

# Appendix A

## The Mathematics of Thermodynamics

### A.1 Exact differential and integrating factor

Consider a function of two independent variables

$$f = f(x, y).$$

The expression

$$df(x, y) = \left. \frac{\partial f}{\partial x} \right|_y dx + \left. \frac{\partial f}{\partial y} \right|_x dy$$

is called the differential of  $f(x, y)$ . Notice that the generalization to more than two variables is obvious. However, for most of our manipulations and transformations of thermodynamic relations this is the relevant case.

Now consider the expression

$$dg(x, y) = pdx + qdy.$$

Provided that

$$\left. \frac{\partial p}{\partial y} \right|_x = \left. \frac{\partial q}{\partial x} \right|_y$$

holds, then  $dg(x, y)$  is an exact differential. An example of an exact differential is

$$dg(x, y) = (3x^2 + y \cos x) dx + (\sin x - 4y^3) dy,$$

because

$$\underbrace{\left. \frac{\partial}{\partial y} (3x^2 + y \cos x) \right|_x}_{=\cos x} = \underbrace{\left. \frac{\partial}{\partial x} (\sin x - 4y^3) \right|_y}_{=\cos x}.$$

An example of a differential which is not exact is

$$dg(x, y) = (3xy^2 + 2y) dx + (2x^2y + x) dy,$$

because

$$\underbrace{\frac{\partial}{\partial y} (3xy^2 + 2y) \Big|_x}_{=6xy+2} \neq \underbrace{\frac{\partial}{\partial x} (2x^2y + x) \Big|_y}_{=4xy+1}.$$

However, in this case we can multiply  $dg(x, y)$  by  $x$ , i.e.

$$\begin{aligned} dh(x, y) &\equiv x dg(x, y) \\ &= (3x^2y^2 + 2yx) dx + (2x^3y + x^2) dy. \end{aligned}$$

Obviously  $dh(x, y)$  again is an exact differential:

$$\underbrace{\frac{\partial}{\partial y} (3x^2y^2 + 2xy) \Big|_x}_{=6x^2y+2x} = \underbrace{\frac{\partial}{\partial x} (2x^3y + x^2) \Big|_y}_{=6x^2y+2x}.$$

Because of this the factor  $x$  is called integrating factor.

Notice that the above  $df(x, y)$  is an exact differential, because the partial derivatives may be exchanged, i.e.

$$\frac{\partial}{\partial x} \frac{\partial f}{\partial y} \Big|_x \Big|_y = \frac{\partial}{\partial y} \frac{\partial f}{\partial x} \Big|_y \Big|_x$$

assuming continuity of the derivatives.

The special importance of exact differentials in thermodynamics is rooted in the following mathematical theorem: Let

$$dA(x, y) = P dx + Q dy,$$

where  $P$ ,  $Q$ ,  $\partial P/\partial y$ , and  $\partial Q/\partial x$  are single-valued and continuous in a simply- (or multiply-)connected region  $\mathcal{R}$  bounded by a simple (or more) closed curve(s)  $\mathcal{C}$ . Then

$$\oint_{\mathcal{C}} dA = \int_{\mathcal{R}} dx dy \left( \frac{\partial Q}{\partial x} \Big|_y - \frac{\partial P}{\partial y} \Big|_x \right).$$

This statement is called Green's theorem in the plane. A proof may be found in Spiegel (1971). We conclude immediately that if  $dA(x, y)$  is an exact differential, and therefore

$$\left. \frac{\partial Q}{\partial x} \right|_y = \left. \frac{\partial P}{\partial y} \right|_x,$$

we have

$$\oint_{\mathcal{C}} dA = 0.$$

This means that if we divide a closed path  $\mathcal{C}$  in the  $x$ - $y$ -plane into two sections, i.e.

$$\mathcal{C} = (x_1, y_1) \xrightarrow{\text{path I}} (x_2, y_2) \xrightarrow{\text{path II}} (x_1, y_1),$$

we find

$$\int_{1, \text{path I}}^2 dA + \int_{2, \text{path II}}^1 dA = 0$$

or

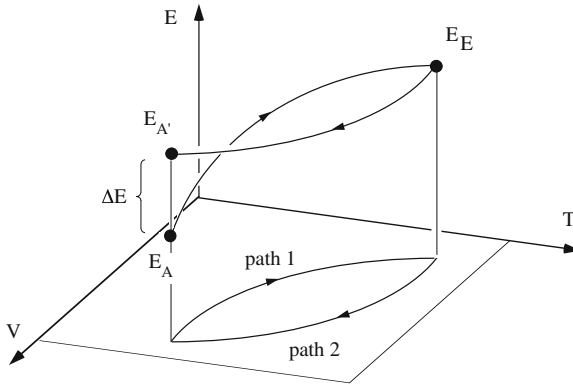
$$\int_{1, \text{path I}}^2 dA = \int_{1, \text{path II}}^2 dA.$$

Therefore the value of  $A(x_2, y_2)$  does not depend on the path along which  $(x_2, y_2)$  is reached. Every function  $A(x, y)$  possessing this property is called a state function. Thus, if  $dA(x, y)$  is an exact differential then  $A(x, y)$  is a state function and vice versa.

**Example: Perpetual Motion Machine.** The physical significance of this is best explained using the internal energy  $E$ . Consider for simplicity a closed system containing a gas. We know from experience that the state of the gas is described completely if we know its temperature,  $T$ , and its volume,  $V$ . We want to study the change of  $E$  along a closed path  $\mathcal{C}$  in the  $T$ - $V$ -plane. Let us assume we find that

$$\oint_{\mathcal{C}} dE = \Delta E \neq 0.$$

If  $\Delta E > 0$  we may generate an arbitrary amount of energy simply by repeating the cyclic path in the  $T$ - $V$ -plane (this situation is depicted in Fig. A.1). If  $\Delta E < 0$  we reverse direction and again generate energy. A machine constructed on this principle is called a perpetual motion machine. However, no such device has been build thus far.



**Fig. A.1** Hypothetical internal energy gain along a closed path in the T-V-plane

**Example:  $dq$  is not an Exact Differential.** Let us study another instructive example. We consider a process involving volume change like the one we have discussed before (see p. 1). We want to show that

$$dq = dE + PdV$$

is not an exact differential. Using  $E = E(T, V)$  we obtain

$$dq = \left. \frac{\partial E}{\partial T} \right|_V dT + \left( \left. \frac{\partial E}{\partial V} \right|_T + P \right) dV.$$

Exact differential would mean that

$$\underbrace{\frac{\partial}{\partial V} \left. \frac{\partial E}{\partial T} \right|_V \bigg|_T}_{\stackrel{(*)}{=} \frac{\partial}{\partial T} \left. \frac{\partial E}{\partial V} \right|_T \bigg|_V} = \frac{\partial}{\partial T} \left( \left. \frac{\partial E}{\partial V} \right|_T + P \right) \bigg|_V.$$

Here (\*) holds, because  $dE$  is an exact differential (cf. above). Therefore we must have

$$\left. \frac{\partial P}{\partial T} \right|_V = 0.$$

This equation obviously cannot be correct, and therefore  $q$  is no state function.

**Remark:** Because we have seen that  $S$  is a state function, we conclude that according to Eq. (2.47)  $1/T$  is an integrating factor.

### A.2 Three Useful Differential Relations

In the following we derive three useful differential relations. Consider  $A = A(x, y)$  and  $z = z(x, y)$ . The differential of  $A$  is

$$dA = \left. \frac{\partial A}{\partial x} \right|_y dx + \left. \frac{\partial A}{\partial y} \right|_x dy,$$

and therefore

$$\left. \frac{\partial A}{\partial x} \right|_z = \left. \frac{\partial A}{\partial x} \right|_y \underbrace{\left. \frac{\partial x}{\partial x} \right|_z}_{=1} + \left. \frac{\partial A}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z$$

or

$$\left. \frac{\partial A}{\partial z} \right|_y = \left. \frac{\partial A}{\partial x} \right|_y \left. \frac{\partial x}{\partial z} \right|_y + \left. \frac{\partial A}{\partial y} \right|_x \underbrace{\left. \frac{\partial y}{\partial z} \right|_y}_{=0}.$$

Thus we find

$$\boxed{\left. \frac{\partial A}{\partial x} \right|_z = \left. \frac{\partial A}{\partial x} \right|_y + \left. \frac{\partial A}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z} \tag{A.1}$$

and

$$\boxed{\left. \frac{\partial A}{\partial z} \right|_y = \left. \frac{\partial A}{\partial x} \right|_y \left. \frac{\partial x}{\partial z} \right|_y} \tag{A.2}$$

The third relation follows if we use  $z = A$  in Eq. (A.1), i.e.

$$\underbrace{\left. \frac{\partial z}{\partial x} \right|_z}_{=0} = \left. \frac{\partial z}{\partial x} \right|_y + \left. \frac{\partial z}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z,$$

and therefore

$$\boxed{\left. \frac{\partial x}{\partial y} \right|_z = - \left. \frac{\partial x}{\partial z} \right|_y \left. \frac{\partial z}{\partial y} \right|_x}, \tag{A.3}$$

where we have used

$$\left. \frac{\partial z}{\partial x} \right|_y = \frac{1}{\left. \frac{\partial x}{\partial z} \right|_y}$$

and

$$\left. \frac{\partial y}{\partial x} \right|_z = \frac{1}{\left. \frac{\partial x}{\partial y} \right|_z}.$$

### A.3 Legendre Transformation

Consider

$$df = udx + vdy$$

where

$$v = \left. \frac{\partial f}{\partial y} \right|_x. \quad (\text{A.4})$$

We define a new function  $g$  via

$$g = f - vy. \quad (\text{A.5})$$

Notice that  $g$ , computed for a certain  $y$ -value, is the intercept of the tangent of  $f$  at this  $y$ -value with the  $f$ -axis ( $f(\dots, y) = f'(\dots, y)y + b$ , where  $b$  is the intercept).

Next we compute  $dg$ , i.e.

$$dg = df - d(vy) = udx + vdy - vdy - ydv.$$

Therefore

$$dg = udx - ydv.$$

This tells us that  $g$  is a function of  $x$  and  $v$ , i.e.  $g = g(x, v)$ . The function  $g(x, v)$  is called the Legendre transform of  $f(x, y)$ . It replaces the dependence on  $y$  by a dependence on  $v$ . The key to this replacement is the validity of  $v = \partial f / \partial y|_x$ .

**Example:**  $f = p(x^2 + y^2)$ . We consider the example

$$f(x, y) = p(x^2 + y^2), \quad (\text{A.6})$$

where  $p$  is a parameter. We find

$$v = \left. \frac{\partial f}{\partial y} \right|_x = 2py \quad \text{and thus} \quad y = \frac{v}{2p}. \quad (\text{A.7})$$

Inserting this into Eq. (A.5) yields

$$g(x, v) = px^2 - \frac{1}{4p}v^2. \quad (\text{A.8})$$

We can use this to illustrate an important point. Assume that the parameter  $p$  is changed, i.e.  $p_{\text{new}} = p_{\text{old}} - \delta p$ . If  $\delta p > 0$  this means that

$$\delta f(x, y)|_{x,y} < 0, \quad (\text{A.9})$$

where  $\delta f = f(x, y; p_{new}) - f(x, y; p_{old})$ . What happens to  $g(x, v)$ ? The answer is

$$\begin{aligned} \delta g|_{x,v} &= (p - \delta p)x^2 - \frac{1}{4(p - \delta p)}v^2 - px^2 + \frac{1}{4p}v^2 \\ &\approx -\delta p x^2 - \frac{1}{4p} \left(1 + \frac{\delta p}{p}\right) v^2 + \frac{1}{4p} v^2 \\ &= - \left(x^2 + \frac{1}{4p^2} v^2\right) \delta p < 0. \end{aligned} \quad (\text{A.10})$$

This means that the decrease of  $f(x, y; p)$  at constant  $x$  and  $y$  is carried over to the Legendre transform  $g(x, v)$  at constant  $x$  and  $v$ . Even though this is not a general proof, we can see easily from Eq. (A.5) in conjunction with Eq. (A.4) that a (local) shift of  $f$  at certain fixed variables  $x$  and  $y$  produces a corresponding shift of  $g$  at the attendant fixed values of  $x$  and  $v$ . This is very useful—as we shall see.

## Appendix B

# Grand-Canonical Monte Carlo: Methane on Graphite

```

"GCMC: adsorption of methane on graphite" ;
  "units = Lennard-Jones units" ;
  "temperature";  $T = 1.53$ ; Print["T=",  $T$ ];
  "target bulk density";  $\rho_{\text{bulk}} = 0.05$ ; Print[" $\rho_{\text{bulk}}$ =",  $\rho_{\text{bulk}}$ ];
  "2nd virial coefficient";
   $B2 = N \int_0^\infty [-2\pi(\text{Exp}[-(4(1/s^{12} - 1/s^6))/T] - 1)s^2,$ 
{s, 0, Infinity}];
  "bulk pressure";  $P = T\rho_{\text{bulk}}(1 + \rho_{\text{bulk}} B2)$ ; Print["P=",  $P$ ];
  "excess chemical potential";  $\mu_{\text{ex}} = 2T\rho_{\text{bulk}} B2$ ; Print[" $\mu_{\text{ex}}$ =",  $\mu_{\text{ex}}$ ];
  "simulation box size (LxLxLz)";  $L = 6$ ;  $Lz = 2L$ ;  $V = L^2 Lz$ ;
   $a = N[V \rho_{\text{bulk}} \text{Exp}[\mu_{\text{ex}}/T]]$ ;
  "cutoff radius";  $r_{\text{cut}} = 3.0$ ;
  "particle coordinates";
  TLIST = Table[{Random[Real, {1, L}], Random[Real, {1, L}],
Random[Real, {1, Lz}], {i, 1, 2}];
   $n = \text{Length}[TLIST]$ ;
  "MC step counter";  $\text{mcsteps} = 0$ ;
  "steps per MC-cycle";  $\text{maxmcsteps} = 1000$ ;
  "cycle counter";  $\text{cycles} = 0$ ;
  "total number of cycles";  $\text{maxcycles} = 4000$ ;
  "initial values in density histogram";  $\text{nint} = 100$ ;  $\rho = \text{Table}[0, \{i, 0, \text{nint}\}]$ ;
   $\text{counter} = 0$ ;
  While[cycles < maxcycles, cycles++;
  While[mcsteps < maxmcsteps,
  "particle insertion";
  "1. random position";
   $x = \{\text{Random}[\text{Real}, L], \text{Random}[\text{Real}, L], \text{Random}[\text{Real}, Lz]\}$ ;
  "2. energy change";
   $\Delta u = 0$ ;
  Do[ $y = \text{Extract}[TLIST, i] - x$ ;

```



```

r = Sqrt[(y[[1]] - LRound[y[[1]]/L]^2 + (y[[2]] - LRound[y[[2]]/L]^2 +
y[[3]]^2);
If[r < rcut, Δu+=4(r^(-12) - r^(-6)), {}], {i, 1, n}];
Δusurf = 17.908(0.4(1.034/x[[3]]^10 - (1.034/x[[3]]^4);
"3. Metropolis ";
If[Min[1, Check[ $\frac{a}{n+1}$ Exp[-(Δu + Δusurf)/T], 0]] ≥ Random[],
{TLIST = Append[TLIST, x]; n++}, {}];
mcsteps++;

"particle removal";
"1. random selection";
p = Random[Integer, {1, n}];
"2. energy change ";
Δu = 0;
Do[y = Extract[TLIST, i] - Extract[TLIST, p];
r = Sqrt[(y[[1]] - LRound[y[[1]]/L]^2 + (y[[2]] - LRound[y[[2]]/L]^2 +
y[[3]]^2);
If[r > 0&& r < rcut, Δu+=4(r^(-12) - r^(-6)), {}], {i, 1, n}];
Δusurf =
17.908(0.4(1.034/Extract[TLIST, p][[3]]^10 -
(1.034/Extract[TLIST, p][[3]]^4);
"3. Metropolis "; If[Min[1, Check[ $\frac{n}{a}$ Exp[(Δu + Δusurf)/T], 0]] ≥ Random[],
{TLIST = Delete[TLIST, p]; n-}, {}];
mcsteps++;

"generate density profile normal to surface";
If[cycles > 5,
{Do[ρ[[Round[Extract[TLIST, i][[3]]/(Lz/nint)]]]++, {i, 1, Length[TLIST]};
counter++; "optional output: histogram ";
If[False, {ListPlot[ρ/(counter V/Length[ρ])}], {}];
Print["cycle ", cycles, " of ", maxcycles], {}]; "optional output: box ";
If[False, {pts = Table[Point[Extract[TLIST, i]], {i, 1, Length[TLIST]};
Show[Graphics3D[{PointSize[0.05], pts}], {}];
"complete density profile ";
hist = {}; Do[hist = Append[hist, {iLz/Length[ρ], ρ[[i]]/(counter V/(nint + 1))}],
{i, 1, Length[ρ]}; ListPlot[hist, Joined → True, AxesLabel → {"z [LJ]", "ρ [LJ]"},
PlotRange → {0, 1}, PlotStyle → Black]
"box ";
If[True, {pts = Table[Point[Extract[TLIST, i]], {i, 1, Length[TLIST]};
Show[Graphics3D[{PointSize[0.05], pts}], {}];

```

**Remark 1:** *bulk* refers to the region far from the surface, where the system is homogeneous.

**Remark 2:** The program assumes that the bulk gas density is low. In particular it uses  $\mu_{ex} \approx 2B_2(T)P$ , where  $B_2(T)$  is the second virial coefficient and  $P$  is the

(bulk) gas pressure. This is obtained by integrating  $\partial\mu/\partial P|_T = 1/\rho(P)$ .  $\rho(P)$  is obtained by inserting the expansion  $\rho = c_1P + c_2P^2 + \dots$  into the virial expansion of the pressure,  $P = T\rho(1 + B_2\rho + \dots)$  and comparing coefficients ( $c_1 = T^{-1}$ ;  $c_2 = -T^{-2}B_2, \dots$ ). Integration and subsequent subtraction of the ideal gas chemical potential yields  $\mu_{ex} = \mu - \mu_{id} = 2B_2P + \dots$ . The integral formula for the second virial coefficient can be found in every textbook on Statistical Mechanics.

**Remark 3:** The quantity  $r = \text{Sqrt}[(y[[1]] - \text{LRound}[y[[1]]/L])^2 + (y[[2]] - \text{LRound}[y[[2]]/L])^2 + y[[3]]^2]$  is the *minimum image distance* between the particle  $x$  to be inserted or removed and another particle  $i$  in the system. The minimum image distance is the smallest distance within the set of all distances between  $x$  and  $i$  as well as  $i$ 's periodic images (parallel to the surface). Subsequently the interactions are calculated only if  $r < r_{cut}$  - a suitable cutoff. In the present program all interactions of  $x$  with other particles or image particles are neglected if  $r \geq r_{cut}$ .  $r_{cut}$  must be large enough to justify the neglect of interactions. Simultaneously it must be small enough to avoid inclusion of interactions from one and the same particle more than once via its periodic images. Notice that the minimum image construction allows the actual particles to be anywhere in space - even outside the simulation box (cf. Frenkel and Smit (1996) or Allen Tildesley (1990)).

## Appendix C

### Constants, Units, Tables

$N_A$	$= 6.02214... \cdot 10^{23} \text{ mol}^{-1}$	Avogadro's number
$R$	$= 8.31447... \text{ J K}^{-1} \text{ mol}^{-1}$	Gas constant
$hN_A$	$= 3.99031... \cdot 10^{-10} \text{ J smol}^{-1}$	$h$ : Planck's constant ( $\hbar = h/(2\pi)$ )
$m_{amu}N_A$	$= 10^{-3} \text{ kg}$	$m_{amu} = \frac{1}{12}m(^{12}\text{C})$ : Atomic mass constant
$F = eN_A$	$= 9.64853... \cdot 10^4 \text{ C mol}^{-1}$	Faraday constant= $eN_A$ ; $e$ : elementary charge
$\epsilon_o$	$= 8.85418... \cdot 10^{-12} \text{ F m}^{-1}$	Electric constant
$\mu_o$	$= 1.25663... \cdot 10^{-6} \text{ N A}^{-2}$	Magnetic constant
$c$	$= 2.99792... \cdot 10^8 \text{ m s}^{-1}$	Vacuum speed of light ( $c = (\epsilon_o\mu_o)^{-1/2}$ )
$g$	$= 9.80665 \text{ m s}^{-2}$	Standard gravitational acceleration
$G$	$= 6.673... \cdot 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$	Gravitational constant
$1 \text{ bar}$	$= 10^5 \text{ Pa}$	$1 \text{ Pa} = 1 \text{ Nm}^{-2}$
$1 \text{ atm}$	$= 101325 \text{ Pa}$	
$1 \text{ psi}$	$= 703.0696 \text{ kg m}^{-2}$	
$1 \text{ cmHg}$	$= 1333.224 \text{ Pa}$	
$1 \text{ Torr}$	$= 133.322 \text{ Pa}$	
$1 \text{ cal}$	$= 4.1858 \text{ J}$	
$1 \text{ eV}$	$= 1.60217... \cdot 10^{-19} \text{ J}$	
	$= 1.16045... \cdot 10^4 \text{ K}$	
$1 \text{ kWh}$	$= 3.6 \cdot 10^6 \text{ J}$	
$0^\circ\text{C}$	$= 273.15 \text{ K}$	

#### Useful Tables:

HCP: D. R. Lide, *Handbook of Chemistry and Physics*. CRC Press

HTTD: D. R. Lide, H. V. Kehiaian (1994) *Handbook of Thermophysical and Thermochemical Data*. CRC Press

**Conversion between Gaussian and SI-units:**

Quantity	Gaussian	SI
Speed of light	$c$	$(\mu_0 \epsilon_0)^{-1/2}$
Electric field	$\vec{E}$	$\sqrt{4\pi \epsilon_0} \vec{E}$
Displacement	$\vec{D}$	$\sqrt{4\pi / \epsilon_0} \vec{D}$
Charge	$q$	$q / \sqrt{4\pi \epsilon_0}$
Magnetic induction	$\vec{B}$	$\sqrt{4\pi / \mu_0} \vec{B}$
Magnetic field	$\vec{H}$	$\sqrt{4\pi \mu_0} \vec{H}$
Magnetization	$\vec{M}$	$\sqrt{\mu_0 / (4\pi)} \vec{M}$

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