# Exact differential for the thermodynamics <br> Masatsugu Sei Suzuki <br> Department of Physics, SUNY at Binghamton <br> Binghamton, NY 13902-6000 <br> (date: September 05, 2018) 

## 1. Exact differential

We work in two dimensions, with similar definitions holding in any other number of dimensions. In two dimensions, a form of the type

$$
A(x, y) d x+B(x, y) d y
$$

is called a differential form. This form is called exact if there exists some scalar function $Q(x, y)$

$$
d Q=\left(\frac{\partial Q}{\partial x}\right)_{y} d x+\left(\frac{\partial Q}{\partial y}\right)_{x} d y=A d x+B d y
$$

if and only if

$$
\left(\frac{\partial A}{\partial y}\right)_{x}=\left(\frac{\partial B}{\partial x}\right)_{y}
$$

or

$$
\left(\frac{\partial}{\partial y}\left(\frac{\partial Q}{\partial x}\right)_{y}\right)_{x}=\left(\frac{\partial}{\partial x}\left(\frac{\partial Q}{\partial y}\right)_{x}\right)_{y}
$$

The vector field $(A, B)$ is a conservative vector field, with corresponding potential $Q$. When a differential $Q$ is exact, the function $Q$ exist,

$$
\int_{i}^{f} d Q=Q(f)-Q(i)
$$

independent of the oath followed.
In thermodynamics, when $\mathrm{d} Q$ is exact, the function Q is a state function of the system. The thermodynamics functions, $E$ ( or $U$ ) , S, $H, F$ (or $A$ ), and $G$ are state functions. An exact differential is sometimes also called a total differential or a full differential.
2. Jacobian

We consider two functions $u$ and $v$ such that

$$
u=u(x, y), \quad v=v(x, y)
$$

The Jacobian is defined as

$$
\frac{\partial(u, v)}{\partial(x, y)}=\left|\begin{array}{ll}
\frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\
\frac{\partial v}{\partial x} & \frac{\partial v}{\partial y}
\end{array}\right|
$$

It clearly has the following properties

$$
\begin{aligned}
& \frac{\partial(v, u)}{\partial(x, y)}=-\frac{\partial(u, v)}{\partial(x, y)} \\
& \frac{\partial(u, y)}{\partial(x, y)}=\left|\begin{array}{ll}
\frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\
\frac{\partial y}{\partial x} & \frac{\partial y}{\partial y}
\end{array}\right|=\left|\begin{array}{cc}
\frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\
0 & 1
\end{array}\right|=\left(\frac{\partial u}{\partial x}\right)_{y} .
\end{aligned}
$$

The following relations also hold:

$$
\begin{aligned}
& \frac{\partial(z, y)}{\partial(x, y)}=\frac{1}{\frac{\partial(x, y)}{\partial(z, v)}} \\
& \left(\frac{\partial z}{\partial x}\right)_{y}=\frac{\partial(z, y)}{\partial(x, y)}=\frac{\frac{\partial(z, y)}{\partial(t, y)}}{\frac{\partial(x, y)}{\partial(t, y)}}=\frac{\left(\frac{\partial z}{\partial t}\right)_{y}}{\left(\frac{\partial x}{\partial t}\right)_{y}} \\
& \frac{\partial(z, y)}{\partial(x, y)} \frac{\partial(x, z)}{\partial(y, z)} \frac{\partial(y, x)}{\partial(z, x)}=-1
\end{aligned}
$$

$$
\begin{aligned}
\left(\frac{\partial u}{\partial x}\right)_{y} & =\frac{\partial(u, y)}{\partial(x, y)} \\
& =-\frac{\partial(u, x)}{\partial(y, x)} \frac{\partial(u, y)}{\partial(u, x)} \\
& =-\frac{\partial(u, x)}{\partial(y, x)} \frac{\partial(y, u)}{\partial(x, u)} \\
& =-\left(\frac{\partial u}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial x}\right)_{u}
\end{aligned}
$$

## 3. Expression of $C_{P}$ and $C_{V}$

The heat capacity:

$$
C_{V}=T\left(\frac{\partial S}{\partial T}\right)_{V}=T \frac{\partial(S, V)}{\partial(T, V)}=T \frac{\frac{\partial(S, V)}{\partial(T, P)}}{\frac{\partial(T, V)}{\partial(T, P)}}=T \frac{\frac{\partial(S, V)}{\partial(T, P)}}{\left(\frac{\partial V}{\partial P}\right)_{T}}
$$

or

$$
\begin{aligned}
C_{V} & =\frac{T}{\left(\frac{\partial V}{\partial P}\right)_{T}}\left|\begin{array}{ll}
\left(\frac{\partial S}{\partial T}\right)_{P} & \left(\frac{\partial S}{\partial P}\right)_{T} \\
\left(\frac{\partial V}{\partial T}\right)_{P} & \left(\frac{\partial V}{\partial P}\right)_{T}
\end{array}\right| \\
& =\frac{T}{\left(\frac{\partial V}{\partial P}\right)_{T}}\left[\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial V}{\partial P}\right)_{T}-\left(\frac{\partial S}{\partial P}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{P}\right] \\
& =T\left(\frac{\partial S}{\partial T}\right)_{P}-\frac{T\left(\frac{\partial S}{\partial P}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{P}}{\left(\frac{\partial V}{\partial P}\right)_{T}}
\end{aligned}
$$

Using the Maxwell's relation

$$
\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P}
$$

and the relation

$$
\left(\frac{\partial V}{\partial P}\right)_{T}=\frac{\partial(V, T)}{\partial(P, T)}=\frac{1}{\frac{\partial(P, T)}{\partial(V, T)}}=\frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T}}
$$

Then we get

$$
C_{V}=C_{P}+\frac{T\left(\frac{\partial V}{\partial T}\right)_{P}^{2}}{\left(\frac{\partial V}{\partial P}\right)_{T}}=C_{P}+T\left(\frac{\partial V}{\partial T}\right)_{P}^{2}\left(\frac{\partial P}{\partial V}\right)_{T}
$$

or

$$
C_{P}=C_{V}-T\left(\frac{\partial V}{\partial T}\right)_{P}^{2}\left(\frac{\partial P}{\partial V}\right)_{T}
$$

For the ideal gas we have the Mayer relation

$$
C_{P}-C_{V}=R
$$

This is one of the most important equations of thermodynamics, and it shows that:
(a) $\left(\frac{\partial P}{\partial V}\right)_{T}<0$, leading to $C_{P}>C_{V}$
(b) As $T \rightarrow 0, C_{P} \rightarrow C_{V}$
(c) $\quad C_{P}=C_{V} \quad$ when $\left(\frac{\partial V}{\partial T}\right)_{P}=0$.
s
For example, at $4^{\circ} \mathrm{C}$ at which the density of water is maximum, $C_{P}=C_{V}$.
Using the volume expansion $\beta$ and isothermal compressibility $\kappa$

$$
\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P}, \quad \kappa=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T}=-\frac{1}{V} \frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T}}
$$

We may write the equation in the form

$$
C_{P}-C_{V}=\frac{T V \beta^{2}}{\kappa}
$$

## 4. Legendre transformation

Legendre transforms appear in two places in a standard undergraduate physics curriculum: (i) in classical mechanics and (ii) in thermodynamics. The Legendre transform simply changes the independent variables in a function of two variables by application of the product rule.

We start with the expression for the internal energy $U$ as

$$
d U=T d S-P d V
$$

## (a) Helmholtz free energy: $F$

Using the relation

$$
d U=d(T S)-S d T-P d V
$$

we have

$$
d(U-T S)=-S d T-P d V
$$

Here we introduce the Helmholtz free energy $F$ as

$$
F=U-S T
$$

Thus we have the relation

$$
d F=-S d T-P d V
$$

## (b) Enthalpy: H

From the relation

$$
\begin{aligned}
d U & =T d S-P d V \\
& =T d S-d(P V)+V d P
\end{aligned}
$$

we have

$$
d(U+P V)=T d S+V d P
$$

Here we introduce the enthalpy $H$ as

$$
H=U+P V
$$

Thus we have

$$
d H=T d S+V d P
$$

(c) Gibbs Free energy:

Using the relation

$$
\begin{aligned}
d F & =-S d T-P d V \\
& =-S d T-d(P V)+V d P
\end{aligned}
$$

we have
$\backslash$

$$
d(F+P V)=-S d T+V d P
$$

We introduce the Gibbs free energy $G$ as

$$
G=F+P V
$$

with

$$
d G=-S d T+V d P
$$

5. Thermodynamic potential


Fig. Born diagram. $E=U$ (internal energy). $A=F$ (Helmholtz free energy).
(a) The internal energy $U=U(S, V)$

For an infinitesimal reversible process, we have

$$
d U=T d S-P d V
$$

showing that

$$
T=\left(\frac{\partial U}{\partial S}\right)_{V}, \quad P=-\left(\frac{\partial U}{\partial V}\right)_{S}
$$

and

$$
\left(\frac{\partial T}{\partial V}\right)_{S}=-\left(\frac{\partial P}{\partial S}\right)_{V} \quad \text { (Maxwell's equation) }
$$

(b) The enthalpy $H=H(S, P)$

The enthalpy $H$ is defined as

$$
H=U+P V
$$

For an infinitesimal reversible process,

$$
d H=d U+P d V+V d P
$$

but

$$
d U=T d S-P d V
$$

Therefore we have

$$
d H=T d S+V d P
$$

showing that

$$
T=\left(\frac{\partial H}{\partial S}\right)_{P}, \quad V=\left(\frac{\partial H}{\partial P}\right)_{S}
$$

and

$$
\left(\frac{\partial T}{\partial P}\right)_{S}=\left(\frac{\partial V}{\partial S}\right)_{P} . \quad \quad \text { (Maxwell's equation) }
$$

(c) The Helmholtz free energy $F=F(T, V)$

The Helmholtz free energy is defined as

$$
F=U-S T
$$

For an infinitesimal reversible process,

$$
\begin{aligned}
d F & =d U-S d T-T d S \\
& =T d S-P d V-S d T-T d S \\
& =-S d T-P d V
\end{aligned}
$$

or

$$
d F=-S d T-P d V
$$

showing that

$$
\begin{array}{lr}
S=-\left(\frac{\partial F}{\partial T}\right)_{V}, & P=-\left(\frac{\partial F}{\partial V}\right)_{T} \\
\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V} & \text { (Maxwell's equation) }
\end{array}
$$

We note that

$$
U=F+S T=F-T\left(\frac{\partial F}{\partial T}\right)_{V}=-T^{2}\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_{V}
$$

(Gibbs-Helmholtz equation)
(d) The Gibbs free energy $G=G(T, P)$

The Gibbs free energy is defined as

$$
G=F+P V=H-T S
$$

For an infinitesimal reversible process,

$$
\begin{aligned}
d G & =d H-S d T-T d S \\
& =T d S+V d P-S d T-T d S \\
& =-S d T+V d P
\end{aligned}
$$

or

$$
d G=-S d T+V d P
$$

with

$$
d H=T d S+V d P
$$

showing that

$$
S=-\left(\frac{\partial G}{\partial T}\right)_{P}, \quad V=\left(\frac{\partial G}{\partial P}\right)_{T}
$$

and

$$
\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P} \quad \text { (Maxwell's equation) }
$$

We note that

$$
H=G+T S=G-T\left(\frac{\partial G}{\partial T}\right)_{P}=-T^{2}\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_{P}
$$

(Gibbs-Helmholtz equation)

## 6. Relations between the derivatives of thermodynamic quantities

(a) First energy equation

$$
\begin{aligned}
& d U=T d S-P d V \\
&\left(\frac{\partial U}{\partial V}\right)_{T}=\left(\frac{\partial}{\partial V}\right)_{T}(T d S-P d V) \\
&=T\left(\frac{\partial S}{\partial V}\right)_{T}-P
\end{aligned}
$$

Using the Maxwell's relation $\quad\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V}$, we get

$$
\left(\frac{\partial U}{\partial V}\right)_{T}=T\left(\frac{\partial P}{\partial T}\right)_{V}-P \quad \quad \text { (First energy equation) }
$$

which is called the first energy equation. For the ideal gas ( $P V=N k_{B} T$ ), we can make a proof of the Joule's law.

$$
\left(\frac{\partial U}{\partial V}\right)_{T}=0
$$

In other words, $U$ is independent of $V: \quad \Delta U=C_{V} \Delta T \quad$ (Joule's law for ideal gas)
(b) Second energy equation

$$
d U=T d S-P d V
$$

$$
\begin{aligned}
\left(\frac{\partial U}{\partial P}\right)_{T} & =\left(\frac{\partial}{\partial P}\right)_{T}(T d S-P d V) \\
& =T\left(\frac{\partial S}{\partial P}\right)_{T}-P\left(\frac{\partial V}{\partial P}\right)_{T}
\end{aligned}
$$

Using the Maxwell's relation $\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P}$, we get

$$
\left(\frac{\partial U}{\partial P}\right)_{T}=-T\left(\frac{\partial V}{\partial T}\right)_{P}-P\left(\frac{\partial V}{\partial P}\right)_{T} \quad \quad \text { (second energy equation) }
$$

which is called the second energy equation. For an ideal gas,

$$
\left(\frac{\partial U}{\partial P}\right)_{T}=-T \frac{R}{P}-P\left(-\frac{R T}{P^{2}}\right)=0
$$

In other words, $U$ is independent of $P: \quad \Delta U=C_{V} \Delta T \quad$ (Joule's law for ideal gas)

## 7. Generalized susceptibility

$\beta_{P}=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P} ; \quad$ isobaric expansivity
$\beta_{S}=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{S} ; \quad$ adiabatic expansivity
$\kappa_{T}=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T} ; \quad$ isothermal compressibility
$\kappa_{S}=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S} ; \quad$ adiabatic compressibility
8. The ratio $\gamma=\frac{C_{P}}{C_{V}}$

$$
\begin{aligned}
\frac{\kappa_{T}}{\kappa_{S}} & =\frac{\left(\frac{\partial V}{\partial P}\right)_{T}}{\left(\frac{\partial V}{\partial P}\right)_{S}} \\
& =\frac{\partial(V, T)}{\partial(P, T)} \frac{\partial(P, S)}{\partial(V, S)} \\
& =\frac{\partial(V, T)}{\partial(V, S)} \frac{\partial(P, S)}{\partial(P, T)} \\
& =\frac{\frac{\partial(P, S)}{\partial(P, T)}}{\frac{\partial(V, S)}{\partial(V, T)}}
\end{aligned}
$$

or

$$
\begin{aligned}
\frac{\kappa_{T}}{\kappa_{S}} & =\frac{\left(\frac{\partial V}{\partial P}\right)_{T}}{\left(\frac{\partial V}{\partial P}\right)_{S}} \\
& =\frac{\partial(V, T)}{\partial(P, T)} \frac{\partial(P, S)}{\partial(V, S)} \\
& =\frac{\partial(V, T)}{\partial(V, S)} \frac{\partial(P, S)}{\partial(P, T)} \\
& =\frac{\frac{\partial(P, S)}{\partial(P, T)}}{\frac{\partial(V, S)}{\partial(V, T)}}
\end{aligned}
$$

or

$$
\frac{\kappa_{T}}{\kappa_{S}}=\frac{\frac{\partial(S, P)}{\partial(T, P)}}{\frac{\partial(S, V)}{\partial(T, V)}}=\frac{T\left(\frac{\partial S}{\partial T}\right)_{P}}{T\left(\frac{\partial S}{\partial T}\right)_{V}}=\frac{C_{P}}{C_{V}}=\gamma
$$

9. Mayer's relation
(a) Relation $C_{P}=C_{V}-T \frac{\left(\frac{\partial P}{\partial T}\right)_{V}^{2}}{\left(\frac{\partial P}{\partial V}\right)_{T}}$

The thermodynamics first law:

$$
\begin{aligned}
& d U=T d S-P d V \\
& C_{P}=\left(\frac{\partial Q}{\partial T}\right)_{P}=T\left(\frac{\partial S}{\partial T}\right)_{P}
\end{aligned}
$$

Transforming $C_{P}$ to the variable $T$ and $P$,

$$
\begin{aligned}
\left(\frac{\partial S}{\partial T}\right)_{P} & =\frac{\partial(S, P)}{\partial(T, P)} \\
& =\frac{\frac{\partial(S, P)}{\frac{\partial(T, V)}{\partial(T, P)}}}{\partial(T, V)} \\
& =\left.\left.\frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T}}\left(\frac{\partial S}{\partial T}\right)_{V}\left(\frac{\partial P}{\partial T}\right)_{V}\left(\frac{\partial S}{\partial V}\right)_{T}\right|^{\left.\frac{\partial P}{\partial V}\right)_{T}}\right|^{\left(\frac{\partial P}{\partial V}\right)_{T}}\left[\left(\frac{\partial S}{\partial T}\right)_{V}\left(\frac{\partial P}{\partial V}\right)_{T}-\left(\frac{\partial S}{\partial V}\right)_{T}\left(\frac{\partial P}{\partial T}\right)_{V}\right] \\
& =\frac{1}{\left(\frac{\partial S}{\partial T}\right)_{V}-\frac{\left(\frac{\partial S}{\partial V}\right)_{T}\left(\frac{\partial P}{\partial T}\right)_{V}}{\left(\frac{\partial P}{\partial V}\right)_{T}}}
\end{aligned}
$$

Here we use the Maxwell's relation,

$$
\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V}
$$

Thus we get

$$
T\left(\frac{\partial S}{\partial T}\right)_{P}=T\left(\frac{\partial S}{\partial T}\right)_{V}-T \frac{\left(\frac{\partial P}{\partial T}\right)_{V}^{2}}{\left(\frac{\partial P}{\partial V}\right)_{T}}
$$

or

$$
C_{P}-C_{V}=-T \frac{\left(\frac{\partial P}{\partial T}\right)_{V}^{2}}{\left(\frac{\partial P}{\partial V}\right)_{T}}
$$

Note that

$$
\begin{aligned}
& \left(\frac{\partial P}{\partial V}\right)_{T}=\frac{\partial(P, T)}{\partial(V, T)}=\frac{1}{\frac{\partial(V, T)}{\partial(P, T)}}=\frac{1}{\left(\frac{\partial V}{\partial P}\right)_{T}} \\
& \left(\frac{\partial P}{\partial T}\right)_{V}=\frac{\partial(P, V)}{\partial(T, V)}=\frac{\frac{\partial(P, V)}{\partial(T, P)}}{\frac{\partial(T, V)}{\partial(T, P)}}=-\frac{\left(\frac{\partial V}{\partial T}\right)_{P}}{\left(\frac{\partial V}{\partial P}\right)_{T}}
\end{aligned}
$$

Then we have

$$
C_{P}-C_{V}=-T \frac{\left(\frac{\partial V}{\partial T}\right)_{P}^{2}}{\left(\frac{\partial V}{\partial P}\right)_{T}}=V T \frac{\beta_{P}^{2}}{\kappa_{T}}
$$



Similarly, transforming $C_{V}$ to the variable $T$ and $V$,

$$
\begin{aligned}
\left(\frac{\partial S}{\partial T}\right)_{V} & =\frac{\partial(S, V)}{\partial(T, V)} \\
& =\frac{\frac{\partial(S, V)}{\frac{\partial(T, P)}{\partial(T, V)}}}{\partial(T, P)} \\
& \left.=\frac{1}{\left(\frac{\partial V}{\partial P}\right)_{T}}\left|\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial V}{\partial T}\right)_{P}\left(\frac{\partial S}{\partial P}\right)_{T}\right|^{\partial P}\right)_{T} \mid \\
& =\frac{1}{\left(\frac{\partial V}{\partial P}\right)_{T}}\left[\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial V}{\partial P}\right)_{T}-\left(\frac{\partial S}{\partial P}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{P}\right] \\
& =\left(\frac{\partial S}{\partial T}\right)_{P}-\frac{\left(\frac{\partial S}{\partial P}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{P}}{\left(\frac{\partial V}{\partial P}\right)_{T}}
\end{aligned}
$$

Using the Maxwell's relation

$$
\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P}
$$

we have

$$
T\left(\frac{\partial S}{\partial T}\right)_{V}=T\left(\frac{\partial S}{\partial T}\right)_{P}+\frac{T\left[\left(\frac{\partial V}{\partial T}\right)_{P}\right]^{2}}{\left(\frac{\partial V}{\partial P}\right)_{T}}
$$

or

$$
C_{P}-C_{V}=-T \frac{\left[\left(\frac{\partial V}{\partial T}\right)_{P}\right]^{2}}{\left(\frac{\partial V}{\partial P}\right)_{T}}=V T \frac{\beta_{P}{ }^{2}}{\kappa_{T}}
$$

## 10. Derivative of $C \mathrm{v}$ with respect to $\boldsymbol{T}$ (Reif, Blundell)

$$
\begin{aligned}
\left(\frac{\partial C_{V}}{\partial V}\right)_{T} & =\left(\frac{\partial}{\partial V}\right)_{T}\left[T\left(\frac{\partial S}{\partial T}\right)_{V}\right] \\
& =T \frac{\partial^{2} S}{\partial V \partial T} \\
& =T \frac{\partial^{2} S}{\partial T \partial V} \\
& =T\left(\frac{\partial}{\partial T}\right)_{V}\left(\frac{\partial S}{\partial V}\right)_{T} \\
& =T\left(\frac{\partial}{\partial T}\right)_{V}\left(\frac{\partial S}{\partial V}\right)_{T}
\end{aligned}
$$

Using the Maxwell's relation

$$
\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V}
$$

we get

$$
\left(\frac{\partial C_{V}}{\partial V}\right)_{T}=T\left(\frac{\partial}{\partial T}\right)_{V}\left(\frac{\partial P}{\partial T}\right)_{V}=T\left(\frac{\partial^{2} P}{\partial T^{2}}\right)_{V}
$$

11. Derivative of $C_{P}$ with respect to $P$ (Reif, Blundell)

$$
\begin{aligned}
\left(\frac{\partial C_{P}}{\partial P}\right)_{T} & =\left(\frac{\partial}{\partial P}\right)_{T}\left[T\left(\frac{\partial S}{\partial T}\right)_{P}\right] \\
& =T \frac{\partial^{2} S}{\partial P \partial T} \\
& =T \frac{\partial^{2} S}{\partial T \partial P} \\
& =T\left(\frac{\partial}{\partial T}\right)_{P}\left(\frac{\partial S}{\partial P}\right)_{T} \\
& =T\left(\frac{\partial}{\partial T}\right)_{P}\left(\frac{\partial S}{\partial P}\right)_{T}
\end{aligned}
$$

Using the Maxwell's relation

$$
\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P}
$$

we get

$$
\left(\frac{\partial C_{P}}{\partial P}\right)_{T}=-T\left(\frac{\partial}{\partial T}\right)_{P}\left(\frac{\partial V}{\partial T}\right)_{P}=-T\left(\frac{\partial^{2} V}{\partial T^{2}}\right)_{P}
$$

## 12. Joule-Thomson expansion

$$
\begin{aligned}
\left(\frac{\partial T}{\partial P}\right)_{H} & =\frac{\partial(T, H)}{\partial(P, H)} \\
& =\frac{\frac{\partial(T, H)}{\partial(P, T)}}{\frac{\partial(P, H)}{\partial(P, T)}} \\
& =\frac{-\left(\frac{\partial H}{\partial P}\right)_{T}}{\left(\frac{\partial H}{\partial T}\right)_{P}}
\end{aligned}
$$

Note that

$$
d H=T d S+V d P
$$

So we get

$$
\begin{aligned}
\left(\frac{\partial H}{\partial P}\right)_{T} & =\left(\frac{\partial}{\partial P}\right)_{T}(T d S+V d P) \\
& =T\left(\frac{\partial S}{\partial P}\right)_{T}+V \\
& =-T\left(\frac{\partial V}{\partial T}\right)_{T}+V
\end{aligned}
$$

$$
\begin{aligned}
\left(\frac{\partial H}{\partial T}\right)_{P} & =\left(\frac{\partial}{\partial T}\right)_{P}(T d S+V d P) \\
& =T\left(\frac{\partial S}{\partial T}\right)_{P} \\
& =C_{P}
\end{aligned}
$$

Thus we have

$$
\left(\frac{\partial T}{\partial P}\right)_{H}=\frac{1}{C_{P}}\left[T\left(\frac{\partial V}{\partial T}\right)_{T}-V\right]
$$

## REFERENCES

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F. Reif, Fundamentals of Statistical and Thermal Physics (McGraw-Hill, 1965).
S. Blundel and K. Blundel, Concepts of Thermal Physics (Oxford, 2015).

## APPENDIX

Stokes theorem and conservative force

## 1 Conservative force

### 1.1 Path integral

The work done by a conservative force on a particle moving between any two points is independent of the path taken by the particle.


$$
\int_{\text {Path }-1} \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=\int_{\text {Path }-2} \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=\int_{\text {Path }-3} \boldsymbol{F}_{c} \cdot d \boldsymbol{r}
$$

for any path connecting two points A and B .

### 1.2 Path integral along the closed path

The work done by a conservative force on a particle moving through any closed path is zero. (A closed path is one for which the beginning point and the endpoint are identical).


$$
\oint \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=0, \quad \text { for any closed path }
$$

## 2 Potential energy $U$

The quantity $\boldsymbol{F}_{c} \cdot d \boldsymbol{r}$ can be expressed in the form of a perfect differential

$$
d U=-W_{c}=-\boldsymbol{F}_{c} \cdot d \boldsymbol{r}
$$

where the function $U(\boldsymbol{r})$ depends only on the position vector r and does not depend explicitly on the velocity and time. A force $\boldsymbol{F}_{\mathrm{c}}$ is conservative and $U$ is known as the potential energy.

$$
\int_{A}^{B} \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=-\int_{A}^{B} d U=U(A)-U(B)
$$

which does not depend on the path of integration but only on the initial and final positions. It is clear that the integral over a closed path is zero

$$
\begin{equation*}
\oint \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=0 \tag{1}
\end{equation*}
$$

which is a different way of saying that the force field is conservative

## Using Stoke's theorem;

For any vector $\boldsymbol{A}$,

$$
\oint \boldsymbol{A} \cdot d \boldsymbol{r}=\int(\nabla \times \boldsymbol{A}) \cdot d \boldsymbol{a} .
$$

Since

$$
\oint \boldsymbol{F}_{c} \cdot d \boldsymbol{r}=\int\left(\nabla \times \boldsymbol{F}_{c}\right) \cdot d \boldsymbol{a}=0
$$

we have

$$
\begin{equation*}
\nabla \times \boldsymbol{F}_{c}=0, \tag{2}
\end{equation*}
$$

where $\nabla$ is a differential operator called del or nabla. The operator can be written in n terms of the Cartesian components $x, y, z$ in the form

$$
\nabla=\hat{\boldsymbol{i}} \frac{\partial}{\partial x}+\hat{\boldsymbol{j}} \frac{\partial}{\partial y}+\hat{\boldsymbol{k}} \frac{\partial}{\partial z}
$$

In this case, $\boldsymbol{F}_{\mathrm{c}}$ can be expressed by

$$
\boldsymbol{F}_{c}=-\nabla U
$$

or

$$
\boldsymbol{F}_{c}=\left(-\frac{\partial U}{\partial x},-\frac{\partial U}{\partial y},-\frac{\partial U}{\partial z}\right)
$$

which leads to the relation

$$
\begin{gathered}
\frac{\partial F_{c x}}{\partial y}=\frac{\partial F_{c y}}{\partial x} \\
\frac{\partial F_{c y}}{\partial z}=\frac{\partial F_{c z}}{\partial y} . \\
\frac{\partial F_{c z}}{\partial x}=\frac{\partial F_{c x}}{\partial z}
\end{gathered}
$$

This relation can be used to decide whether a force is conservative or not on physical grounds.
We note that

$$
\begin{aligned}
\nabla \times \boldsymbol{F}_{c} & =\left|\begin{array}{ccc}
\hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\
\frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\
F_{c x} & F_{c y} & F_{c z}
\end{array}\right|=\hat{\boldsymbol{i}}\left|\begin{array}{cc}
\frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\
F_{c y} & F_{c z}
\end{array}\right|-\hat{\boldsymbol{j}}\left|\begin{array}{cc}
\frac{\partial}{\partial x} & \frac{\partial}{\partial z} \\
F_{c x} & F_{c z}
\end{array}\right|+\hat{\boldsymbol{k}}\left|\begin{array}{ll}
\frac{\partial}{\partial x} & \frac{\partial}{\partial y} \\
F_{c x} & F_{c y}
\end{array}\right| \\
& =\hat{\boldsymbol{i}}\left(\frac{\partial F_{c z}}{\partial y}-\frac{\partial F_{c y}}{\partial z}\right)-\hat{\boldsymbol{j}}\left(\frac{\partial F_{c z}}{\partial x}-\frac{\partial F_{c x}}{\partial z}\right)+\hat{\boldsymbol{k}}\left(\frac{\partial F_{c y}}{\partial x}-\frac{\partial F_{c x}}{\partial y}\right)
\end{aligned}
$$

## 3 Stoke's theorem

Stokes' theorem (or Stokes's theorem) in differential geometry is a statement about the integration of differential forms which generalizes several theorems from vector calculus. It is named after Sir George Gabriel Stokes (1819-1903), although the first known statement of the theorem is by William Thomson (Lord Kelvin) and appears in a letter of his to Stokes. The theorem acquired its name from Stokes' habit of including it in the Cambridge prize examinations. In 1854, he asked his students to prove the theorem on an examination. It is unknown if anyone was able to do so.

Let's start off with the following surface with the indicated orientation.


Around the edge of this surface we have a curve $C$. This curve is called the boundary curve. The orientation of the surface $S$ will induce the positive orientation of $\boldsymbol{C}$. To get the positive orientation of $C$ think of yourself as walking along the curve. While you are walking along the curve if your head is pointing in the same direction as the unit normal vectors while the surface is on the left then you are walking in the positive direction on $C$.
Now that we have this curve definition out of the way we can give Stokes' Theorem.

## Stokes' Theorem

Let $S$ be an oriented smooth surface that is bounded by a simple, closed, smooth boundary curve C with positive orientation. Also let $\boldsymbol{F}$ be a vector field, then

$$
\oint \boldsymbol{F} \cdot d \boldsymbol{r}=\int(\nabla \times \boldsymbol{F}) \cdot d \boldsymbol{a}=\int(\nabla \times \boldsymbol{F}) \cdot \boldsymbol{n} d a
$$

In this theorem note that the surface $S$ can actually be any surface so long as its boundary curve is given by $C$. This is something that can be used to our advantage to simplify the surface integral on occasion.

## 4. Path integral and conservative force

((Example)) Serway Problem 7-15
A force acting on a particle moving in the $x y$ plane is given by

$$
\boldsymbol{F}=\left(2 y \hat{i}+x^{2} \hat{j}\right) N
$$

where $x$ and $y$ are in meters. The particle moves from the origin to a final position having coordinates $x=5.00 \mathrm{~m}$ and $y=5.00 \mathrm{~m}$ as in Fig. Calculate the work done by $F$ along (a) OAC, (b) OBC, (c) OC. (d) Is $F$ conservative or nonconservative? Explain.

((Solution))

$$
\boldsymbol{F} \cdot d \boldsymbol{r}=F_{x} d x+F_{y} d y=2 y d x+x^{2} d y
$$

## Path OAC

On the path $\mathrm{OA} ; x=0-5, y=0 ; \boldsymbol{F}=x^{2} \hat{j}$ and $\mathrm{d} y=0$.

$$
\int_{O}^{A} \boldsymbol{F} \cdot d \boldsymbol{r}=0
$$

On the path AC; $x=5, y=0-5 ; \boldsymbol{F}=5^{2} \hat{j}=25 \hat{j}$

$$
\int_{A}^{C} \boldsymbol{F} \cdot d \boldsymbol{r}=\int_{0}^{5} 25 d y=125
$$

Then we have

$$
\int_{o}^{C} \boldsymbol{F} \cdot d \boldsymbol{r}=125 J \text { for the path OAC }
$$

## Path OBC

On the path $\mathrm{OB} ; x=0, y=0-5$;

$$
\boldsymbol{F} \cdot d \boldsymbol{r}=2 y d x \text { and } \mathrm{d} x=0
$$

or

$$
\int_{O}^{B} \boldsymbol{F} \cdot d \boldsymbol{r}=0
$$

On the path BC; $x=0-5, y=5 ; \boldsymbol{F} \cdot d \boldsymbol{r}=2 y d x=10 d x$

$$
\int_{B}^{C} \boldsymbol{F} \cdot d \boldsymbol{r}=\int_{0}^{5} 10 d x=50
$$

Then we have

$$
\int_{o}^{c} \boldsymbol{F} \cdot d \boldsymbol{r}=50 \mathrm{~J} \text { for the path } \mathrm{OBC}
$$

Path OC
$x=t, \mathrm{y}=t$ for $t=0-5$.

$$
\begin{aligned}
& 2 y d x+x^{2} d y=2 t d t+t^{2} d t=\left(t^{2}+2 t\right) d t \\
& \int_{0}^{c} \boldsymbol{F} \cdot d \boldsymbol{r}=\int_{0}^{5}\left(t^{2}+2 t\right) d t=\frac{125}{3}+2 \frac{5^{2}}{2}=\frac{200}{3} J
\end{aligned}
$$

for the path OC line. Then the force is non-conservative.
((Note))

$$
\boldsymbol{F}=\left(2 y \hat{\boldsymbol{i}}+x^{2} \hat{\boldsymbol{j}}\right) N
$$

$$
\begin{aligned}
& \frac{\partial F_{x}}{\partial y}=2 \\
& \frac{\partial F_{y}}{\partial x}=2 x
\end{aligned}
$$

This implies that the force is not conservative.

