Exercise 4C: Partial derivatives and the van der Waals gas

Objectives:

- Derive (examples of) Maxwell's relations.

- Qualitative understanding of van der Waals gas equation of state.

- Qualitative understanding of partial derivatives in many variable calculus.

- Adiabatic vs. Isentropic

Useful results from previous lectures

- Fundamental relation for energy $dE = -pdV + \tau d\sigma$

- Fundamental relation for free energy $dF = -pdV - \sigma d\tau$

- Equipartition theorem applied to ideal gas $E = \frac{3}{2}N\tau$

- Sackur Tetrode equation for entropy of ideal gas $\sigma = N \ln\left(\frac{V}{N\lambda_T^3}\right) + \frac{5}{2}N$

1) Maxwell's relations

1. Show that
$$\left(\frac{\partial p}{\partial \tau}\right)_V = \left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

   Hint: Take second derivatives of the free energy.

$$F = -pdV - \sigma\, dT$$

$$-P = \left(\frac{\partial F}{\partial V}\right)_\tau \qquad -\sigma = \left(\frac{\partial F}{\partial T}\right)_V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\right)_V\left(\frac{\partial}{\partial V}\right)_\tau F = -\left(\frac{\partial}{\partial V}\right)_\tau\left(\frac{\partial}{\partial T}\right)_V F = \left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

2. (Optional) Find another Maxell relation using the energy E rather than the free energy.

2) Van der Waals Gas

1. Consider the van der Waals equation of state
$$\left(p + N^2 a/V^2\right)(V - Nb) = N\tau$$

   What are physical interpretations of the a and b terms?

   The $N^2 a/V^2$ term is the interaction term. It is proportional to the number of molecules squared, N^2.

   The b term is the volume excluded by the molecules.

2. What is the energy as a function of τ for a van der Waals Gas when V is very large?

$E = \frac{3}{2} N \tau$ because it goes to an ideal gas as $V \to \infty$

3. Suppose you now compress the gas. Calculate $(\partial E/\partial V)_T$ for this system.

$$\left(\frac{\partial E}{\partial V}\right)_\tau = -p + \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau = -p + \tau \left(\frac{\partial p}{\partial \tau}\right)_V = -\frac{N\tau}{V-Nb} + \frac{N^2 a}{V^2} + \tau \frac{N}{V-Nb}$$

$$= \frac{N^2 a}{V}$$

4. What is $E(V, T)$ for a van der Waals gas?

$$E(V, \tau) = \frac{3}{2} N \tau + \int_\infty^V \left(\frac{dE}{dV}\right)_\tau dV = \frac{3}{2} N\tau + \int_\infty^V \frac{N^2 a}{V^2} dV = \frac{3}{2} N\tau - \frac{N^2 a}{V}$$
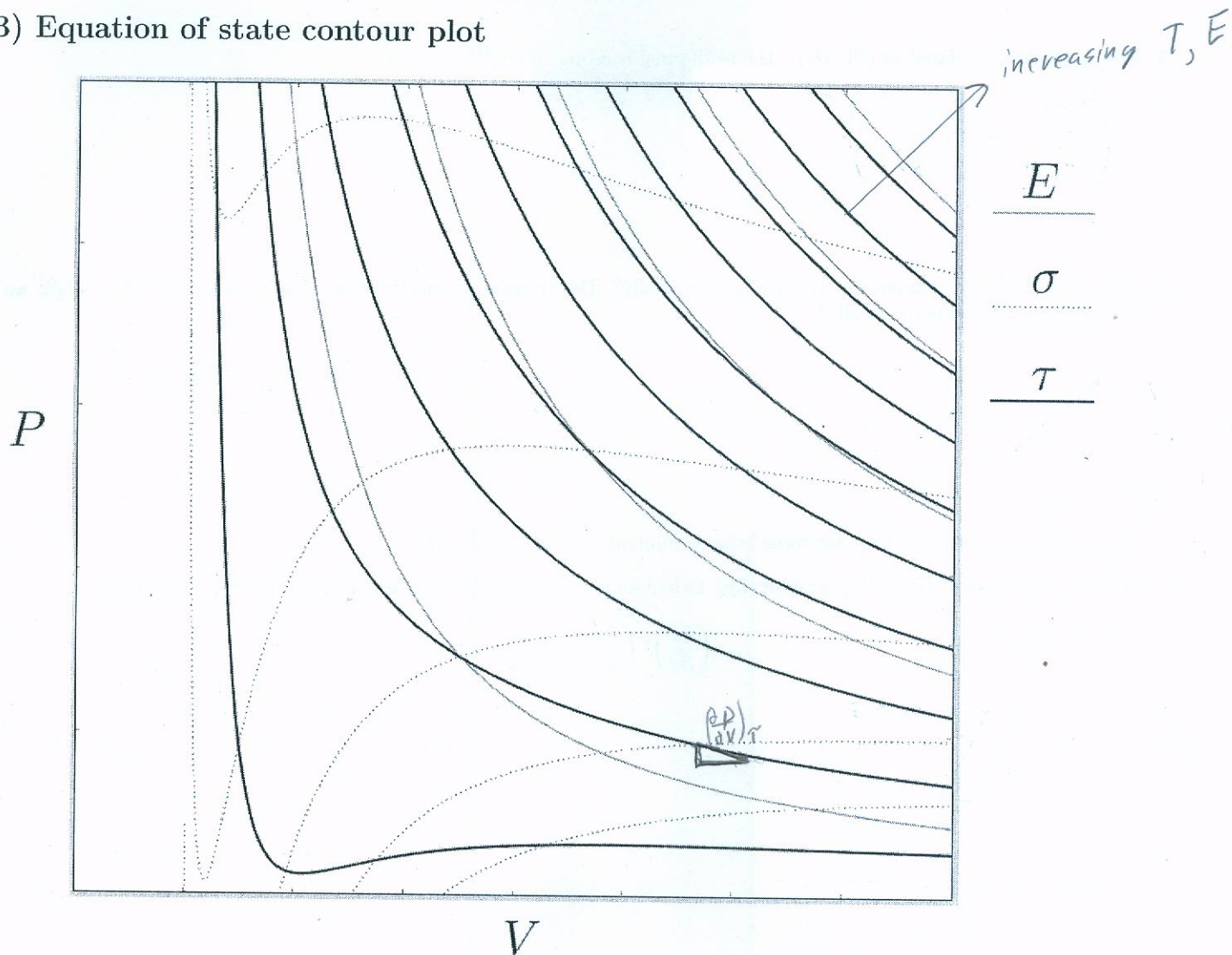
5. Compare the energy of the van der Waals gas with that of the ideal gas. Which of the parameters a, b are relevant, and way?

Only a because b is just like an Ideal gas in a smaller box.

6. (Optional) By a similar process, show that for a van der Waals Gas

$$\sigma = N \ln \left(\frac{V - Nb}{N \lambda_T^3} \right) + \frac{5}{2} N$$

2

3) Equation of state contour plot

increasing T, E

E

σ

τ

P

V

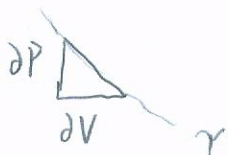1. Using the results from the previous section you can find the following

$$p(T,V) = \frac{N\tau}{V - Nb} - \frac{N^2 a}{V^2}$$

$$p(E,V) = \frac{2}{3(V - Nb)}\left(E - \frac{N^2 a}{V}\right) - \frac{N^2 a}{V}$$

$$p(\sigma, V) = \frac{N}{V - Nb}\left(\frac{V - Nb}{N\alpha^3}\exp\left(\frac{5}{2} - \frac{1}{2}\frac{\sigma}{N}\right)\right)^{2/3} - \frac{N^2 a}{V^2}$$

Curves of constant T, constant E, and constant σ are shown in the plot. Take some time to familiarize yourself with this figure. Which direction is increasing T? Increasing E? Increasing σ?

2. Represent $(\partial p/\partial V)_\tau$ graphically in the figure. Calculate an expression for it. How might you measure this derivative experimentally?

∂P / ∂V $\quad \gamma$

3. How is $(\partial p/\partial V)_\tau$ related to $(\partial V/\partial p)_\tau$, the isothermal compressability?

$$\left(\frac{\partial p}{\partial V}\right)_\tau = \left(\left(\frac{\partial V}{\partial p}\right)_\tau\right)^{-1}$$
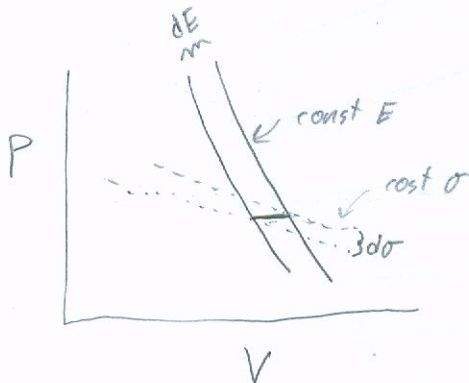
4. How does $(\partial p/\partial V)_\tau$ compare to $(\partial p/\partial V)_\sigma$ graphically? Do we need to specify what is held constant? How might we measure the latter experimentally?

$\left(\partial p\right)_\tau$

$\left(\partial P\right)_\sigma$ dV σ τ

5. Graphically represent $(\partial x/\partial y)_z$ for some other combination(s) of P, V, T, σ, E.

6. How do you represent $(\partial \sigma/\partial V)_E$ graphically? Calculate an expression for it. *Hint: you can use the relationship*

dE

P

const E

cost σ

$3d\sigma$

V

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

7. Graphically prove that the cyclic relation from the last question using P, V and T as the three variables.

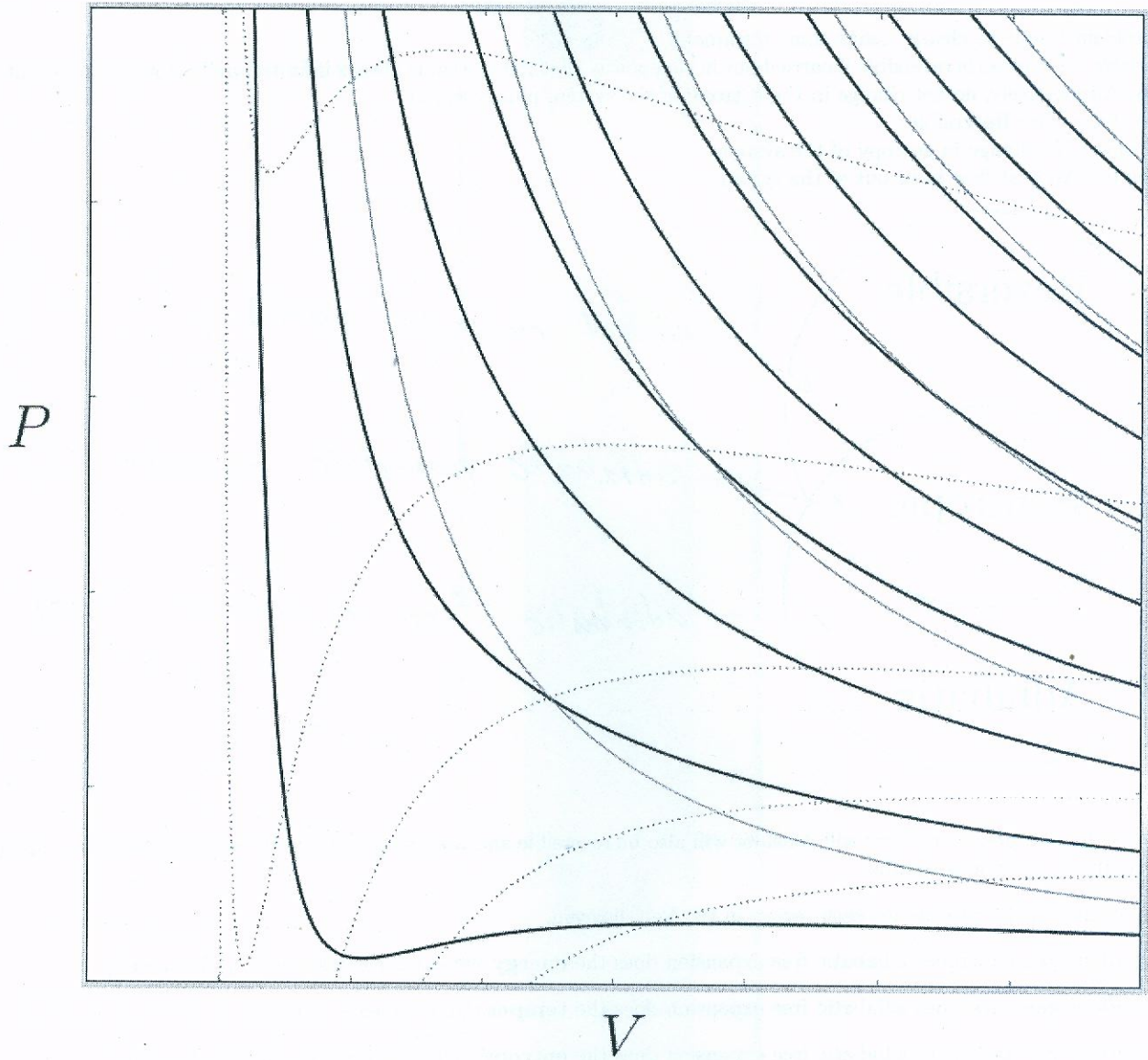dP $\frac{-dP}{dV}$ dV

8. Which of the following equations hold if we were to use a system other than a van der Waals gas?

   (a) $dE = -pdV + \tau d\sigma$ holds   for   all   systems
   (b) Maxwell's relations   "   "   "   "
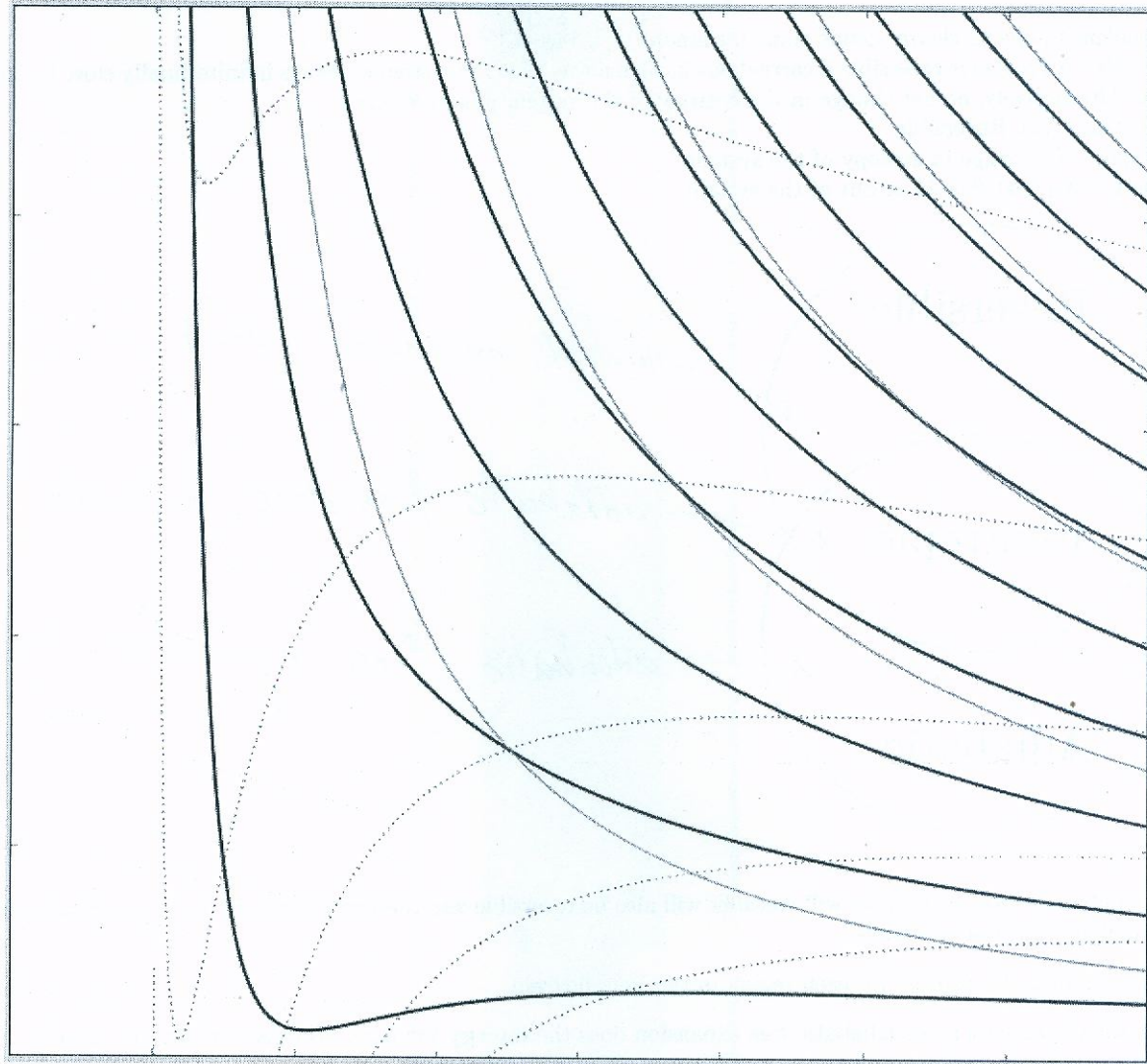   (c) The equation of state   will   be   different
   (d) The cyclic relationship   holds   for   all   systems

P

V

E

σ

τ

P

V

E

σ

τ

6

4) Adiabatic Vs. Isentropic expansion

In this problem I hope to clearly define some terminology.

Reversible - A process is reversible if carried out in such a way that the system is always infinitesimally close to the equilibrium condition. Alternatively, no net change in the entropy of the system plus reservoir.

Quasi-static - See Reversible

Isentropic - No change in entropy of the system.

Adiabatic - No heat flow in or out of the system.

isothermal expansion (slow)

adiabatic quasi-static expansion (medium)

adiabatic free expansion (fast)
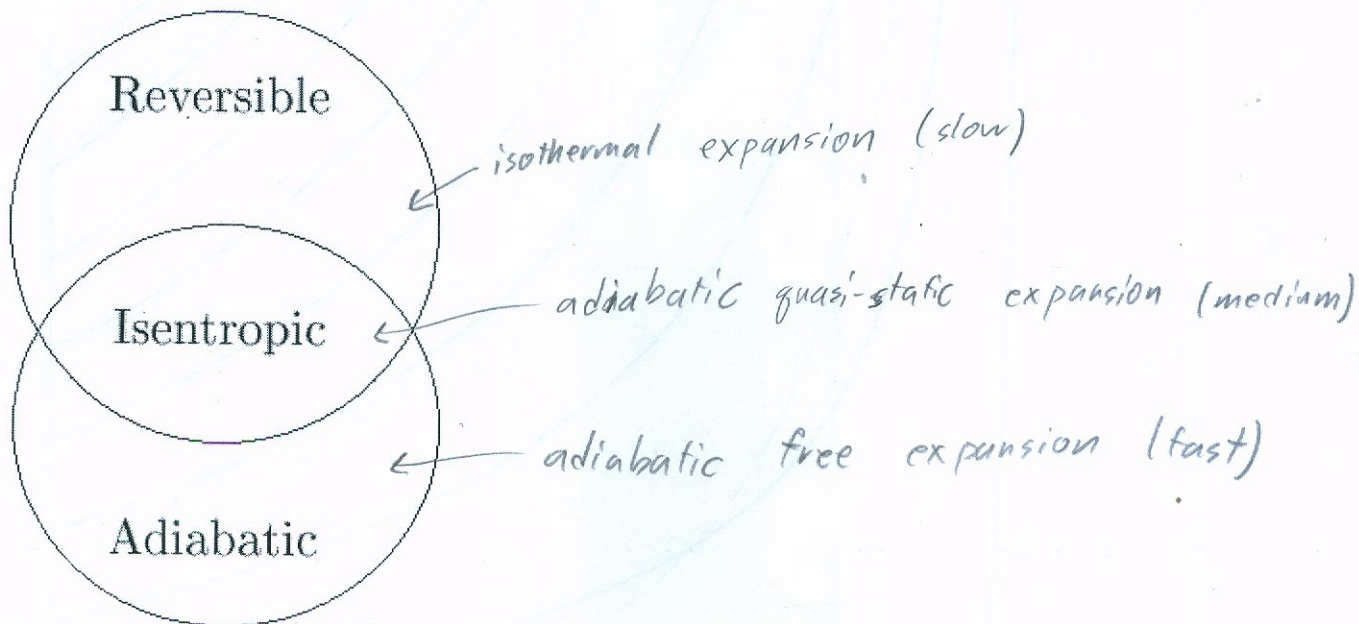
Often adiabatic processes that we will consider will also be reversible and therefor isentropic. One exception is free expansion which is adiabatic but not reversible.

1. Give examples of a process for each region in the Ven diagram.

2. If an **ideal gas** undergoes adiabatic free expansion does the **energy** increase, decrease, or stay the same?

3. If an **ideal gas** undergoes adiabatic free expansion does the **temperature** increase, decrease, or stay the same?

4. If an **ideal gas** undergoes adiabatic free expansion does the **entropy** increase, decrease, or stay the same?

5. If an **van der Waals** gas undergoes adiabatic free expansion does the **energy** increase, decrease, or stay the same?

6. If an **van der Waals** gas undergoes adiabatic free expansion does the **temperature** increase, decrease, or stay the same?

$$E = \frac{3}{2}NT - \frac{N^2 a}{V}$$