WEEK # 5

DIFFERENTIALS AND PROCESSES

- OFTENTIMES WE ARE INTERESTED IN THE CHANGE df IN SOME function f ~~WHEN WE~~ OF OUR THERMODYNAMIC VARIABLES WHEN WE TAKE OUR SYSTEM FROM SOME ~~POINT~~ STATE

$$\vec{x}_0 = (x_{01}, x_{02}, \ldots, x_{0N})$$ TO

SOME NEARBY STATE

$$\vec{x}_0 + d\vec{x}$$ WHERE

$$d\vec{x} = (dx_1, dx_2, \ldots, dx_N)$$

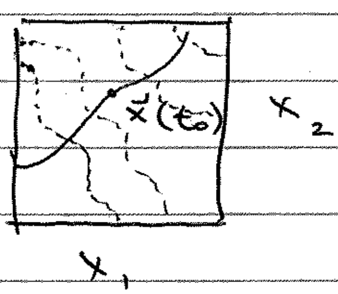
Q_1: SHOW THAT, TO FIRST ORDER IN THE dx_i, WE CAN WRITE

$$(1): \quad df = \sum_{i=1}^{N} \left.\frac{\partial f}{\partial x_i}\right|_{x_j, j \neq i} (\vec{x}_0)\, dx_i = \vec{\nabla} f(\vec{x}_0) \cdot d\vec{x}$$

q1 cont

hint: $df = f(\vec{x} + d\vec{x}) - f(\vec{x})$

IF WE DON'T WANT TO THINK IN TERMS OF DIFFERENTIALS df AND $d\vec{x}$, WE CAN ALTERNATIVELY CONSIDER A TRAJECTORY $\vec{x}(t)$ REPRESENTING SOME PROCESS AND ASK ABOUT THE RATE OF CHANGE OF SOME FUNCTION $f(\vec{x}(t))$ AT SOME TIME t_0



.......: CURVES OF CONSTANT f

———: $\vec{x}(t)$

Q2: SHOW THAT:

$$\frac{d}{dt}\Big|_{t=t_0} f(\vec{x}(t)) = \sum_{i=1}^{N} \frac{\partial f}{\partial x_i}\Big|_{x_j,\, j\neq i} (\vec{x}(t_0)) \frac{d}{dt}\Big|_{t=t_0} x_i(t)$$

So that, if we ask about the change df in f going from t_0 to $t_0 + dt$ we get:

$$df = \left[\sum_{i=1}^{N} \frac{\partial f}{\partial x_i}\bigg|_{x_j,\, j \neq i} (\vec{x}(t_0)) \frac{d}{dt}\bigg|_{t=t_0} x_i(t) \right] dt$$

So, making the associations

$$\vec{x}(t_0) \longleftrightarrow \vec{x}_0$$

$$\frac{d}{dt}\bigg|_{t=t_0} \vec{x} \longleftrightarrow d\vec{x}$$

we find we are describing equivalent methods.

The upshot is that to determine the change in some function $f(\vec{x})$ of our system at some point $\vec{x}_0$ for some process, we need to

SPECIFY THE <u>TANGENT VECTOR</u> $d\vec{x}$

$\left(\text{OR } \left. \frac{d}{dt} \right|_{t_0} \vec{x} \equiv \dot{\vec{x}} \right)$ CHARACTERIZING THE

PROCESS.

IF OUR ~~DE~~ SYSTEM IS DESCRIBED

BY N VARIABLES, THEN WE

NEED $N-1$ CONSTRAINTS (i.e. EQUATIONS) TO SPECIFY

A <u>DIRECTION</u> FOR THE TANGENT

VECTOR [THE LEN<u>GT</u>H OF THE VECTOR

IS NOT IMPORTANT SINCE ~~THIS WILL~~ WE ARE

NOT CONCERNED IN GENERAL W/ THE

ABSOLUTE RATE OF CHANGE, ONLY

RELATIVE RATES].

LET'S DETERMINE THE TANGENT

VECTORS ASSOCIATED W/ THE

PROCESSES DESCRIBED ON QUESTION 2

OF THE HOMEWORK.

OUR SYSTEM HAS 6 VARIABLES:

$U_1, V_1, N_1, U_2, V_2, N_2$

IN PART a) WE ARE ASKING

TO CONSIDER A TRANSFER OF

ENERGY dU TO SYSTEM #1

FROM SYSTEM #2. [I USED

TO GET CONFUSED AT THIS PART.

HOW BIG IS dU?! HERE'S THE

ANSWER: dU IS SMALL ENOUGH

THAT EQN (1) (1st PAGE) APPLIES. IF THAT

DOESN'T SATISFY YOU THEN REFORMULATE

THE PROBLEM IN TERMS OF TRAJECTORIES

AND RATES OF CHANGE AS I SHOWED

EARLIER]

THE TRANSFER OCCURS VIA A

WALL THAT IS IMPERMEABLE

AND FIXED.

Q3: a) THE CONSTRAINT OF IMPERMEABILITY

IMPLIES WHAT TWO CONSTRAINTS?

b) WHAT ABOUT FOR THE FIXED WALL?

c) WHAT IS THE 5^{TH} (AND FINAL)

CONSTRAINT? (HINT: WHAT'S EVEN MORE

IMPORTANT THAN THE 2^{ND} LAW OF

T.D.?)

d) WRITE DOWN THE VECTOR

$d\vec{X} \equiv (dU_1, dV_1, dN_1, dU_2, dV_2, dN_2)$

IN TERMS OF dU

Q3 CONT:

e) ~~WRITE DOWN~~ SUPPOSE OUR SYSTEM MOVE ALONG A TRAJECTORY

$$\vec{x}(t) = \vec{x}_0 + d\vec{x} \cdot t$$

WHERE $\vec{x}_0 \equiv (U_{0_1}, V_{0_1}, N_{0_1}, U_{0_2}, V_{0_2}, N_{0_2})$

AND $d\vec{x}$ AS DEFINED IN PART d)

WRITE DOWN AN EXPRESSION FOR $\left.\frac{d}{dt}\right|_{t_0} S(\vec{x}(t))$.

FOR WHICH $\vec{x}_0$ IS THIS RATE OF CHANGE NON ZERO?

Q4: LOOKING NOW AT QUESTION 2c), WHAT DOES THE ISOTHERMAL CONSTRAINT IMPLY ABOUT THE dU_i, dV_i, dN_i?

ANSWERS

Q1: $f(\vec{x}_0 + d\vec{x}) =$

$$f(x_{01} + dx_1, x_{02} + dx_2, \ldots, x_{0N} + dx_N) \simeq$$

$$f(x_{01}, x_{02} + dx_2, \ldots, x_{0N} + dx_N)$$

$$+ \frac{\partial}{\partial x_1} f \Bigg|_{x_2, \ldots, x_N} (x_{01}, x_{02} + dx_2, \ldots, x_{0N} + dx_N) \cdot dx_1 \simeq$$

$$f(x_{01}, x_{02}, \ldots, x_{0N} + dx_N)$$

$$+ \frac{\partial}{\partial x_2} f \Bigg|_{x_1, x_3, \ldots, x_N} (x_{01}, x_{02}, \ldots, x_{0N} + dx_N)\, dx_2$$

$$+ \frac{\partial}{\partial x_1} f \Bigg|_{x_2, \ldots, x_N} (x_{01}, x_{02} + dx_2, \ldots, x_{0N} + dx_N)\, dx_1 \simeq$$

$$\vdots$$

$$= f(x_{01}, x_{02}, \ldots, x_{0N})$$

$$+ \sum_i^N \frac{\partial}{\partial x_i} \Bigg|_{x_j, j \neq i} f(x_{01}, x_{02}, \ldots, x_{0N})\, dx_i$$

+ HIGHER ORDER IN THE dx_i

(E.G. $dx_i dx_j$, $dx_i dx_j dx_k$, ETC.)