2.B. State Variables and Exact Differentials

Read Reichl's Chapter 1, §2.A, and the opening paragraphs of §2.B.

For convenience, definitions of some basic terms are listed below.

Equilibrium state ≡ Time-independent macroscopic state characterized by a few state variables.

Extensive variables are state variables that are proportional to the volume V or particle number N of the system. They take the role of generalized displacements in thermodynamics and will be denoted by $\boldsymbol{X} = \{X_j\}$.

Intensive variables are state variables that are independent of V or N. They take the role of generalized forces in thermodynamics and will be denoted by $\boldsymbol{Y} = \{Y_j\}$.

Intensive & extensive variables form conjugate pairs so that the work done by the system takes the form

$$\bar{d}\, W = -\boldsymbol{Y} \cdot \bar{d}\, \boldsymbol{X} = -\sum_j Y_j \bar{d}\, X_j \tag{2.1a}$$

where $\bar{d}$ is an inexact differential [to be defined later].

(Equilibrium) thermodynamics studies the dynamics of a system on a time-scale that is long enough so that the system can be described by an equilibrium state at every "instance".

Each equilibrium state of the system is denoted by a point in the phase space $\{\boldsymbol{X}, \boldsymbol{Y}\}$ and the evolution of the system by a path in it. Inexact differentials are differentials whose integration is path dependent.

Consider the differential form ϕ of two variables

$$\phi = c_1(x_1, x_2)\, d x_1 + c_2(x_1, x_2)\, d x_2 \tag{2.1b}$$

where c_1 & c_2 are some functions of x_1 & x_2.

Let

$$\left(\frac{\partial f}{\partial x}\right)_y = \text{derivative of } f \text{ with respect to } x \text{ while } y \text{ is held constant.} \tag{2.1c}$$

If

$$\left(\frac{\partial c_1}{\partial x_2}\right)_{x_1} = \left(\frac{\partial c_2}{\partial x_1}\right)_{x_2} \tag{2.1d}$$

then there exists a twice differentiable function $F(x_1, x_2)$ such that

$$c_1 = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} \qquad c_2 = \left(\frac{\partial F}{\partial x_2}\right)_{x_1} \tag{2.1e}$$

ϕ is then an exact differential commonly denoted by $d F$ so that (2.1b) becomes

$$d F = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} d x_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} d x_2 \tag{2.1}$$

while (2.1d) now reads

$$\left(\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right)_{x_1} = \left(\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right)_{x_2} \tag{2.2}$$

By (2.1), the differential of any given function is always exact.

On the other hand, if (2.1d) is not satisfied, ϕ is called an inexact differential and shall be denoted by $\bar{d} F$ so that (2.1b) becomes

$$\bar{d}F = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} dx_2 \qquad (2.2a)$$

The violation of (2.1d) means that the entity F obtained by integrating (2.2a) is path dependent. Hence, F cannot be a function, even though we shall continue to interpret $\left(\frac{\partial F}{\partial x_j}\right)_{x_k}$ via (2.1c).

In contrast, the significance of (2.2) is that it guarantees that dF is independent of directions. In other words, dF is a scalar and (2.1) can be written as

$$dF = \nabla F \cdot d\boldsymbol{r}$$

where ∇F and $d\boldsymbol{r}$ are vectors in the (x_1, x_2) space with components

$$\nabla F = \left(\left(\frac{\partial F}{\partial x_1}\right)_{x_2}, \left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right) \qquad d\boldsymbol{r} = (dx_1, dx_2)$$

Thus, the line integral

$$\int_A^B dF = F(B) - F(A) \qquad (2.2a)$$

is path independent and vanishes for any closed path

$$\oint dF = 0 \qquad (2.2b)$$

Given dF, one can always integrate to get the function (or scalar field) F to within an additive constant.

The foregoing can easily be generalized to the case of n variables $\boldsymbol{x} = \{x_1, \ldots, x_n\}$. Thus, the differential form

$$\phi = \sum_{j=1}^{n} c_j \, dx_j \qquad (2.3)$$

is exact if and only if

$$\left(\frac{\partial}{\partial x_j}\left(\frac{\partial F}{\partial x_k}\right)_{\{x_m \neq x_k\}}\right)_{\{x_m \neq x_j\}} = \left(\frac{\partial}{\partial x_k}\left(\frac{\partial F}{\partial x_j}\right)_{\{x_m \neq x_j\}}\right)_{x_m \neq x_k\}} \qquad (2.4)$$

for all $j, k = 1, \ldots, n$.

An example for $n = 3$ is

$$\phi = c_1 \, dx + c_2 \, dy + c_3 \, dz$$

which is exact if and only if

$$\left(\frac{\partial c_1}{\partial y}\right)_{x,z} = \left(\frac{\partial c_2}{\partial x}\right)_{y,z} \qquad \left(\frac{\partial c_1}{\partial z}\right)_{x,y} = \left(\frac{\partial c_3}{\partial x}\right)_{z,y} \qquad \left(\frac{\partial c_2}{\partial z}\right)_{y,x} = \left(\frac{\partial c_3}{\partial y}\right)_{z,x}$$

By definition, the differential of any state variable is exact.

Let x, y & z be 3 state variables satisfying

$$F(x, y, z) = 0 \qquad (2.5a)$$

which means only 2 of them are independent. Also, let w be a function of any two of x, y & z.

We shall prove the following useful identities known as the Maxwell relations.

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \qquad (2.5)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{2.6}$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z \tag{2.7}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z \tag{2.8}$$

To begin, (2.5a) implies $x = x(y, z)$ and $y = y(x, z)$. Hence,

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{(dx)_z}{(dy)_z} = \left[\frac{(dy)_z}{(dx)_z}\right]^{-1} = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}$$

which proves (2.5).

(2.5a) also implies $z = z(x, y)$ so that

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Keeping z constant then gives

$$0 = \left(\frac{\partial z}{\partial x}\right)_y (dx)_z + \left(\frac{\partial z}{\partial y}\right)_x (dy)_z$$

$$\to \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{(dx)_z}{(dy)_z} = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\therefore \quad \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial z}{\partial y}\right)_x\right]^{-1} \left(\frac{\partial z}{\partial x}\right)_y = -1$$

which is just (2.6) since

$$\left[\left(\frac{\partial z}{\partial y}\right)_x\right]^{-1} = \left(\frac{\partial y}{\partial z}\right)_x \qquad \text{[(2.5) used.]}$$

From $x = x(y, z)$, we have

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\to \quad \frac{dx}{dw} = \left(\frac{\partial x}{\partial y}\right)_z \frac{dy}{dw} + \left(\frac{\partial x}{\partial z}\right)_y \frac{dz}{dw} \tag{2.8a}$$

where dw is any exact differential. Keeping z constant and setting $w = w(x, y)$, (2.8a) becomes

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z$$

which proves (2.7).

Finally, consider $x = x(y, w)$ so that

$$dx = \left(\frac{\partial x}{\partial y}\right)_w dy + \left(\frac{\partial x}{\partial w}\right)_y dw \tag{2.8b}$$

Setting $w = w(y, z)$ gives

$$dw = \left(\frac{\partial w}{\partial y}\right)_z dy + \left(\frac{\partial w}{\partial z}\right)_y dz$$

so that (2.8b) becomes

$$dx = \left(\frac{\partial x}{\partial y}\right)_w dy + \left(\frac{\partial x}{\partial w}\right)_y \left[\left(\frac{\partial w}{\partial y}\right)_z dy + \left(\frac{\partial w}{\partial z}\right)_y dz\right]$$

Setting $z = \text{const}$ then gives

$$(dx)_z = \left(\frac{\partial x}{\partial y}\right)_w (dy)_z + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z (dy)_z$$

$$\rightarrow \quad \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$$

which proves (2.8)

Ex.2.1.

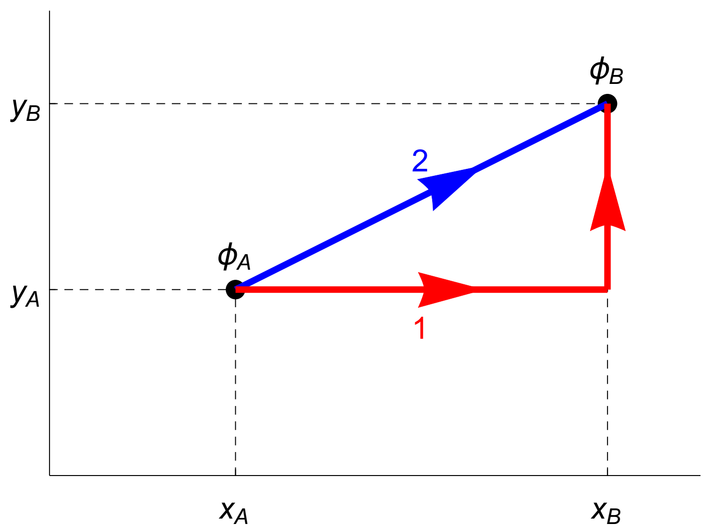
Consider the differential

$$d\phi = (x^2 + y)\, dx + x\, dy \qquad \text{(1a)}$$

(a) Show that it is an exact differential.

(b) Integrate $d\phi$ between the points A & B in the figure below, along the paths, 1 & 2.

(c) Integrate $d\phi$ between the points A & B using indefinite integrals.



Answer (a)

Writing (1a) as

$$d\phi = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy$$

we have

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial \phi}{\partial x}\right)_y\right]_x = \left(\frac{\partial (x^2 + y)}{\partial y}\right)_x = 1$$

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial \phi}{\partial y}\right)_x\right]_y = \left(\frac{\partial x}{\partial x}\right)_y = 1$$

Hence, the criterion (2.4) is satisfied and $d\phi$ is exact.

Answer (b)

Along path 1,

$$\int_A^B d\phi = \int_{x_A}^{x_B} dx \left(\frac{\partial \phi}{\partial x}\right)_y + \int_{y_A}^{y_B} dy \left(\frac{\partial \phi}{\partial y}\right)_x$$
$$= \int_{x_A}^{x_B} dx \left(x^2 + y\right)_{y=y_A} + \int_{y_A}^{y_B} dy \left(x\right)_{x=x_B}$$
$$= \int_{x_A}^{x_B} dx \left(x^2 + y_A\right) + \int_{y_A}^{y_B} dy\, x_B$$
$$= \frac{1}{3}\left(x_B^3 - x_A^3\right) + (x_B - x_A)\, y_A + (y_B - y_A)\, x_B$$
$$= \frac{1}{3}\left(x_B^3 - x_A^3\right) - x_A\, y_A + y_B\, x_B \qquad (1)$$

Along path 2,

$$y = y_A + \frac{y_B - y_A}{x_B - x_A}(x - x_A)$$

so that

$$dy = \frac{y_B - y_A}{x_B - x_A} dx$$

and (1a) becomes

$$d\phi = \left[x^2 + y_A + \frac{y_B - y_A}{x_B - x_A}(x - x_A)\right] dx + x \frac{y_B - y_A}{x_B - x_A} dx$$
$$= \left[x^2 + y_A + \frac{y_B - y_A}{x_B - x_A}(2x - x_A)\right] dx$$

$$\rightarrow \quad \int_A^B d\phi = \int_{x_A}^{x_B} dx \left[x^2 + y_A + \frac{y_B - y_A}{x_B - x_A}(2x - x_A)\right]$$
$$= \frac{1}{3}\left(x_B^3 - x_A^3\right) + (x_B - x_A)\, y_A + \frac{y_B - y_A}{x_B - x_A}\left[x_B^2 - x_A^2 - (x_B - x_A)\, x_A\right]$$
$$= \frac{1}{3}\left(x_B^3 - x_A^3\right) + (x_B - x_A)\, y_A + (y_B - y_A)\, x_B$$
$$= \frac{1}{3}\left(x_B^3 - x_A^3\right) - x_A\, y_A + y_B\, x_B \qquad (2)$$

which agrees with (1).

Answer (c)

Treating y as a constant, we have

$$\int dx \left(\frac{\partial \phi}{\partial x}\right)_y = \int dx \left(x^2 + y\right) = \frac{1}{3}x^3 + x\,y + K_1(y) \qquad (3)$$

where $K_1(y)$ is some function of y.

Treating x as a constant, we have

$$\int dy \left(\frac{\partial \phi}{\partial y}\right)_x = \int dy\, x = x\,y + K_2(x) \qquad (4)$$

where $K_2(x)$ is some function of x.

(3) & (4) are the same if we set

$$K_1(y) = C \qquad K_2(x) = \frac{1}{3}x^3 + C$$

where C is a constant. Hence,

$$\phi = \int d\,\phi = \frac{1}{3}x^3 + x\,y + C$$

so that

$$\int_A^B d\,\phi = \phi_B - \phi_A = \frac{1}{3}\left(x_B^3 - x_A^3\right) + x_B\,y_B - x_A\,y_A$$

in agreement with (1).

Ex.2.1.a

Consider the differential

$$d\,\phi = 2\left(x^2 + y\right)d\,x + x\,d\,y \qquad (5)$$

(a) Show that it is an inexact differential.

(b) Integrate $d\,\phi$ between the points A & B in the figure above, along the paths, 1 & 2.

Answer (a)

Writing (5) as

$$d\,\phi = \left(\frac{\partial\,\phi}{\partial\,x}\right)_y d\,x + \left(\frac{\partial\,\phi}{\partial\,y}\right)_x d\,y$$

we have

$$\left[\frac{\partial}{\partial\,y}\left(\frac{\partial\,\phi}{\partial\,x}\right)_y\right]_x = \left(\frac{\partial\,2\left(x^2 + y\right)}{\partial\,y}\right)_x = 2$$

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial\,\phi}{\partial\,y}\right)_x\right]_y = \left(\frac{\partial x}{\partial x}\right)_y = 1$$

Hence, the criterion (2.4) is not satisfied and $d\,\phi$ is inexact.

Answer (b)

Along path 1,

$$\begin{aligned}\int_A^B d\,\phi &= \int_{x_A}^{x_B} d\,x\left(\frac{\partial\,\phi}{\partial\,x}\right)_y + \int_{y_A}^{y_B} d\,y\left(\frac{\partial\,\phi}{\partial\,y}\right)_x \\ &= \int_{x_A}^{x_B} d\,x\,2\left(x^2 + y\right)_{y=y_A} + \int_{y_A}^{y_B} d\,y\left(x\right)_{x=x_B} \\ &= \int_{x_A}^{x_B} d\,x\,2\left(x^2 + y_A\right) + \int_{y_A}^{y_B} d\,y\,x_B \\ &= 2\left[\frac{1}{3}\left(x_B^3 - x_A^3\right) + \left(x_B - x_A\right)y_A\right] + \left(y_B - y_A\right)x_B \\ &= \frac{2}{3}\left(x_B^3 - x_A^3\right) - 2\,x_A\,y_A + \left(y_B + y_A\right)x_B \qquad (6)\end{aligned}$$

Along path 2,

$$y = y_A + \frac{y_B - y_A}{x_B - x_A}(x - x_A)$$

so that

$$d\,y = \frac{y_B - y_A}{x_B - x_A}\,d\,x$$

and (5) becomes

$$d\,\phi = 2\left[x^2 + y_A + \frac{y_B - y_A}{x_B - x_A}(x - x_A)\right]d\,x + x\,\frac{y_B - y_A}{x_B - x_A}\,d\,x$$
$$= \left[2\,x^2 + 2\,y_A + \frac{y_B - y_A}{x_B - x_A}(3\,x - 2\,x_A)\right]d\,x$$

$$\rightarrow \quad \int_A^B d\,\phi = \int_{x_A}^{x_B} d\,x\left[2\,x^2 + 2\,y_A + \frac{y_B - y_A}{x_B - x_A}(3\,x - 2\,x_A)\right]$$
$$= \frac{2}{3}(x_B^3 - x_A^3) + 2\,(x_B - x_A)\,y_A + \frac{y_B - y_A}{x_B - x_A}\left[\frac{3}{2}(x_B^2 - x_A^2) - 2\,(x_B - x_A)\,x_A\right]$$
$$= \frac{2}{3}(x_B^3 - x_A^3) + 2\,(x_B - x_A)\,y_A + \frac{1}{2}(y_B - y_A)\,(3\,x_B - x_A)$$

which is not the same as (6).

Code

In[130]:=
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     Red, Arrow[{A, F}], Arrow[{F, B}], Text["1", 1/2 (A + F) - off]
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