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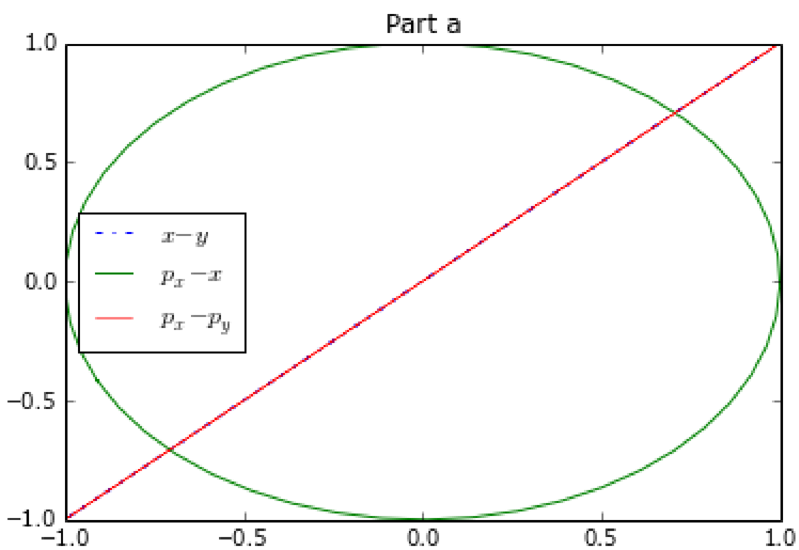
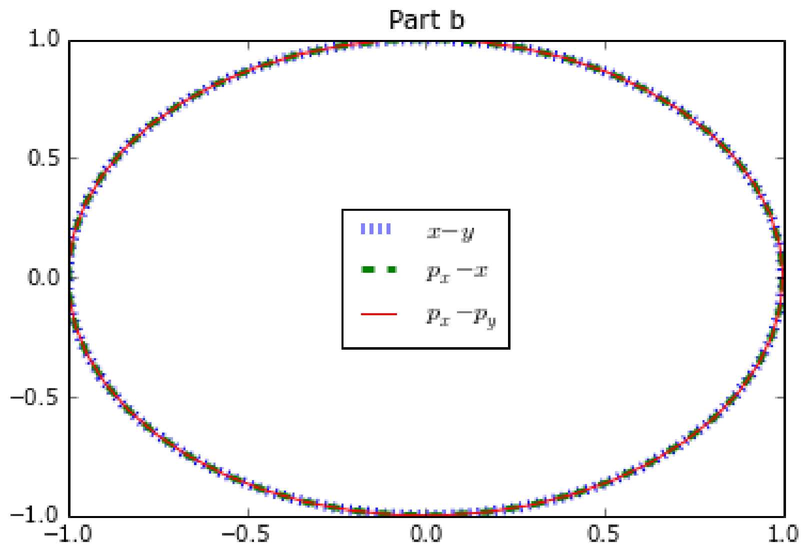
HW 3

Problem 1

In [1]:
```
import numpy as np
import matplotlib.pyplot as plt
%matplotlib inline
def shm(t,w=1,alpha=2,delta=3):
    x  =  np.cos(w*t+delta)
    px = -np.sin(w*t+delta)*w
    y  =  np.cos(w*t+alpha)
    py = -np.sin(w*t+alpha)*w
    return x,y,px,py
t = np.linspace(0,2*np.pi)
x,y,px,py = shm(t,w=1,alpha=2,delta=2)
plt.plot(x,y,label='$x-y$',ls='-.')
plt.plot(px,x,label='$p_x - x$')
plt.plot(px,py,label='$p_x - p_y$',ls='-',lw=0.5)
plt.legend(loc='best')
g=plt.title('Part a')
```

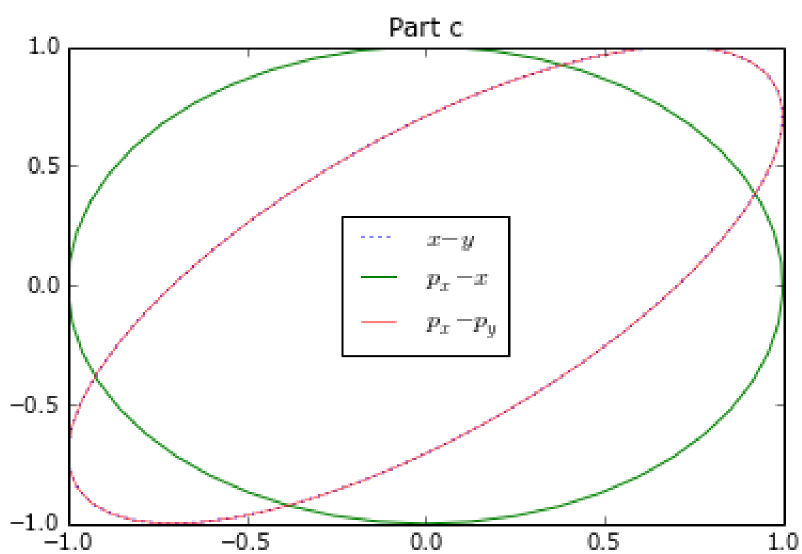


In [2]:
```
plt.figure()
x,y,px,py = shm(t,w=1,alpha=2,delta=2+np.pi/2)
plt.plot(x,y,label='$x-y$',ls=':',lw=5)
plt.plot(px,x,label='$p_x - x$',ls='--',lw=3)
plt.plot(px,py,label='$p_x - p_y$',ls='-',lw=1)
plt.legend(loc='center')
g=plt.title('Part b')
```



In [3]:
```
plt.figure()
x,y,px,py = shm(t,w=1,alpha=2,delta=2-np.pi/4)
plt.plot(x,y,label='$x-y$',ls=':')
plt.plot(px,x,label='$p_x - x$')
plt.plot(px,py,label='$p_x - p_y$',ls='-',lw=0.5)
plt.legend(loc='best')
plt.title('Part c')
print("It is interesting how the phase space changes as we change the
phase of x and y relative to each other")
```

```
It is interesting how the phase space changes as we change the phase o
f x and y relative to each other
```



Problem 2

1. We need to relate the height of the cylindrical portion and the radius of the silo to its volume: $V = c = \pi r^2 h + \pi \frac{2}{3} r^3$
2. Now we need surface area: $A = 2\pi r h + 2\pi r^2$
3. The auxiliary function is: $F = 2\pi r h + 2\pi r^2 - \lambda \left(\pi r^2 h + \pi \frac{2}{3} r^3 - c \right)$
4. There are two partial derivatives:
   $\frac{\partial F}{\partial h} = 2\pi r - \lambda \left(\pi r^2 \right)$

   $\frac{\partial F}{\partial r} = 2\pi h + 4\pi r - \lambda \left(2\pi r h + \pi 2 r^2 \right)$
5. We then have:
   $2\pi r h - \lambda \pi r^2 h = 0$
   $2\pi r h + 4\pi r^2 - 2\lambda \pi r^2 h + 2\lambda \pi r^3 = 0$
   Simplifying

   - $2\pi r = \lambda \pi r^2$
     $r = 0, \frac{2}{\lambda}$
   - $h \left[2\pi r - 2\lambda \pi r^2 \right] = -4\pi r^2 - 2\lambda \pi r^3$
     $h = \frac{4\pi r^2 + 2\lambda \pi r^3}{2\lambda \pi r^2 - 2\pi r}$

     $h = \frac{4\pi \left(\frac{2}{\lambda}\right)^2 + 2\lambda\pi \left(\frac{2}{\lambda}\right)^3}{2\lambda\pi \left(\frac{2}{\lambda}\right)^2 - 2\pi \frac{2}{\lambda}} = \frac{4\pi \frac{2}{\lambda} + 2\lambda\pi \left(\frac{2}{\lambda}\right)^2}{2\lambda\pi \frac{2}{\lambda} - 2\pi} = \frac{\frac{8\pi}{\lambda} + \frac{4 \cdot 2\lambda\pi}{\lambda^2}}{2 \cdot 2\pi - 2\pi} = \frac{\frac{8\lambda\pi + 8\lambda\pi}{\lambda^2}}{2\pi} = \frac{16\lambda\pi}{2\pi\lambda^2} = \frac{8}{\lambda} = 4r$
6. Finally: $V = c = \pi r^2 4r + \pi \frac{2}{3} r^3 = 4\pi r^3 + \pi \frac{2}{3} r^3 = \frac{14}{3} r^3$
   $r = \sqrt[3]{\frac{3c}{14}}, h = 4r$

Problem 3

The partition function of an ideal gas of diatomic molecules in an external electric field is

$$Q(N,V,T,E)=\frac{[q(V,T,E)]^N}{N!}$$

Where

- $q(V,T,E)=V\Lambda^3\cdot q_r\cdot q_v\cdot\left(\frac{kT}{\mu E}\right)\sinh\left(\frac{\mu E}{kT}\right)$
- $q_r=\frac{8\pi^2 IkT}{h^2}$
- $q_v=\frac{\exp\left(\frac{-h\nu}{2kT}\right)}{1-\exp\left(\frac{-h\nu}{kT}\right)}$

I is the moment of inertia of the molecule, ν is the molecule's fundamental vibrational frequency, and μ is the molecule's permanent dipole moment. Using this partition function and the thermodynamic relation

$$\mathrm{d}A=-S\mathrm{d}T-P\mathrm{d}V-N\langle\mu\rangle\mathrm{d}E$$

show that

$$\langle\mu\rangle=\mu\left[\coth(\beta\mu E)-\frac{1}{\beta\mu E}\right]$$

where $\langle\mu\rangle$ is the average dipole moment of a molecule in the direction of the external field. Then sketch the functionality of the dimensionless dipole moment $\mu^+=\frac{\langle\mu\rangle}{\mu}$ result versus the dimensionless field E^+ $\left(E^+=\beta\mu E\right)$ from $E^+=0$ to $E^+=\infty$ and interpret what you see.

▶ Details

Answer

1. $\mathrm{d}A=-S\mathrm{d}T-P\mathrm{d}V-N\langle\mu\rangle\mathrm{d}E$

   $\frac{\mathrm{d}A}{\mathrm{d}E}=-N\langle\mu\rangle=\frac{\mathrm{d}(-kT\ln Q)}{\mathrm{d}E}$
2. $\ln Q=\ln\left(\frac{[q(V,T,E)]^N}{N!}\right)=N\ln(q(V,T,E))-(N\ln N-N)$
3. $\ln q=\ln\left(V\Lambda^3\right)+\ln(\cdot q_r)+\ln(q_v)+\ln\left(\frac{kT}{\mu E}\right)+\ln\left(\sinh\left(\frac{\mu E}{kT}\right)\right)$

   $\ln q=\ln\left(V\Lambda^3\right)+\ln\left(\frac{8\pi^2 IkT}{h^2}\right)+\ln\left(\frac{\exp\left(\frac{-h\nu}{2kT}\right)}{1-\exp\left(\frac{-h\nu}{kT}\right)}\right)+\ln\left(\frac{kT}{\mu E}\right)+\ln\left(\sinh\left(\frac{\mu E}{kT}\right)\right)$
4. $\frac{\mathrm{d}(-kT\ln Q)}{\mathrm{d}E}=-kT\left[N\ln(q(V,T,E))-(N\ln N-N)\right]$

   $=-kTN\frac{\mathrm{d}\left[\ln\left(\frac{1}{E}\right)+\ln\left(\sinh\left(\frac{\mu E}{kT}\right)\right)\right]}{\mathrm{d}E}\qquad=-kTN\frac{\mathrm{d}\left[-\ln(E)+\ln\left(\sinh\left(\frac{\mu E}{kT}\right)\right)\right]}{\mathrm{d}E}$

   $=-kTN\left(\frac{-1}{E}+\frac{\mathrm{d}\left[\ln\left(\sinh\left(\frac{\mu E}{kT}\right)\right)\right]}{\mathrm{d}E}\right)$

In [4]:
```
import sympy
from sympy import symbols, Symbol
sympy.init_printing()
Q,N,V,T,E=symbols('Q,N,V,T,E')
q,L,qr,qv,k,T,mu,I,nu = symbols('q,L,q_r,q_v,k,T,\\mu,I,\\nu')
eq=sympy.diff(sympy.ln(sympy.sinh(mu*E/(k*T))),E) # I have no idea wha
t the derivative is,
eq                                                  # so calculate it.
```

Out[4]:

$$\frac{\mu \cosh\left(\frac{E\mu}{Tk}\right)}{Tk \sinh\left(\frac{E\mu}{Tk}\right)}$$

5. $\frac{\mathrm{d}(-kT\ln Q)}{\mathrm{d}E} = -kTN\left[\frac{-1}{E} + \frac{\mu}{kT}\coth\left(\frac{\mu E}{kT}\right)\right] = \left[\frac{-kTN}{E} + \mu N\coth\left(\frac{\mu E}{kT}\right)\right]$

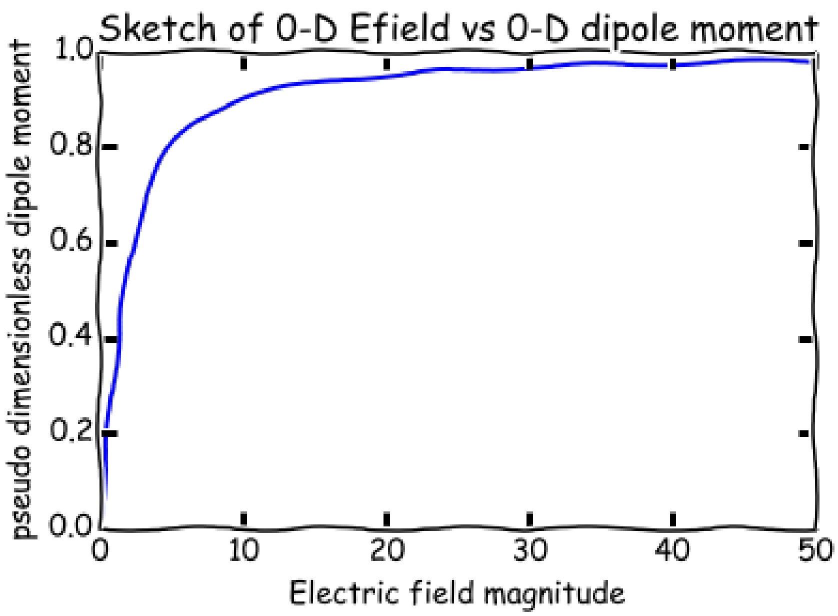
6. $\frac{\mathrm{d}A}{\mathrm{d}E} = -N\langle\mu\rangle, \beta = \frac{1}{kT}$

$$\langle\mu\rangle = \frac{\left[\frac{-kTN}{E} + \mu N\coth\left(\frac{\mu E}{kT}\right)\right]}{N} = \left[\frac{-kT}{E} + \mu\coth\left(\frac{\mu E}{kT}\right)\right] = \mu\left[\coth\left(\beta\mu E\right) - \frac{1}{\beta\mu E}\right]$$

In [5]:

```python
E = np.linspace(1e-6,50,1000)
mu = 1/np.tanh(E)-1/E
plt.xkcd(randomness=5)
plt.figure()
plt.plot(E,mu)
plt.xlabel('Electric field magnitude')
plt.ylabel('pseudo dimensionless dipole moment')
plt.title('Sketch of 0-D Efield vs 0-D dipole moment')
plt.xkcd(False)
print("We see that the Dipole moment approaches unity as the electric field magnitude increases, which makes sense.")
```

```
We see that the Dipole moment approaches unity as the electric field m
agnitude increases, which makes sense.
```



Problem 4

A rigid diatomic molecule rotates freely in three dimensions in a zero potential-energy field. The Hamiltonian may be expressed in terms of the moment of inertia as

$$H = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)$$

where θ ranges from 0 to π, ϕ ranges from 0 to 2π and

$$p_\theta = I\dot{\theta}\,, p_\phi = I\dot{\phi}\sin^2\theta$$

Evaluate the classical molecular partition function, Q_{cl} (excluding the $N!$ term). Note that there are only two applicable coordinates, θ and ϕ, because the distance between the atoms is fixed and translational motion is not considered.

$$Q_{cl}=\frac{1}{N!h^{3N}}\int\limits_{\tau}e^{-\beta H}\mathrm{d}\tau=\int\limits_{\phi}\int\limits_{\theta}e^{-\beta H}\mathrm{d}\theta\mathrm{d}\phi=\int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}e^{-\beta H}\mathrm{d}\theta\mathrm{d}\phi$$
$$=\int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}e^{-\beta\frac{1}{2I}\left(p_\theta^2+\frac{p_\phi^2}{\sin^2\theta}\right)}\mathrm{d}p_\theta\mathrm{d}p_\phi\mathrm{d}\theta\mathrm{d}\phi$$

$$=\int\limits_{0}^{\pi}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}e^{-\beta\frac{1}{2I}\left(p_\theta^2+\frac{p_\phi^2}{\sin^2\theta}\right)}\mathrm{d}p_\theta\mathrm{d}p_\phi\mathrm{d}\theta\int\limits_{0}^{2\pi}\mathrm{d}\phi$$
$$=\int\limits_{0}^{\pi}\int\limits_{-\infty}^{\infty}e^{-\beta\frac{1}{2I}\left(\frac{p_\phi^2}{\sin^2\theta}\right)}\mathrm{d}p_\phi\mathrm{d}\theta\int\limits_{-\infty}^{\infty}e^{-\beta\frac{1}{2I}\left(p_\theta^2\right)}\mathrm{d}p_\theta\int\limits_{0}^{2\pi}\mathrm{d}\phi$$
$$\int\limits_{-\infty}^{\infty}e^{-\frac{2}{3}x^2}\mathrm{d}x=\sqrt{\frac{3\pi}{2}}$$

$$Q_{cl}=\int\limits_{0}^{\pi}\int\limits_{-\infty}^{\infty}e^{-\beta\frac{1}{2I}\left(\frac{p_\phi^2}{\sin^2\theta}\right)}\mathrm{d}p_\phi\mathrm{d}\theta\sqrt{\frac{2I\pi}{\beta}}2\pi=\int\limits_{0}^{\pi}\sqrt{\pi 2IkT}\sin(\theta)\mathrm{d}\theta=\frac{2\sqrt{2\pi IkT}}{h^{3N}N!}$$

Problem 5

▶ Details

Derive the classical canonical partition function for an ideal monatomic gas contained within a cubic box of length L on a side if the particles experience a gravitational field in the z direction; i.e., the potential energy of each particle is given by $U(z)=mgz$.

$$Q_{cl}=\frac{Z}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$$

$$Z=\int e^{-U/kT}dq\Rightarrow Z=\int_0^L e^{-\frac{mgz}{kT}}dz=-\frac{mg}{kT}\left(e^{-\frac{mgz}{kT}}-1\right)$$

$$Q_{cl}=\frac{-\frac{mg}{kT}\left(e^{-\frac{mgz}{kT}}-1\right)}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$$

Problem 6

▶ Details

$$P = -kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{\partial}{\partial V}\ln\frac{(V-Nb)^N}{N!\Lambda^{3N}} + \frac{N^2 a}{VkT}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{\partial}{\partial V}\ln(V-Nb)^N + \frac{N^2 a}{VkT}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{\partial}{\partial V}N\ln(V-Nb) + \frac{N^2 a}{VkT}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = N\frac{1}{V-Nb} - \frac{N^2 a}{V^2 kT}$$

$$P = -NkT\frac{1}{V-Nb} - \frac{N^2 a}{V^2} = \frac{RT}{V-Nb} - \frac{N^2 a}{V^2}$$

Part b

$$A = -kT\ln Q$$

$$\frac{A^* - A}{kT} = \ln\left(\frac{Q_{int}(V-Nb)^N}{N!\Lambda^{3N}}\exp\left(\frac{N^2 a}{VkT}\right)\right) - \ln\left(\frac{(V-Nb)^N}{N!\Lambda^{3N}}\exp\left(\frac{N^2 a}{VkT}\right)\right) =$$

$$\ln\left(\frac{Q_{int}(V-Nb)^N}{N!\Lambda^{3N}}\right) - \ln\left(\frac{(V-Nb)^N}{N!\Lambda^{3N}}\right) = \ln Q_{int}$$