

On the Helmholtz Potential Metric: The Isotherm Length-Work Theorem

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In this paper we introduce the Isotherm Length-Work theorem using the Helmholtz potential metric and the virial expansion of pressure in inverse power of molar volume. The theorem tells us what length of a thermodynamical system described by equation of state through virial expansion along isotherms actually is with such a metric. We also give explicit solutions for thermodynamic length along isotherms in the case of first, second and third order expansion.

KEY WORDS: Geometry of thermodynamics; equilibrium thermodynamics; thermodynamic length.

1. INTRODUCTION

Gibbs⁽⁵⁾ introduced in his work a geometrical interpretation of equilibrium thermodynamics which was followed by Caratheodory^(3,4) who proved that the state space is endowed with the canonical contact structure that underlines the first law of thermodynamics (energy balance law). Different representations of this structure in a canonical (D'Arbois) chart are related to different forms of the energy balance law written through internal energy, entropy, Helmholtz free energy, etc.^(7,9)

Hermann⁽⁶⁾ and Mrugala⁽⁷⁾ suggested that the “extended phase space” of a homogeneous thermodynamic system endowed with the contact structure does represent the natural geometrical space for description of equilibrium thermodynamics.

Later, a thermodynamic metric was explicitly introduced by Weinhold⁽¹⁸⁾ and, from a different point of view, by Ruppeiner.⁽¹⁰⁾ These

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metrics were defined on the space of thermodynamic states of a system using different thermodynamic potentials, respectively, internal energy U and entropy S , and set of extensive variables, respectively (S, V, N_1, \dots) and (U, V, N_1, \dots) . It became clear, then, that a physical interpretation of path-length between two states had to be investigated. These studies were conducted using mostly the internal energy formalism of a single component system⁽¹⁴⁻¹⁷⁾ and some results were obtained for systems at constant entropy, volume, pressure and temperature.⁽¹⁴⁻¹⁶⁾ In particular, it was shown⁽¹⁴⁾ that, using Weinhold metric for an Ideal gas, a reversible process at constant temperature gives length equal to zero. Thus, the following question arises: what is the meaning of thermodynamic length of a quasi-static process along isotherms even for more complex systems in which inter-particle interaction occurs?

It is important to note that, in the molar energy representation, the temperature T is function of the extensive variables s and v , namely $T = T(s, v)$, and, therefore, analytical procedures become considerably awkward. The standard approach, then, would be to consider the Helmholtz free energy as thermodynamic potential obtained by Legendre transformation of the energy function with temperature and volume as independent variables and, then, define a *new* metric as the Hessian of the Helmholtz free energy. Thus, this manuscript will unfold in a sequence of two main points. First, we shall define and study the Helmholtz potential metric of a two-dimensional thermodynamic system. In particular, we shall see that the tangent space at any point on the equilibrium surface is the Lorentzian space $E^{1,1}$. Second, we shall study path-length along isotherms using the virial expansion in inverse power of molar volume.

Let's, now, introduce the concepts of contact structure, thermodynamic metric and thermodynamic length.

We shall define the extended phase space as a $(2n + 1)$ -dimensional manifold P endowed with the contact structure given by a differential 1-form θ such that^(6,7)

$$\theta \wedge (d\theta)^n \neq 0,$$

where θ is called the contact form.

In a local (Darboux) chart $(\Phi, (Y_i, X_i))$ with $i = 1, \dots, n$, any contact form θ can be represented as⁽¹⁾

$$\theta = d\Phi - \sum_1^n Y_i dX^i.$$

A Legendre manifold $S \subset P$ is a n -dimensional maximal integral submanifold of the Pfaff equation $\theta = 0$. On such a manifold we consider Φ

to be the thermodynamic potential, $Y_i = \partial\Phi/\partial X^i$ to be the intensive variables and X_i to be the extensive variables with $i = 1, \dots, n$. Equilibrium states form such a maximal integral surface of contact form θ in the space P by the choice of n extensive variables and thermodynamic potential as function of these variables. Equilibrium surface is then geometrically described by constitutive relation $\Phi = \Phi(X_i)$. Another choice of external variables and thermodynamic potential leads to another equilibrium surface corresponding, in general, to another constitutive relation.^(7,9)

On such equilibrium surface, thermodynamic metrics are defined by the constitutive relation $\Phi = \Phi(X_i)$. The general form is given by

$$\eta_\Phi = \frac{\partial^2 \Phi}{\partial X^i \partial X^j} dX_i \otimes dX_j$$

and the corresponding matrix representation is denoted by Mrugala⁽⁸⁾

$$\eta_{\Phi_{ij}} = \frac{\partial^2 \Phi}{\partial X^i \partial X^j}.$$

1.1. Thermodynamic Metrics

Weinhold introduced a metric⁽¹⁸⁾ in the space of thermodynamic states as second derivative of internal energy with respect to extensive variables X_i and X_j , namely $\eta_{U_{ij}} = \partial^2 U / \partial X^i \partial X^j$. In a general setting, constitutive relation $U = U(X_1, \dots, X_n)$ represents the energy surface in which, for example, $X_1 = S$, $X_2 = V$, etc., where S is the entropy and V is the volume of our system. Such a metric gives us a way to define distances and angles and, therefore, it enables us to study the geometry of the energy surface.

Ruppeiner, instead, introduced a metric⁽¹¹⁾ by the choice $\Phi = S$ as thermodynamic potential and defined it as second momenta of entropy with respect to the fluctuations, namely $\eta_{S_{ij}} = -(\partial^2 S / \partial X^i \partial X^j)$. In this case constitutive relation $S = S(X_1, \dots, X_n)$ represents the entropy surface in which, for example, $X_1 = U$, $X_2 = V$, etc.

As we have already mentioned, a different choice of thermodynamic potential and extensive variables leads to a different equilibrium surface geometrically described by a certain constitutive relation. Since the most familiar thermodynamic potentials are the Legendre transformations⁽²⁾ of the internal energy, namely Helmholtz free energy, Enthalpy, Gibbs free energy, and since this manuscript is concerned with the meaning of thermodynamic length which it has been studied mostly using Weinhold metric,⁽¹²⁻¹⁷⁾ we shall focus our attention to the energy surface and its

geometry. We shall see that Legendre transformations of a thermodynamic potential change the “nature” of the thermodynamic state space.

1.2. Thermodynamic Length

The metric $\eta_{U_{ij}}$ can be interpreted locally as the distance⁽¹⁴⁾ between the energy surface and the linear space tangent to this surface at some point where $\eta_{U_{ij}}$ is evaluated. Indeed, let's denote by coordinates (X_1^0, \dots, X_n^0) a particular energy state. The tangent space is attached to the energy surface at point $(U^0, X_1^0, \dots, X_n^0)$. If we move away a little to a new energy state (X_1, \dots, X_n) then the availability^(12,14) or the available work⁽¹²⁾ of the system is the distance between the point on the surface (U, X_1, \dots, X_n) and the tangent space. This is naturally a local interpretation since it requires just small displacements, like for fluctuations, from the given point $(U^0, X_1^0, \dots, X_n^0)$ on the surface.

On the other hand, we could study thermodynamic length taking the metric $\eta_{U_{ij}}$ globally. In this situation we consider a path ϕ on the energy surface between two states a_0 and a_1 and study the length of the path

$$L_{a_0 a_1} = \int_{a_0}^{a_1} \left[\sum_{i,j} \eta_{U_{ij}} dX_i dX_j \right]^{1/2}.$$

It was shown⁽¹⁴⁾ that the thermodynamic length L does, in general, represent the change in mean molecular velocity depending on the particular nature of the thermodynamic process defining the path ϕ and that its dimension is square root of energy. But thermodynamic length was explicitly studied⁽¹⁴⁾ just in the Ideal case. In particular, it was found that, for a reversible adiabatic Ideal Gas from state (p_0, V_0) to state (p_1, V_1) , length represents the change in flow velocity of a gas undergoing an isentropic expansion, like in rarefaction waves, and it is given by Salamon *et al.*⁽¹⁴⁾

$$L^s = \frac{2}{\gamma - 1} \sqrt{\gamma p_0 V_0} \left[1 - \left(\frac{p_1}{p_0} \right)^{\frac{\gamma-1}{2\gamma}} \right]$$

with $\gamma = \frac{C_p}{C_v}$.

Moreover, in our previous manuscript, we have shown an explicit⁽¹⁷⁾ relation between thermodynamic length and work for an isentropic Ideal

and quasi-Ideal Gas along isotherms, namely

$$L^s = \sqrt{\frac{1}{RT}} W.$$

Such a relation was considered to be a way to measure the amount of work done by the system along isotherms. But its interpretation in relation with work turned out to be much more complex than what we had expected. Indeed, we realized that such a case was the trivial one, namely that length in an isentropic Ideal and quasi-Ideal Gas along isotherms is zero, and gave a generalization of that relation no longer at constant temperature.⁽¹⁵⁾ In particular, we found that thermodynamic length of an isentropic Ideal or quasi-Ideal Gas measures the difference of the square roots of the energies of two given states, namely⁽¹⁵⁾

$$L^s = 2\sqrt{\frac{c_p}{R}} \left[\sqrt{u_2 + W_{\text{in}}} - \sqrt{u_2} \right] = 2\sqrt{\frac{c_p}{R}} \left[\sqrt{u_1} - \sqrt{u_2} \right]$$

and

$$-L^s = 2\sqrt{\frac{c_p}{R}} \left[\sqrt{u_2} - \sqrt{u_2 - W_{\text{out}}} \right] = 2\sqrt{\frac{c_p}{R}} \left[\sqrt{u_2} - \sqrt{u_1} \right],$$

where W_{in} and W_{out} are the work done on the system and the work done by the system. (Note that we require length to be positive). Therefore thermodynamic length is zero if there is no work.

So far we have been able to physically interpret thermodynamic length for an isentropic Ideal and quasi-Ideal Gas. As a special case we have shown that along isotherms such a length vanishes. Thus, the following question arises, namely: what is the physical meaning of length for an isothermal thermodynamic system?

Remark 1. Note that we are no longer considering thermodynamic systems at constant entropy. Just constant temperature.

Naturally, we cannot use the same mathematical approach using Weinhold metric on the equilibrium surface described by constitutive relation $u = u(s, v)$. We would like to *change* set of extensive variables in such a way to include temperature as one of them. The standard way to do that is to consider the Legendre transformation of internal energy which replaces the molar entropy with the temperature. Therefore, we would need to consider the molar Helmholtz free energy with corresponding energy surface described by constitutive relation $f = f(T, v)$ as the *natural* setting for such a problem.

2. THERMODYNAMIC LENGTH WITH THE HELMHOLTZ POTENTIAL METRIC

We have already mentioned that thermodynamic metrics are geometrically defined on Legendre submanifolds (equilibrium surfaces) of the thermodynamical phase space by the choice of a set of extensive variables and of a thermodynamic potential like internal energy, entropy, Helmholtz free energy, enthalpy, etc. By such a choice we are able to study, through constitutive relation, the geometrical structure of that particular equilibrium surface. It is on such equilibrium surface that we can define a metric as second derivative of the thermodynamic potential with respect to the extensive variables. All these metrics are naturally well-defined on the corresponding Legendre submanifold through Legendre transformation.

Here we will consider the Helmholtz free energy as thermodynamic potential and we will study the metric of a two-dimensional thermodynamic system defined by such a choice. We shall see that the equilibrium surface defined by constitutive relation $f = f(T, v)$ has, as a tangent space at any point, the Lorentzian space $E^{1,1}$ since the eigenvalues of the relative matrix metric have opposite sign, as long as we avoid points of degeneracy. The length of any vector on such a space is either positive, zero or pure imaginary. Naturally, the length of any curve (thermodynamic process) on the equilibrium surface can be parametrized and, thus, can be expressed in terms of rate of change of position vectors with respect to the parameter. Such vectors belong to the Lorentzian space at any point. For paths in a constant direction, length is either positive, zero or pure imaginary. We will define a volume-like vector, a temperature-like vector and a null vector on the Lorentzian space $E^{1,1}$ at each point q on the surface S .

We shall see that length is computed in its generality using virial expansion of pressure in inverse molar volume and just in the Ideal and quasi-Ideal case is proportional to work along isotherms.

It is known that the Helmholtz (molar) potential f is the Legendre transformation of the molar internal energy u that replaces the molar entropy s by the temperature T as independent variable. That is

$$f = f(T, v)$$

Now, since $f = u - Ts$, we have the following differential,⁽²⁾

$$df = -s dT - p dv$$

with

$$\left(\frac{\partial f}{\partial T}\right)_v = -s$$

and

$$\left(\frac{\partial f}{\partial v}\right)_T = -p.$$

If we define the metric $\eta_{f_{ij}} = \partial^2 f(x)/\partial x_i \partial x_j$, we have

$$\eta_{f_{ij}} = \begin{pmatrix} \frac{-c_v}{T} & -\frac{\alpha}{k_T} \\ -\frac{\alpha}{k_T} & \frac{1}{vk_T} \end{pmatrix}, \tag{2.1}$$

where

- (1) c_v is the molar heat capacity at constant volume:

$$c_v = T \left(\frac{\partial s}{\partial T}\right)_v,$$

- (2) c_p is the molar heat capacity at constant pressure:

$$c_p = T \left(\frac{\partial s}{\partial T}\right)_p,$$

- (3) α is the thermal coefficient of expansion:

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p,$$

- (4) κ_T is the isothermal compressibility:

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T.$$

Local conditions of stability require that the Helmholtz free energy be a concave function of the temperature and a convex function of the volume.⁽²⁾ It is easy to see that $\det(\eta_{f_{ij}}) = -c_p/Tv\kappa_T = c_p/T(\partial p/\partial v)_T$ and that the characteristic equation of (2.1) is given by

$$\lambda^2 + \left(\frac{c_v}{T} - \frac{1}{v\kappa_T} \right) \lambda - \frac{c_p}{T v \kappa_T} = 0. \quad (2.2)$$

It follows that the eigenvalues are given by

$$\lambda_{1/2} = \frac{1}{2} \left[\left(\frac{1}{v\kappa_T} - \frac{c_v}{T} \right) \pm \sqrt{\Delta} \right], \quad (2.3)$$

where

$$\Delta = \left(\frac{1}{v\kappa_T} + \frac{c_v}{T} \right)^2 + 4 \left(\frac{\alpha}{\kappa_T} \right)^2 > 0. \quad (2.4)$$

Now, since Δ is always positive, the eigenvalues $\lambda_{1/2}$ are both real and distinct and, since $\det(\eta_{ij}) = \lambda_1 \lambda_2$, then we have the following result

Lemma 1. Let $T > 0$. Since $c_p - c_v = \frac{vT\alpha^2}{\kappa_T}$, then if $c_p > 0$ and $(\frac{\partial p}{\partial v})_T < 0$ then $\det(\eta_{fij}) < 0$ and $\lambda_1 < 0$, $\lambda_2 > 0$.

Let's assume that the eigenvalues are both non-zero. Then the metric (2.1) is diagonalizable. Since η_{fij} is a real symmetric matrix, it can be diagonalized by an orthogonal change of basis of the tangent space $T_q S$ at point q to the surface S . In the eigenvector basis, the shape of the equilibrium surface S becomes obvious. Direction along eigenvectors with negative eigenvalues have curvature downward and direction with positive eigenvalues have upward curvature. Moreover, each eigenvector would represent a particular perturbation of the surface. Naturally, both eigenvalues and eigenvector would depend on the point (T, v) . It follows that the matrix of eigenvalues is given by

$$\Lambda_{ij} = \frac{1}{2} \begin{pmatrix} (\frac{1}{v\kappa_T} - \frac{c_v}{T}) - \sqrt{\Delta} & 0 \\ 0 & (\frac{1}{v\kappa_T} - \frac{c_v}{T}) + \sqrt{\Delta} \end{pmatrix} \quad (2.5)$$

The corresponding eigenvectors corresponding to λ_1 and λ_2 are given by

$$\xi_1 = \begin{pmatrix} 1 \\ -\frac{\kappa_T}{2\alpha} \left[\left(\frac{1}{v\kappa_T} + \frac{c_v}{T} \right) - \sqrt{\Delta} \right] \end{pmatrix} \quad (2.6)$$

and

$$\xi_2 = \begin{pmatrix} \frac{\kappa_T}{2\alpha} \left[\left(\frac{1}{v\kappa_T} + \frac{c_v}{T} \right) - \sqrt{\Delta} \right] \\ 1 \end{pmatrix} \quad (2.7)$$

Now, since the two eigenvalues are distinct then the set $[\xi_1, \xi_2]$ is linearly independent.

Let's denote, now, the matrix $P = (\xi_1, \xi_2)$. In particular,

$$P = \begin{pmatrix} 1 & \frac{\kappa_T}{2\alpha} [(\frac{1}{v\kappa_T} + \frac{c_v}{T}) - \sqrt{\Delta}] \\ -\frac{\kappa_T}{2\alpha} [(\frac{1}{v\kappa_T} + \frac{c_v}{T}) - \sqrt{\Delta}] & 1 \end{pmatrix} \tag{2.8}$$

and the inverse P^{-1} is given by

$$P^{-1} = \frac{1}{1 + \frac{\kappa_T^2}{4\alpha^2} [(\frac{1}{v\kappa_T} + \frac{c_v}{T}) - \sqrt{\Delta}]^2} \times \begin{pmatrix} 1 & -\frac{\kappa_T}{2\alpha} [(\frac{1}{v\kappa_T} + \frac{c_v}{T}) - \sqrt{\Delta}] \\ \frac{\kappa_T}{2\alpha} [(\frac{1}{v\kappa_T} + \frac{c_v}{T}) - \sqrt{\Delta}] & 1 \end{pmatrix}. \tag{2.9}$$

It is evident that $\eta_{f_{ij}}$ can be decomposed in the very special form

$$\eta_{f_{ij}} = P \Lambda_{ij} P^{-1}, \tag{2.10}$$

where P is a matrix composed of eigenvectors, P^{-1} is its inverse and Λ_{ij} is the matrix of eigenvalues of $\eta_{f_{ij}}$.

Let's, now, define with E_{λ_1} and E_{λ_2} the eigenspaces of λ_1 and λ_2 . Naturally, the basis for the one-dimensional eigenspaces E_{λ_1} and E_{λ_2} are given by ξ_1 and ξ_2 .

If we denote by $|\xi_i|$, $i = 1, 2$, the length of the eigenvectors, then we can normalize them obtaining a orthonormal basis for the two-dimensional tangent space at any point q on the surface considering the important fact that normalizing a vector of imaginary length can require multiplication by a negative scalar

$$B = \left(\frac{\xi_1}{|\xi_1|}, \frac{\xi_2}{|\xi_2|} \right) = (\xi_1^-, \xi_2^-) \tag{2.11}$$

The tangent space $T_q S$ at any point q on S is a vector space endowed with a pseudo-Riemannian metric given by

$$\Lambda_{ij} = \frac{1}{2} \begin{pmatrix} (\frac{1}{v\kappa_T} - \frac{c_v}{T}) - \sqrt{\Delta} & 0 \\ 0 & (\frac{1}{v\kappa_T} - \frac{c_v}{T}) + \sqrt{\Delta} \end{pmatrix}. \tag{2.12}$$

Such a metric at any point on the domain, say (T_0, v_0) , is equivalent to a Lorentz metric of the form

$$A_{ij}|_{(T_0, v_0)} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.13)$$

The tangent space $T_q S$ at a point q on the surface S is, therefore, a Lorentzian two-space and denoted by $E^{1,1}$.

This implies that the length of any vector is either positive, zero or pure imaginary.

Now, it is known that the equilibrium surface defined by the energy function $u = u(s, v)$ has a metric at any point of its domain of the form

$$\Lambda_{ij}|_{(s_0, v_0)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Moreover, the Helmholtz potential f is the Legendre transformation of u , which replaces the molar entropy s by the temperature $T = \partial u / \partial s$. Then, it is exactly the one variable Legendre transformation which change the signature of the metric. In other words, it locally change the Euclidean metric in a Lorentzian one and viceversa.

Remark 2. Note that the same argument is true in case we would consider Enthalpy as thermodynamic potential which is the Legendre transformation of internal energy that replaces the molar volume by the pressure as independent variables. In our future work, we'll show that also such a metric is Lorentzian. As we will show that, given Gibbs free energy as thermodynamic potential, which is a double-variable Legendre transformation, the metric related to it has signature $(-1, -1)$ which is equivalent to the Euclidean signature $(1, 1)$. As far this paper is concerned we are just considering length along isotherms and, therefore, we leave such a remark as introduction to future work.

Let's, thus, define positive length to be volume-like and pure imaginary to be temperature-like. We stress again that pure imaginary length is temperature-like due to the one variable Legendre transformation which replaces s with T .

From now on, we'll study length along isotherms. An isothermal process typically occurs when a system is in contact with an outside thermal reservoir, and the system changes slowly enough to allow it to adjust to the temperature of the reservoir.

Now, considering

$$L_{a_0 a_1} = \int_{a_0}^{a_1} \left[\sum_{i,j} \eta_{fij} dX_i dX_j \right]^{1/2} \quad (2.14)$$

to be the length of a path between two states a_0 and a_1 , the thermodynamic length with the Helmholtz potential metric becomes

$$L = \int \left[-\frac{c_v}{T} (dT)^2 - 2\frac{\alpha}{\kappa_T} dT dv + \frac{1}{v\kappa_T} (dv)^2 \right]^{1/2} \quad (2.15)$$

$$= \int_{\xi_i}^{\xi_f} \left[-\frac{c_v}{T} \left(\frac{dT}{d\xi} \right)^2 - 2\frac{\alpha}{\kappa_T} \frac{dT}{d\xi} \frac{dv}{d\xi} + \frac{1}{v\kappa_T} \left(\frac{dv}{d\xi} \right)^2 \right]^{1/2} d\xi. \quad (2.16)$$

Using (2.12), we have that

$$(dL)^2 = \lambda_1 (dT)^2 + \lambda_2 (dv)^2. \quad (2.17)$$

The expression above is not positive definite. Therefore the usual concept of length has to be abandoned.

In particular, as we stated previously, we consider constant directional paths in which we also allow zero and pure imaginary length. As mention above, we will restrict our attention to the study of thermodynamic length at constant temperature which is given by

$$L^T = \int \sqrt{\frac{1}{v\kappa_T}} dv = \int \sqrt{\left(-\frac{\partial p}{\partial v}\right)_T} dv = \int \sqrt{-\frac{T}{c_p} \det \eta_{ijf}} dv = \int \sqrt{\eta_{22}} dv. \quad (2.18)$$

3. THE ISOTHERM LENGTH-WORK THEOREM

The *Isotherm Length-Work Theorem* uses the virial expansion in inverse power of molar volume which is given by,⁽²⁾

$$p = \frac{RT}{v} + \frac{RTB(T)}{v^2} + \frac{RTC(T)}{v^3} + \frac{RTD(T)}{v^4} + \dots, \quad (3.1)$$

where $B(T)$, $C(T)$, etc. are the virial coefficients.

If we expand p up to the n th power, then, we might express (3.1) as

$$p = \frac{RT}{v} + \frac{RTB(T)}{v^2} + \frac{RTC(T)}{v^3} + \frac{RTD(T)}{v^4} + \dots + \frac{RTY(T)}{v^{n-1}} + \frac{RTZ(T)}{v^n}, \tag{3.2}$$

where $Y(T)$ and $Z(T)$ are the $(n - 1)$ th and the n th virial coefficients.

Now, since the temperature is constant, say $T = T_0$, let's set $B(T_0) = B$, $C(T_0) = C$, etc. and so, recalling the second integral in (2.18), we have

$$\begin{aligned} L^T &= \int \sqrt{\left(-\frac{\partial p}{\partial v}\right)_T} dv \\ &= \int \sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}} dv. \end{aligned} \tag{3.3}$$

Theorem 1. Isotherm Length-Work Theorem.

Let T and v be non-zero. Then, along isotherms, thermodynamic length is given by any of the following:

$$\begin{aligned} L^T &= \frac{1}{\sqrt{RT}} \left[n \int \frac{p dv}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} - (n-1) \int \frac{RT dv}{v \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} \right. \\ &\quad \left. - (n-2) \int \frac{RTB dv}{v^2 \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} - \dots \right] \end{aligned} \tag{3.4}$$

$$\begin{aligned} &= \frac{n}{\sqrt{RT}} \left[\frac{W}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} \right. \\ &\quad \left. - \int \frac{Bv^{2n-4} + 3Cv^{2n-5} + \dots}{v^{\frac{n-1}{2}} [v^{n-1} + 2Bv^{n-2} + 3Cv^{n-3} + \dots]^{\frac{3}{2}}} W dv \right] \\ &\quad - \sqrt{RT} \left[\int \frac{(n-1)dv}{v \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} \right. \\ &\quad \left. + \int \frac{(n-2)Bdv}{v^2 \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} + \dots \right] \end{aligned} \tag{3.5}$$

$$= \sqrt{RT} \left[\int \frac{dv}{v \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} + \int \frac{2B dv}{v^2 \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} + \int \frac{3C dv}{v^3 \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} + \dots \right], \tag{3.6}$$

where W is work.

Proof. Consider (3.3),

$$L^T = \int \sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}} dv. \tag{3.7}$$

It can be rewritten as

$$\begin{aligned} L^T &= \int \frac{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}{\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} dv \\ &= \int \frac{\frac{1}{v} \left[\frac{RT}{v} + \frac{RTB}{v^2} + \frac{RTC}{v^3} + \dots + \frac{RTY}{v^{n-1}} + \frac{RTZ}{v^n} \right]}{\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} dv \\ &\quad + \int \frac{\frac{1}{v} \left[\frac{RTB}{v^2} + \frac{RTC}{v^3} + \dots + \frac{RTY}{v^{n-1}} + \frac{RTZ}{v^n} \right]}{\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} dv \\ &\quad + \int \frac{\frac{1}{v} \left[\frac{RTC}{v^3} + \dots + \frac{RTY}{v^{n-1}} + \frac{RTZ}{v^n} \right]}{\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} dv \\ &\quad + \dots + \int \frac{\frac{1}{v} \left[\frac{RTZ}{v^n} \right]}{\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} dv, \end{aligned}$$

which gives

$$\begin{aligned} L^T &= \int \frac{p dv}{v \sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} \\ &\quad + \int \frac{\left(p - \frac{RT}{v} \right) dv}{v \sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} \end{aligned}$$

$$\begin{aligned}
 & + \int \frac{(p - \frac{RT}{v} - \frac{RTB}{v^2})dv}{v\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}} \\
 & + \dots + \int \frac{(p - \frac{RT}{v} - \frac{RTB(T)}{v^2} - \frac{RTC(T)}{v^3} - \dots - \frac{RTY(T)}{v^{n-1}})}{v\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{(n-1)RTY}{v^n} + \frac{nRTZ}{v^{n+1}}}}
 \end{aligned}$$

Therefore, after rearranging, and considering that

$$\sqrt{\frac{RT}{v^2} + \frac{2RTB}{v^3} + \frac{3RTC}{v^4} + \dots + \frac{nRTZ}{v^{n+1}}} = \frac{\sqrt{RT}}{v} \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots + \frac{nZ}{v^{n-1}}}$$

we get

$$\begin{aligned}
 L^T = \frac{1}{\sqrt{RT}} \left[n \int \frac{p dv}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} - (n-1) \int \frac{RT dv}{v \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} \right. \\
 \left. - (n-2) \int \frac{RTB dv}{v^2 \sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} - \dots \right], \tag{3.8}
 \end{aligned}$$

where we drop the n th integral for simplicity.

Considering the first integral, we can integrate by parts considering variables ξ and W , (work), such that

$$\xi = \frac{1}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots + \frac{nZ}{v^{n-1}}}} \quad dW = p dv$$

and, since

$$\frac{d\xi}{dv} = \frac{Bv^{2n-4} + 3Cv^{2n-5} + \dots}{v^{\frac{n-1}{2}} [v^{n-1} + 2Bv^{n-2} + 3Cv^{n-3} + \dots]^{3/2}},$$

then we have

$$\begin{aligned}
 & \int \frac{p dv}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} = \frac{W}{\sqrt{1 + \frac{2B}{v} + \frac{3C}{v^2} + \dots}} \\
 & - \int \frac{Bv^{2n-4} + 3Cv^{2n-5} + \dots}{v^{\frac{n-1}{2}} [v^{n-1} + 2Bv^{n-2} + 3Cv^{n-3} + \dots]^{3/2}} W dv. \tag{3.9}
 \end{aligned}$$

Substituting (3.9) into (3.8), we get our final result (3.5). (3.6) is immediate from (3.4). ■

Remark 3. Note that while (3.5) gives evidence that thermodynamic length is *also* work, (3.6) is easier for computational purposes.

Let's now look at specific cases. In particular, let's look at the first, second and third expansion; i.e. $n=1$, $n=2$ and $n=3$.

For $n=1$, we have the Ideal (or quasi-Ideal) case.

Corollary 1. Let

$$p = \frac{RT}{v}. \tag{3.10}$$

Then, along isotherms,

$$L^T = \frac{1}{\sqrt{RT}} W = \sqrt{RT} \ln \left(\frac{v_2}{v_1} \right), \tag{3.11}$$

where W is work given by $W = \int_{v_1}^{v_2} p dv$.

Proof I. In this case, all the virial coefficients are zero and $n=1$. So, from (3.5) and (3.6), we get (3.11) immediately.

During an isothermal process, the internal energy of an Ideal gas remains constant because the gas temperature does not change. Thus, $du = 0$, which implies, by the first law of thermodynamics, that if we do some work on a gas to compress it, the same amount of energy will appear as heat transferred from the gas as it is compressed. Thermodynamic length, in this case, seems to be a measure of them up to a constant.

Always along isotherms, it is easy to show that thermodynamic length is work also in the case in which we consider the volume occupied by molecules (quasi-ideal).

In particular, if $p = RT/v - b$ then (3.11) still holds.

Proof II. We look at the case in which

$$\left(\frac{\partial^2 f}{\partial v^2} \right)_T = \frac{1}{RT} \left[\left(\frac{\partial f}{\partial v} \right)_T \right]^2, \tag{3.12}$$

where f is the molar Helmholtz potential. Naturally, (3.12) is equivalent to

$$\left(\frac{\partial p}{\partial v} \right)_T + \frac{1}{RT} p^2 = 0 \tag{3.13}$$

since $(\partial f/\partial v)_T = -p$. Now, (3.13) is a separable first order ordinary differential equation whose solution is given by

$$p = \frac{RT}{v-b}$$

from which we have $f = -RT \ln|v-b| + h$, where h is any constant. Then, by (2.18)

$$\begin{aligned} L^T &= \int \sqrt{\left(\frac{\partial^2 f}{\partial v^2}\right)_T} dv = \int \sqrt{\frac{1}{RT} \left(\frac{\partial f}{\partial v}\right)_T^2} dv = \int \sqrt{\frac{1}{RT}} \left|\left(\frac{\partial f}{\partial v}\right)_T\right| dv \\ &= \sqrt{\frac{1}{RT}} \int |p| dv = \sqrt{\frac{1}{RT}} W. \quad \blacksquare \end{aligned} \quad (3.14)$$

Let's consider, now, the case $n=2$ in which the only non-zero virial coefficient is B .

Corollary 2. Let

$$p = \frac{RT}{v} + \frac{RTB}{v^2}. \quad (3.15)$$

Then, along isotherms,

$$\begin{aligned} L^T &= \frac{1}{\sqrt{RT}} W + \sqrt{RT} \left[\ln \left(\frac{1 + \frac{B}{v_2} + \sqrt{1 + \frac{2B}{v_2}}}{1 + \frac{B}{v_1} + \sqrt{1 + \frac{2B}{v_1}}} \right) - B \left(\frac{v_2 - v_1}{v_1 v_2} \right) \right. \\ &\quad \left. - 2 \left(\sqrt{1 + \frac{2B}{v_2}} - \sqrt{1 + \frac{2B}{v_1}} \right) \right] \end{aligned} \quad (3.16)$$

$$= 2\sqrt{RT} \left[\ln \left(\frac{\sqrt{(v_2 + 2B)} + \sqrt{v_2}}{\sqrt{(v_1 + 2B)} + \sqrt{v_1}} \right) - \left(\sqrt{1 + \frac{2B}{v_2}} - \sqrt{1 + \frac{2B}{v_1}} \right) \right], \quad (3.17)$$

where the length is evaluated from volume v_1 to v_2 and work is given by $W = RT[\ln(\frac{v_2}{v_1}) + B(v_2 - v_1/v_1 v_2)]$.

Proof. From (3.5) and (3.6) after some calculation.

Expression (3.17) might be re-written in a more compact form by setting $\rho_i = \sqrt{1 + \frac{2B}{v_i}}$ with $i=1, 2$. Then we get

$$L^T = 2\sqrt{RT} \left[\ln \left(\sqrt{\frac{v_2}{v_1}} \left(\frac{\rho_2 + 1}{\rho_1 + 1} \right) \right) - (\rho_2 - \rho_1) \right].$$

Let's, now, denote by W_{ideal} , the work done on an Ideal gas (see Corollary 1). It is interesting to note that, since $W = RT[\ln(v_2/v_1) + B(v_2 - v_1/v_1v_2)] = W_{\text{ideal}} + RTB(v_2 - v_1/v_1v_2)$, then expression (3.16) can be written as

$$\begin{aligned}
 L^T &= \frac{1}{\sqrt{RT}} W_{\text{ideal}} + \sqrt{RT} \left[\ln \left(\frac{1 + \frac{B}{v_2} + \sqrt{1 + \frac{2B}{v_2}}}{1 + \frac{B}{v_1} + \sqrt{1 + \frac{2B}{v_1}}} \right) \right. \\
 &\quad \left. - 2 \left(\sqrt{1 + \frac{2B}{v_2}} - \sqrt{1 + \frac{2B}{v_1}} \right) \right] \\
 &= L_{\text{ideal}}^T + \sqrt{RT} \left[\ln \left(\frac{1 + \frac{B}{v_2} + \sqrt{1 + \frac{2B}{v_2}}}{1 + \frac{B}{v_1} + \sqrt{1 + \frac{2B}{v_1}}} \right) - 2 \left(\sqrt{1 + \frac{2B}{v_2}} - \sqrt{1 + \frac{2B}{v_1}} \right) \right]
 \end{aligned}
 \tag{3.18}$$

It is evident that the second term on the right side of expression (3.18) gives the contribution to the thermodynamic length of an isothermal quasi-static “real” process between two states due to inter-particle interaction. ■

Remark 4. This result would help us to understand what thermodynamic length is along isotherms for TD systems in which some interaction is occurring. Note that, if $B = 0$, like in the corollary 1, then length reduces to (3.11).

APPENDIX A

We include the case $n = 3$ as a curiosity. We have the following

Corollary 3. Let

$$p = \frac{RT}{v} + \frac{RTB}{v^2} + \frac{RTC}{v^3}
 \tag{A.1}$$

Then, along isotherms,

$$\begin{aligned}
 L^T = \sqrt{RT} & \left[\ln \left(\frac{\sqrt{v_2^2 + 2Bv_2 + 3C + v_2 + B}}{\sqrt{v_1^2 + 2Bv_1 + 3C + v_1 + B}} \right) \right. \\
 & + \frac{B}{\sqrt{3C}} \left[\ln \left(\frac{\sqrt{3C}\sqrt{v_2^2 + 2Bv_2 + 3C} - Bv_2 - 3C}{\sqrt{3C}\sqrt{v_1^2 + 2Bv_1 + 3C} - Bv_1 - 3C} \right) \right. \\
 & \left. \left. - \ln \left(\frac{v_2}{v_1} \right) \right] - \left(\sqrt{1 + \frac{2B}{v_2} + \frac{3C}{v_2^2}} - \sqrt{1 + \frac{2B}{v_1} + \frac{3C}{v_1^2}} \right) \right] \quad (\text{A.2})
 \end{aligned}$$

4. CONCLUSIONS

It would be interesting to see what thermodynamic length would be along isotherms for different values of B and C or what the physical meaning of length is, since, for $n=2$ above, work is just a part of it. For example, the Van der Waals gas would be a good starting point.

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Dedicated to Francesco Santoro, Benedetta Mazzuti and Carlo Santoro.

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