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The geometry of separation processes: A horse-carrot theorem for steady flow systems

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Abstract. – The horse-carrot theorem bounding the entropy production in processes with a fixed number of relaxations is extended to steady flow processes. The dissipation turns out to be related to a path of flows rather than states. The example of fractional distillation is presented and shows how null directions for the geometry turn out to be useful in the analysis. The implied distillation column design offers potentially significant energy savings.

Introduction. – The Riemannian structure of thermodynamic theory contains important and hitherto barely tapped information concerning a physical system. The structure runs deep; its presence can be felt at all levels of physical description. At the quantum-mechanical level, the distance equals the angle between pure states [1]. For mixed quantum states, the distance measures the reliability of an experiment designed to optimally distinguish between the two states along a one-parameter family of density operators [2]. At the statistical mechanical level, distance is the number of statistically distinguishable intermediate states [3] as we transform one state into another. In this context, statistical distance was originally introduced by R.A. Fisher to measure genetic drift [4] and is the basis for Amari's information geometry [5]. Ruppeiner [6], [7] and Diosi *et al.* [8] have used the requirement of covariance with respect to this geometry to give an important correction to fluctuation theory. Numerous authors have speculated about the meaning of the curvature defined by this geometry as a measure of stability or interaction strength [6], [7], [9], [10]. Finally, at the macroscopic level, this same distance [11] between two equilibrium states of a thermodynamic system equals the minimum entropy produced in a process that transforms one state into the other, multiplied by twice the number of relaxations during the transformation [12], [13]. This result, known as the horse-carrot theorem, is the focus of the present paper.

The horse-carrot theorem. – The horse-carrot theorem involves a process in which a system (the horse) is coaxed along a sequence of states by successive contacts with generalized baths (the carrots). In the first version of the theorem [13], the generalized baths change continuously

in time. The entropy production from the coupling between the system and the bath is bounded by

$$\Delta S_u \geq L^2 \bar{\epsilon} / \tau, \quad (1)$$

where ΔS_u is the entropy produced, L is the length of the process measured in a geometry whose metric tensor equals the second derivative of the entropy of the system with respect to its extensive variables, $\bar{\epsilon}$ is a mean relaxation time, and τ is the total time of the process. While representing a useful and general bound that mixes static and dynamic properties of the system, the inequality has several shortcomings hidden in the averaging process leading to $\bar{\epsilon}$. It was recently shown [14], [15] that the equality version of the theorem represents the minimum entropy production only for a fixed total number of relaxations, *i.e.* for fixed $\int_0^\tau dt/\epsilon$, where ϵ is the instantaneous relaxation time. This fact severely limits the usefulness of this version of the theorem as a starting point for optimal control in a fixed time. The fixed-time problem turns out to require a constant rate of entropy production.

Our concern in the present paper is the second version of the horse-carrot theorem [12]. This version applies for process times τ that are many times the relaxation time of the system. This discrete form of the theorem asks the question: where along a given sequence of states should k generalized baths be located so as to minimize the total entropy produced when the system relaxes successively from a state of equilibrium with bath $j - 1$ to a state of equilibrium with bath j , $j = 1, \dots, k$? Although the process time no longer plays an explicit role, this version of the theorem has relevance for finite-time processes that proceed by stages in which each stage represents a state of equilibrium. A number of important processes are of this type, including fractional distillation. The theorem again gives a bound on the entropy production in terms of the thermodynamic distance traversed and the number of relaxations

$$\Delta S_u \geq \frac{L^2}{2k}. \quad (2)$$

This version of the theorem gives a specific recipe for how the minimum may be achieved: The k baths to which the system equilibrates should be placed at k equidistant positions along the curve the system is to traverse.

The sequence of equilibrations to intensities of a bath bears a strong resemblance to traditional textbook descriptions of a quasistatic process [16]. The trouble is, many processes cannot be so realized. One example of a process which cannot, is the change in scale of a system. The usual description of a quasistatic process does not allow for such changes since they cannot occur as a system responding to intensity differences. In the geometry, such changes represent zero distances, *i.e.* if the scale of the system is not fixed, the structure is only semi-Riemannian. Null directions result from the linear growth of the entropy as we scale any one phase. This linearity makes the second derivative, *i.e.* the components of the metric tensor, vanish along such directions. Forming an appropriate combination of such null directions by simultaneously scaling two phases of a pure substance can represent a phase transition [17], [18]. It follows that such phase transitions appear to have no “intrinsic” irreversibility associated.

Another example of a process that, at least at first glance, appears to be unrealizable as a horse-carrot process, is the separation of a solution into its pure constituents. In the present paper, we show how to associate a horse-carrot process to such a separation. Surprisingly, it turns out that the corresponding path is not a one-parameter sequence of states of the system along the process but rather a one-parameter sequence of material flows. The example we treat is fractional distillation and forces a direct confrontation with the null directions problem described above. Rather than posing difficulties, the null directions are essential for splicing the stages of the process into one continuous path.

Thermodynamic length and entropy production. – The thermodynamic length L is given by the line element [19]

$$(\mathrm{d}L)^2 = -\mathrm{d}Z^t D^2 S \mathrm{d}Z = -\mathrm{d}W \mathrm{d}Z \quad (3)$$

$$= \frac{\mathrm{d}X^t D^2 U \mathrm{d}X}{T} = \frac{\mathrm{d}Y \mathrm{d}X}{T}, \quad (4)$$

where Z is the vector of extensive variables of the system $Z = (U, V, \dots)$, $W = \partial S / \partial Z = (1/T, p/T, \dots)$, and $D^2 S$ is the matrix of partial derivatives $\partial^2 S / \partial Z_i \partial Z_j$. Similarly, in the energy representation, $X = (S, V, \dots)$, $Y = \partial U / \partial X = (T, -p, \dots)$, and $D^2 U$ is the matrix of partial derivatives $\partial^2 U / \partial X_i \partial X_j$.

The key to the discrete horse-carrot theorem is the correspondence between the line element of the geometry, $(\mathrm{d}L)^2$, and the dissipation in a small equilibration with a bath [12]. The dissipation is given by

$$\mathrm{d}S_u = \mathrm{d}S_{\text{system}} + \mathrm{d}S_{\text{bath}} \quad (5)$$

$$= \sum_{i=1}^n (W_i - W_i^0) \mathrm{d}Z_i, \quad (6)$$

where n is the number of degrees of freedom, and a zero superscript indicates a quantity referring to the bath. We have also made use of the conservation laws $\mathrm{d}Z_i = -\mathrm{d}Z_i^0$. Integrating to equilibrium at $W_i = W_i^0$ gives, to second order in $\Delta Z = Z - Z^0$,

$$\Delta S_u = \frac{(\Delta L)^2}{2} = \frac{\Delta Z^t D^2 S \Delta Z}{2}. \quad (7)$$

The horse-carrot theorem follows by minimizing the sum of such $(\Delta L_j)^2$ corresponding to the j -th step along a k -step process while keeping

$$L = \sum_{j=1}^n \Delta L_j \quad (8)$$

fixed [20].

In our analysis below, we exploit the correspondence between the square of the line element and the entropy production for a small step. This will enable us to identify a path in the state space of the mixture with the steady-state operation of the distillation column. Our presentation begins with a description of the column and the associated entropy production.

Dissipation in a distillation column. – Fractional distillation is a process used to separate a mixture of compounds to specified purities. The separation is based on the difference in the boiling points of the components. Fractional distillation is performed within a vertical column divided into trays which constitute the k stages for the process. The mixture to be separated is introduced near the middle of the column at the feed tray and the separated components are removed at the top as distillate D and at the bottom as bottoms B . (See fig. 1.) Boiling occurs on each tray resulting in the formation of vapor which is then bubbled through the liquid at the next higher tray. Each tray is also equipped with an overflow tube which returns excess liquid to the next lower tray. For steady-state operation, the net difference between these two flows must equal D at each tray-tray interface above the feed and B at each interface below the feed.

Conventionally, a heat source is connected at the bottom tray and a heat sink is connected at the top tray creating a temperature gradient along the column. This results in the net upward

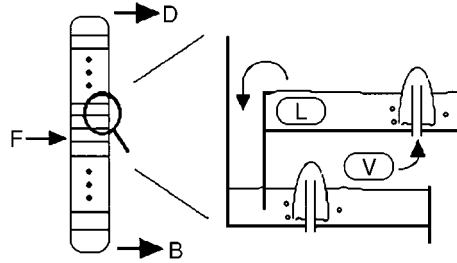


Fig. 1. – A schematic distillation column with flows: feed F , distillate D and bottoms B . The close-up shows two adjacent trays including overflow tubes for downward flow of liquid L and bubble caps for upward flow of vapor V .

motion of low boiling component and downward motion of high boiling component. We depart from the conventional design and use additional heat sources (sinks) along the column to adjust the temperature at each plate. We then ask for the sequence of temperatures which minimizes the total dissipation inside the column. This being our goal, we take the transport of heat and matter between the column and its surroundings as reversible. For convenience and brevity, we treat only a binary mixture and assume that the pressure is constant throughout the column.

Since we assume that each stage is in equilibrium, the losses occur as the upward flow of vapor and downward flow of liquid equilibrate at the next trays. For concreteness, consider the bubble of vapor going up —the analysis for the downward flow of liquid proceeds similarly. The losses can be counted by a conceptual rearrangement of what occurs. We consider the bubble of vapor to be isolated except for the exchange of heat and pdV work with the two phase fluid in the tray above. Accordingly, this fluid acts as a bath with a certain temperature and pressure. In this manner, the bubble is brought to equilibrium at the temperature and pressure of the next tray by a horse-carrot process whose irreversibility is given by the distance squared. Since this squared distance is an extensive quantity, the size of each bubble does not matter; the scale is set by the number of moles of material moving per unit time. In the final state of each bubble, some of the vapor has condensed to liquid, but each phase is exactly at the composition in the next tray. Thus if we now allow mass transfer between the bubble and its surroundings, the mixing is reversible [21]. Our conceptual rearrangement of events is justified since in either case the net effect is the complete equilibration between the bubble of vapor and the equilibrium system in the next tray.

Since for the present calculation we assume constant pressure, the second form of the metric in eq. (4) is the most convenient and gives

$$\Delta S_u = \frac{1}{2}(\Delta L)^2 = \frac{1}{2} \frac{\Delta T \Delta U}{T} = \frac{1}{2} \frac{C_\sigma (\Delta T)^2}{T}, \quad (9)$$

where C_σ is the constant pressure saturation heat capacity of the two-phase mixture in equilibrium [22]. We get the same expression for the liquid, although ΔT has the opposite sign. Since the dissipation only depends on $(\Delta T)^2$, we would get the same entropy production if the liquid were also going up the column. In this way we construct a path from $T_0 = T_{\text{bottoms}}$ to $T_k = T_{\text{distillate}}$ rescaling between each tray to readjust the quantity of vapor, V , and liquid, L , at each temperature.

To specify the path and thus be able to apply the horse-carrot theorem, it remains to set the scales of V and L at each stage. This is achieved by the mass balance conditions

$$V - L = \begin{cases} D & \text{above feed,} \\ -B & \text{below feed,} \end{cases} \quad (10)$$

$$yV - xL = \begin{cases} x_D D & \text{above feed,} \\ -x_B B & \text{below feed,} \end{cases} \quad (11)$$

and the temperatures of the two trays which determine the mole fractions y and x , in the gaseous and liquid phases, respectively. If the temperatures of the trays are taken sufficiently close to allow neglecting terms in $(\Delta T)^3$, V and L are smooth functions of T except at the feed plate where we switch between the appropriate balance conditions. The whole process becomes a continuous, piecewise smooth path in the state space of the two-phase system by including a rescaling branch at the feed plate which contributes length zero. This path is known in the literature [23] as the minimum reflux values of V and L at each T .

We have hereby established a path such that the dissipation of small steps along this path equals the squared length of the corresponding displacement. Therefore, the horse-carrot theorem applies and we can conclude that, to minimize total entropy production, the tray temperatures should be adjusted to equalize the thermodynamic distance between trays, or perhaps more accurately, between the tray-tray interfaces. To find the optimal temperature profile, we need to find temperatures T_j such that

$$\int_{T_j}^{T_{j+1}} \sqrt{\frac{C_\sigma}{T}} dT = \frac{1}{k} \int_{T_0}^{T_k} \sqrt{\frac{C_\sigma}{T}} dT, \quad j = 0, \dots, k-1. \quad (12)$$

Comparing the entropy production of the conventional column with the entropy production using our temperature control offers very significant savings. For example, for a 71-tray column separating a 50-50 mole percent benzene-toluene mixture into 99% pure constituents reduces the entropy production by about a factor of four over the conventional process. Such savings, widely applied, would offer a significant reduction in industrial energy consumption; over 10% of such consumption is used for distillation processes [24]. Despite this fact, the economic advantages of an equal thermodynamic distance column remain unclear. The design requires more plates than conventional columns and a heat pump which can carry out the requisite temperature controls at each tray. This however is offset by significant reductions in the size of the reboiler and the condenser.

Conclusions. – The derivations above extended the discrete horse-carrot theorem to the steady-state operation of a separation process. The results express the dissipation in terms of the length of a path in the equilibrium state space of the mixture and show how to optimally control the temperatures of the stages along such a separation. The derivations assume that the mixing on each tray is sufficiently good to assure complete equilibration.

Our findings show how to associate a path and a quasistatic process to a steady flow process. Surprisingly, the quantities in the associated quasistatic process are the flows rather than the states along the process. The procedure is readily adapted to any staged steady flow process

in the limit of many stages. We start from the flow vectors along the process. Since these flows equilibrate at the next stage, the entropy produced by such small relaxations is the square of a length element. For the purpose of counting dissipation, all flows can be taken unidirectional and summed exactly as for distillation. The corresponding path consists of the flows for the process in the limit of infinitely many stages.

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REFERENCES

- [1] WOOTTERS W. K., *Phys. Rev. D*, **23** (1981) 357.
- [2] BRAUNSTEIN S. L. and CAVES C. M., *Phys. Rev. Lett.*, **72** (1994) 3439.
- [3] The precise meaning here is as follows: To some level of confidence (which defines our unit) we say that two distributions are distinguishable if a χ^2 test will distinguish them in a sample of size N . The number of distinguishable distributions along a path in distribution space will grow as \sqrt{N} . The distance is given by the ratio of the number of distinguishable states to \sqrt{N} in the limit as $N \rightarrow \infty$.
- [4] FISHER R. A., *Proc. Camb. Soc.*, **22** (1925) 700.
- [5] AMARI S., *Differential Geometrical Methods in Statistics* (Springer Verlag, New York) 1985.
- [6] RUPPEINER G., *Rev. Mod. Phys.*, **67** (1995) 605.
- [7] RUPPEINER G., *Phys. Rev. A*, **20** (1979) 1608; **24** (1981) 488.
- [8] DIOSI L., FORGACS G., LUKACS B. and FRISCH H. L., *Phys. Rev. A*, **29** (1984) 3343.
- [9] JANYSZEK H. and MRUGALA R., *Phys. Rev. A*, **39** (1989) 6515; *J. Phys. A*, **23** (1990) 467.
- [10] JANYSZEK H., *J. Phys. A*, **23** (1990) 477.
- [11] SALAMON P., NULTON J. D. and BERRY R. S., *J. Chem. Phys.*, **82** (1985) 2433.
- [12] NULTON J., SALAMON P., ANDRESEN B. and ANMIN QI, *J. Chem. Phys.*, **83** (1985) 334.
- [13] SALAMON P. and BERRY R. S., *Phys. Rev. Lett.*, **51** (1983) 1127.
- [14] SPIRKL W. and RIES H., *Phys. Rev. E*, **52** (1995) 3485.
- [15] DIOSI L., KULACSY K., LUKACS B. and RACZ A., *J. Chem. Phys.*, **105** (1996) 11220.
- [16] See for example CALLEN H., *Thermodynamics* (J. Wiley & Sons, New York) 1985.
- [17] WEINHOLD F., *J. Chem. Phys.*, **63** (1975) 2479, 2484, 2488, 2496. These papers were the first to introduce the geometry at the macroscopic thermodynamic level, albeit in the conformally related form using the second derivative of the internal energy.
- [18] WEINHOLD F., *J. Chem. Phys.*, **65** (1976) 559. See in particular fig. 1.
- [19] The products in eqs. (3) and (4) are symmetric tensor products of the differentials involved. See SALAMON P., IHRIG E. and BERRY R. S., *J. Math. Phys.*, **24** (1983) 2515.
- [20] The number of relaxations, k , needs to be sufficiently large to allow neglecting all terms higher than second order in counting the entropy production during each relaxation.
- [21] This is true only for distillation of binary mixtures. For more than two components, equilibration of additional degrees of freedom is needed.
- [22] See, for example, ROWLINSON J. S., *Liquids and Liquid Mixtures* (Plenum Press, New York) 1969.
- [23] KING C. J., *Separation Processes* (McGraw-Hill, New York) 1971.
- [24] HUMPHREY J. L. and SEIBERT A. F., *Chem. Eng. Progr.*, **32**, March Issue (1992).