \int \frac{dp_i}{h^3}1-\frac{\epsilon}{\hbar}[\frac{p_i^2}{2m}+U(q_{i+1})]e^{ip_i\cdot(q_{i+1}-q_i)/\hbar} \\
&= \left(\frac{m}{2\pi\hbar\epsilon}\right)^{3/2}\exp\{-\frac{\epsilon}{\hbar}\left[\frac{1}{2}m\dot{q}_i^2+U(q_{i+1})\right]\} \qquad (60)
\end{aligned}$$

we find the partition function

$$Z = \left(\frac{m}{2\pi\hbar\epsilon}\right)^{3N/2}\int\left(\prod_{i=0}^{N-1}dq_i\right)\left(\prod_{i=0}^{N-1}\exp\{-\frac{\epsilon}{\hbar}\left[\frac{1}{2}m\dot{q}_i^2+U(q_{i+1})\right]\}\right) notag \qquad (61)$$

$$= \int\left[\prod_{i=0}^{N-1}\left(\frac{mN}{2\pi\hbar^2\beta}\right)^{3/2}dq_i\right]\exp\{-\sum_{i=0}^{N-1}\frac{\epsilon}{\hbar}\left[\frac{1}{2}m\dot{q}_i^2+U(q_{i+1})\right]\} \qquad (62)$$

In the limit $\epsilon \to 0$ and $N \to 0$, this becomes

$$Z = \int Dq\exp[-\frac{1}{\hbar}S(q,\dot{q})] \qquad (63)$$

where the action S is

$$S(q,\dot{q}) = \int_0^{\beta\hbar}d\tau[\frac{1}{2}m\dot{q}^2+U(q)] \qquad (64)$$

Here, the path interal is taken over all paths with $q(0)=q(\beta\hbar)$, since $q_0=q_N$.

2. In the semiclassical limit $\hbar \to 0$, the path integral is dominated by paths for which the action is stationary. To find such paths, we take the variation $q \to q+\delta q$.

$$\begin{aligned}
\delta S &= \int_0^{\beta\hbar}d\tau\left(m\dot{q}\frac{\partial\delta q}{\tau}+\frac{\partial U}{\partial q}\delta q\right) \\
&= \int_0^{\beta\hbar}d\tau\left(-m\ddot{q}+\frac{\partial U}{\partial q}\right)\delta q \qquad (65)
\end{aligned}$$

which gives

$$m\ddot{q} = U'(q) \qquad (66)$$

In the low-temperature regime $\beta|U_0| >> 1$, we have $q_0 < a$, the finite distance for which the potential is negative. In this region, we can approximate the potential by

$$U(q) \approx U(0)+\frac{1}{2}m\omega^2q^2 \qquad (67)$$

and so the stationary paths are given by $\ddot{q}=\omega^2 q$. With the boundary condition $q(0)=q(\beta\hbar)=q_0$, the solutions are the classical paths

$$q_c(\tau) = q_0\frac{\cosh[\omega(\tau-\beta\hbar/2)]}{\cosh[\omega\beta\hbar/2]} \qquad (68)$$

Such paths give the classical action

$$S_c(q,\dot{q}) = \int_0^{\beta\hbar} d\tau[\frac{1}{2}m\dot{q}_c^2 + U(0) + \frac{1}{2}m\omega^2 q_c^2]$$
$$= m\omega q_0^2 \tanh\left(\frac{\beta\hbar\omega}{2}\right) + \beta\hbar U(0) \tag{69}$$

So the partition function is

$$Z = \int Dq \exp[-\frac{1}{\hbar}S_c(q,\dot{q})]$$
$$\approx \left(\sqrt{fracm\omega 2\pi\hbar \sinh(\beta\hbar\omega)}\int_{-\infty}^{\infty} dq_0 \exp\left[-\frac{m\omega q_0^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]\right)^3 \exp(-\beta U(0))$$
$$= \left[\frac{1}{2\sinh(\beta\hbar\omega/2)}\right]^3 \exp(-\beta U(0)) \tag{70}$$

To evaluate the partition function

$$Z = tre^{-\beta\mathcal{H}}$$
$$= \int d^3q\langle q|e^{-\beta\mathcal{H}}|q\rangle \tag{71}$$

we divide $\beta\hbar$ into N infinitesimal parts of length ϵ and write

$$\langle q|e^{-\beta\mathcal{H}}|q\rangle = \int\left(\prod_{i=1}^{N-1} dq_i\right)\left(\prod_{i=0}^{N-1}\langle q_{i+1}|e^{-\epsilon\mathcal{H}/\hbar}|q\rangle\right) \tag{72}$$

where $q_0 = q_N = q$. Computing

$$\langle q_{i+1}|e^{-\epsilon\mathcal{H}/\hbar}|q_i\rangle = \langle_{i+1}|1 - \frac{\epsilon}{\hbar}\mathcal{H} + O(\epsilon^2)|q_i|q_i\rangle$$
$$\approx \langle q_{i+1}|1 - \frac{\epsilon}{\hbar}[\frac{p^2}{2m} + U(q)]|q_i\rangle$$
$$= \left(\frac{m}{2\pi\hbar\epsilon}\right)^{3/2} \exp\{-\frac{\epsilon}{\hbar}[\frac{1}{2}m\dot{q}_i^2 + U(q_{i+1})]\} \tag{73}$$

Therefore, the partition function is

$$Z = \left(\frac{m}{2\pi\hbar\epsilon}\right)^{3N/2}\int\left(\prod_{i=0}^{N-1} dq_i\right)\left(\prod_{i=0}^{N-1}\exp\{-\frac{\epsilon}{\hbar}[\frac{1}{2}m\dot{q}_i^2 + U(q_{i+1})]\}\right)$$
$$= \int\left[\prod_{i=0}^{N-1}\left(\frac{mN}{2\pi\hbar^2\beta}\right)^{3/2} dq_i\right]\exp\{-\sum_{i=0}^{N-1}\frac{\epsilon}{\hbar}[\frac{1}{2}m\dot{q}_i^2 + U(q_{i+1})]\} \tag{74}$$

In the limit $\epsilon \to 0$ and $N \to \infty$, this becomes

$$Z = \int Dq \exp[-\frac{1}{\hbar}S(q,\dot{q})] \tag{75}$$

where the action S is

$$S(q,\dot{q}) = \int_0^{\beta\hbar} d\tau[\frac{1}{2}m\dot{q}^2 + U(q)] \tag{76}$$

Here, the path integral is taken over all paths with $q(0) = q(\beta\hbar)$, since $q_0 = q_N$.
the partitition function is

$$\begin{aligned} Z &= \int Dq \exp[-\frac{1}{\hbar} S_c(q, \dot{q})] \\ &= \frac{1}{(2\sinh(\beta\hbar\omega/2))^3} \exp(-\beta U(0)) \end{aligned} \tag{77}$$

3, The free energy is

$$\begin{aligned} F &= -kT \ln Z \\ &= U(0) + 3kT \ln(2\sinh(\beta\hbar\omega/2)) \end{aligned} \tag{78}$$

The partition function of a three dimensional harmonic oscillator at T is

$$Z_{h.o} = \frac{1}{(2\sinh(\beta\hbar\omega/2))^3} \tag{79}$$

Therefore it has free energy

$$F_{h.o} = 3kT \ln(2\sinh(\beta\hbar\omega/2)) \tag{80}$$

Therefore, the free energy of the system in the low temperature regime is the same as that of a three dimensional oscillator shifted by $U(0)$.