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GRAPHICAL DEPICTION OF CONCAVITY AND CONVEXITY IN THE CONTEXT OF THERMODYNAMIC STABILITY

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Abstract. Thermodynamic stability of systems at equilibrium represents a fundamental and crucial topic within the realm of thermodynamics. The stability of thermodynamic systems at equilibrium is inherently related to the concavity of the entropy (S) or the convexity of the internal energy (U), the functions those encountered in mathematics. It can be demonstrated that for entropy representation formalism $S = S(U, V, N)$ for a stable system, entropy versus internal energy at constant volume (V) and constant number of particles (N expressed in moles) is characterized as a concave function. As a result when energy is transferred between subsystems, at constant volume and constant number of particles within the subsystems, the entropy does not demonstrate an increase. In other words a closed system (the internal energy, volume and all the mole numbers are constant) at equilibrium reaches a state of maximum entropy. This study has been shown that by using the graphical illustration of both convex and concave functions, and by transforming one function into the other via rotation, the notion of thermodynamic stability within the context of entropy representation can be transformed to the framework of internal energy representation. By a ninety-degree counterclockwise rotation, a concave function is converted into a convex function, similarly by rotation an $S - U$ graph a $U - S$ graph will be obtained that represents the convexity of internal energy as a function of entropy. Hence if the entropy transferred between subsystems at constant volume and constant number of particles within the subsystems the internal energy does not show a decrease. In other words the closed system achieves its minimum internal energy value at equilibrium; no net entropy transfer occurred.

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1. Introduction

One of the main problems in thermodynamics is studying the stability of systems at equilibrium [1] and the cornerstone of the study and investigation of stability at equilibrium state in thermodynamics is entropy [2, 3].The third postulate of thermodynamics asserts that entropy is both continuous and differentiable, serving as a monotonically increasing function of internal energy. The proposed monotonic property suggests that the partial derivative $(\partial S/\partial U)_{V,N}$ must be a positive quantity [4]. Notably, this postulate does not provide insights into whether the entropy versus internal energy is a concave or convex function. Although the concept of concavity and convexity of functions is well-known in mathematical discourse, a few chemistry textbooks have thoroughly explored this concept and its critical relevance to the stability of equilibrium systems in thermodynamics [4, 5]. However the thermodynamics text books mostly mention the importance of the subject and leave the details of proving mathematical equations to the reader.

In this article the stability of thermodynamic systems at equilibrium is analyzed from the perspective of the mathematical view of the concavity of entropy and the convexity of internal energy. As well as their interrelationships with the stability of thermodynamic systems employing both algebraic and graphical approaches have been investigated. It has been shown that a graphical representation can facilitate the understanding of the concept of thermodynamic stability from the perspective of concavity and convexity of entropy and internal energy functions. Furthermore, graphical representation introduces a novel conceptual framework for the transformation of thermodynamic stable systems, transforming from an entropy representation, characterized as a concave function to an internal energy representation, which is a convex function. Some scholars believe that the fundamental structure of thermodynamics is purely algebraic [6]. It seems that the graphical perspective may not only provide a novel methodology for enhancing the comprehension of thermodynamic stability but also suggest an innovative framework for the transformation of thermodynamic potentials.

2. Discussion

2.1 A Graphical Representation for Concavity and Convexity

Theorem 2.1. *Let the function f have a continuous derivative f' over an interval I. Furthermore, let it be the case that the second derivative f'' exists and retains a consistent sign across all interior points of I (monotonic function). Under these conditions, f*

exhibits concavity (concave downward) throughout I if f'' is negative at each interior point of I [7, 8].

Figure 1, shows a concave function on a desired interval. As the figure shows, the concave curve, represented by the blue solid-curve lies above the red dash-dot straight line. Therefore it is clearly seen that for a concave function any vertical lines located in the desired interval $[x_1, x_2]$, intersects the red dash-dot line below the concave curve. This result can be represented by equation (2.1):

$$Y\left[\frac{1}{2}(x_1+x_2)\right] \geqslant \frac{1}{2}\left[Y(x_1)+Y(x_2)\right] \tag{2.1}$$

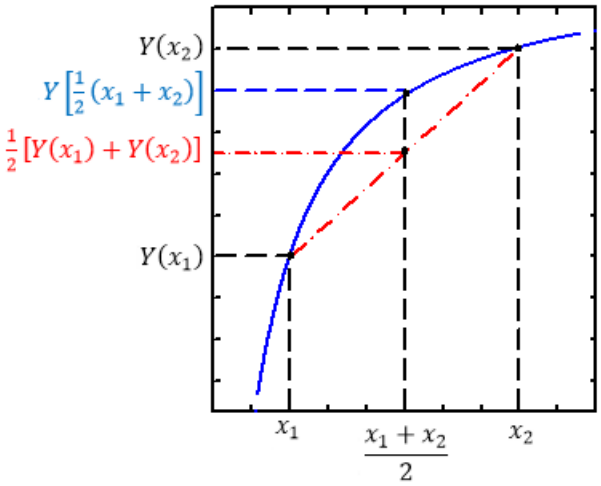


FIGURE 1. A concave or concave downward curve the blue solid-curve, which lies above the red dash-dot straight line in desired interval $[x_1, x_2]$.

Theorem 2.2. *Let the function f have a continuous derivative f' over an interval I. Furthermore, let it be the case that the second derivative f'' exists and retains a consistent sign across all interior points of I (monotonic function). Under these conditions, f exhibits convexity (concave upward) throughout I if f'' is positive at each interior point of I* [7, 8].

Figure 2, shows a convex function within the specified interval. As the figure shows, the convex curve, represented by the blue solid-curve lies below the red dash-dot straight line. Therefore it is clearly seen that for a convex function any vertical lines located in desired

interval $[y_1, y_2]$, intersects the red dash-dot line above the convex curve. This relationship is mathematically expressed in equation (2.2):

$$X\left[\frac{1}{2}(y_1 + y_2)\right] \leqslant \frac{1}{2}\left[X(y_1) + X(y_2)\right] \tag{2.2}$$

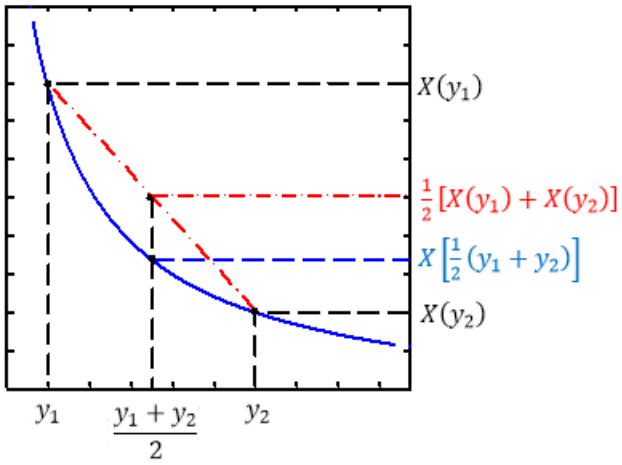


FIGURE 2. A convex or concave upward curve the blue solid-curve, which lies below the red dash-dot straight line in the desired interval $[y_1, y_2]$.

It can be clearly seen that Figure 2, results from a ninety-degree counterclockwise rotation of Figure 1. This operation has effectively transformed the concave curve into a convex curve through the application of the rotation operator. The feature that is used subsequently for thermodynamic concepts and its importance will be discussed.

2.2 Stability Conditions for Entropy

A similar approach that was used in part (2.1) can be utilized for the entropy (S) versus the internal energy (U) graph when the volume (V) and the particle numbers (N) are held constant. In Figure 3, the entropy is plotted versus the internal energy. As the figure is clearly shows the $S - U$ graph is a concave graph for a stable thermodynamic system. When the system is divided into two subsystems, the transfer of energy between the subsystems—while keeping the total internal energy constant—will not lead to an increase in entropy. This dictates that the system is at its maximum entropy, no net energy is transferred between hypothetical subsystems and the system maintains thermodynamic stability.

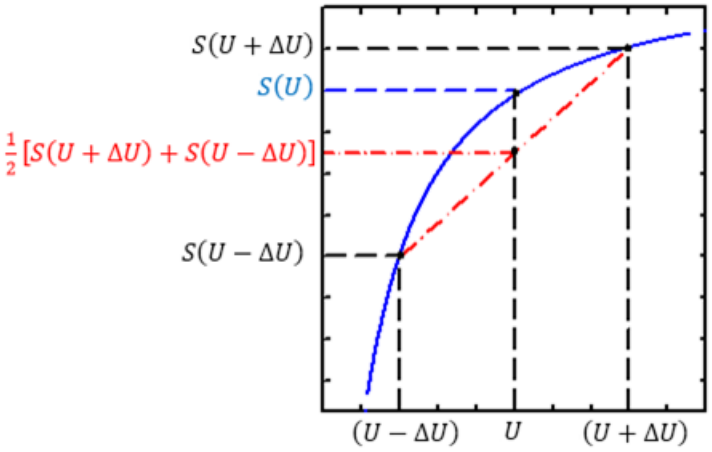


FIGURE 3. Concavity of entropy versus internal energy the blue solid-curve at constant V and N. For a concave curve represented by the blue solid curve, the entropy $S(U)$ is greater than or equal to any amount of entropy associated with the $S-U$ graph that is positioned beneath the concave curve e. g. red dash-dot line in the specified interval.

As illustrated in Figure 3, the blue solid-curve lies above the red dash-dot line, and serves as a graphical representation of concavity. In mathematical terms $S(U,V,N)$ is greater than or equal to $(1/2)[S(U+\Delta U,V,N)+S(U-\Delta U,V,N)]$, where $\pm\Delta U$ represents the quantity of internal energy that is exchanged between one subsystem and another subsystem.

Equation(2.3) demonstrates that the criterion for stability—when entropy changes as small changes in internal energy—is upon the concavity of the entropy function [9, 10]. The equation is in full agreement with the second law [2].

$$S(U+\Delta U,V,N)+S(U-\Delta U,V,N)\leqslant 2S(U,V,N) \tag{2.3}$$

To investigate the relationship between entropy and infinitesimal changes in internal energy, the entropy function is expanded about internal energy utilizing the Taylor expansion. It is crucial to emphasize that this approach considers other extensive parameters (V and N) have been constant, hence a single-variable Taylor expansion is applied. The Taylor expansion for m independent variables [11] expressed in the closed form is represented by equation (2.4):

$$f(x_j)=\sum_{n=0}^{\infty}\frac{t^n}{n!}\left(\sum_{i=1}^{m}\alpha_i\frac{\partial}{\partial x_i}\right)^n f(x_k)\big|_{x_k=x_{k0}} \tag{2.4}$$

where $\alpha_j t = x_j - x_{j0}$. Equation (2.5) shows the expansion of entropy about internal energy, for conciseness, both increases and decreases in internal energy are encapsulated within a single equation, utilizing a plus and minus ($\pm$) symbol.

$$S(U \pm \Delta U, V, N) = S(U, V, N) + \frac{dS}{dU}(\pm \Delta U) + \frac{1}{2}\frac{d^2S}{dU^2}(\pm \Delta U)^2 + ... \tag{2.5}$$

As the limit ΔU approaches zero, cubic and higher-order terms can be neglected. By substituting the right-hand side of equation (2.5) into the left-hand side of equation (2.3), equation (2.6) is derived:

$$2S(U, V, N) \geqslant 2S(U, V, N) + \frac{d^2S}{dU^2}(\Delta U)^2 \tag{2.6}$$

Taking into account that the squared term is always positive, it can be deduced that $(d^2S/dU^2) \leqslant 0$ at constant volume and particle number. This inference is fully consistent with the findings detailed in reference [2] and corresponds with equation (2.7).

$$\lim_{\Delta U \longrightarrow 0} \left[\frac{S(U + \Delta U) + S(U - \Delta U) - 2S(U)}{(\Delta U)^2} \right] = \left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N} \leqslant 0 \tag{2.7}$$

This inequality yields a significant outcome in the field of thermodynamics, aligning with the empirical property regarding as the second derivatives, such as the molar heat capacity at constant volume and the isothermal compressibility [12]. The molar heat capacity at constant volume, is defined as

$$c_v \equiv (T/N)\big(\partial S/\partial T\big)_V = 1/N\big(dQ/dT\big)_V.$$

According to the definition of temperature, $(\partial U/\partial S)_{V,N} \equiv T$, and equation (2.7), $(\partial^2 S/\partial U^2)_{V,N} = -(1/NT^2 c_v) \leqslant 0$ it is anticipated that the molar heat capacity at constant volume always is nonnegative in a closed equilibrium system. This observation is consistent with empirical results, as the transfer of heat into a closed equilibrium system doesn't lead to a decrease in temperature.

The same approach that has been employed to entropy changes with change of internal energy, can be employed to entropy changes with change of volume. The $S - V$ graph should exhibit a concavity to ensure the stability of the system. The equation (2.8) shows the concavity of entropy governing the transfer of volume, between one subsystem and another subsystem:

$$S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \leqslant 2S(U, V, N) \tag{2.8}$$

At constant internal energy and particle number, the differential expression for equation (2.8) becomes $(d^2S/dV^2) \leqslant 0$. This aligns with the empirical property known as isothermal compressibility, one of the second derivatives in thermodynamics. The isothermal compressibility is defined as

$$\kappa_T \equiv (-1/v)\big(\partial v/\partial P\big)_T = -(1/V)\big(\partial V/\partial P\big)_T \geqslant 0$$

will be a nonnegative quantity by utilizing equation (2.8). It is rational to assert that in any closed equilibrium system at constant temperature, a decrease in volume doesn't lead to a decrease in pressure.

Similar to the preceding equations (2.8) and (2.3), the concave behavior of entropy in relation to simultaneous variations in two parameters—internal energy and volume—is illustrated in equation (2.9).

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \leqslant 2S(U,V,N) \tag{2.9}$$

To investigate the changes of entropy as changes of two extensive parameters simultaneously—internal energy and volume—Taylor's expansion, equation (2.4) is employed, where m equals two for the two independent variables. The mathematical representation of this expansion is articulated in equation (2.10):

$$f(x+dx, y+dy) = f(x,y) + dx\frac{\partial f}{\partial x} + dy\frac{\partial f}{\partial y} + \frac{1}{2!}\Big[(dx)^2\frac{\partial^2 f}{\partial x^2} + 2dxdy\frac{\partial^2 f}{\partial x \partial y} + (dy)^2\frac{\partial^2 f}{\partial y^2}\Big] + \ldots \tag{2.10}$$

Utilizing equation (2.10), one can deduce equation (2.11) for $S(U \pm \Delta U, V \pm \Delta V, N)$. For conciseness, both the plus and minus symbol $(\pm)$ are encapsulated within a single equation, utilizing a plus and minus $(\pm)$ symbols.

$$\begin{aligned} S(U \pm \Delta U, V \pm \Delta V, N) = S(U,V,N) &+ \frac{\partial S}{\partial U}(\pm\Delta U) + \frac{\partial S}{\partial V}(\pm\Delta V) \\ &+ \frac{1}{2}\Big[\frac{\partial^2 S}{\partial U^2}(\pm\Delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}(\pm\Delta U)(\pm\Delta V) + \frac{\partial^2 S}{\partial V^2}(\pm\Delta V)^2\Big] \end{aligned} \tag{2.11}$$

Cubic and higher-order terms, wherein ΔU and ΔV approache towards zero, are neglected. By substituting equation (2.11) into the left-hand side of equation (2.9), and doing some manipulations, equation (2.12) can be derived:

$$\left(\frac{\partial^2 S}{\partial V^2}\right)\left(\frac{\partial^2 S}{\partial U^2}\right) - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geqslant 0 \tag{2.12}$$

2.3 Stability Conditions for Internal Energy

As shown in part (2.1), the application of a counterclockwise rotation of ninety degrees to a concave curve results in the formation of a convex curve within a specified interval. This approach can similarly be utilized for the $S-U$ graph illustrated in Figure 3, with the resulting graph depicted in Figure 4. As evidenced in the figure, the concavity in the entropy curve has been transformed into the convexity of the internal energy curve.

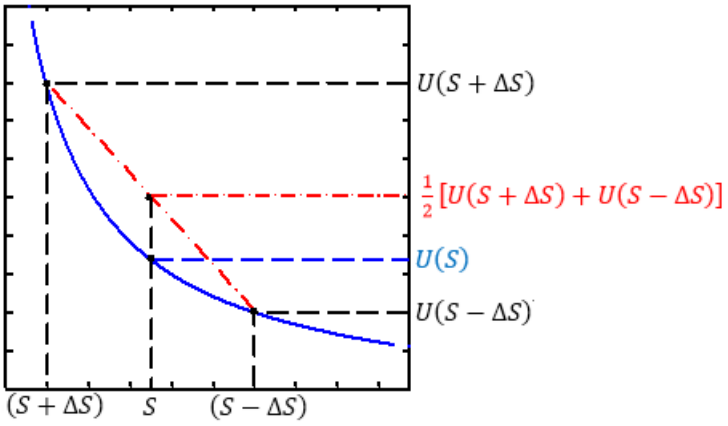


FIGURE 4. Convexity of internal energy versus entropy the blue solid-curve at constant V and N. For a convex curve represented by the blue solid curve, the internal energy $U(S)$ is lower than or equal to any amount of internal energy associated with the $S-U$ graph that is positioned above the convex curve e. g. red dash-dot line in the specified interval.

Figure 4 shows that the blue solid curve lies below the red dash-dot line. Mathematically is less than or equal to $(1/2)[U(S+\Delta S,V,N)+U(S-\Delta S,V,N)]$ where $\pm\Delta S$ denotes the amount of the entropy exchanged between one subsystem and another, which graphically expresses the convexity of the internal energy. Equation (2.13) indicates that the stability condition—where internal energy varies with small changes of entropy—relies on the convexity of the internal energy [13].

$$U(S+\Delta S,V,N)+U(S-\Delta S,V,N)\leqslant 2U(S,V,N) \tag{2.13}$$

The concave curve within the specified interval, lies below each of its tangent lines, while conversely, a convex curve within the specified interval lies above each of its tangent lines. This result as well as two-dimensional, can be generalized to three-dimensional

and also multidimensional space (equations (2.3), (2.8), (2.9), and (2.13)). Therefore for three-dimensional $S-U-V$ subspace, the global condition for thermodynamic stability necessitates that the entropy surface $S(U,V,N)$ lies below its tangent planes, while conversely, that the internal energy surface $U(S,V,N)$ lies above its tangent planes [5, 13] as shown in equations (2.14) and (2.15).

$$U(S+\Delta S,V+\Delta V,N)+U(S-\Delta S,V-\Delta V,N)\geqslant 2U(S,V,N) \tag{2.14}$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)\left(\frac{\partial^2 U}{\partial V^2}\right)-\left(\frac{\partial^2 V}{\partial S\partial V}\right)^2\geqslant 0 \tag{2.15}$$

Equation (2.15) holds significant importance within the realm of thermodynamic stability, as it can be generalized to Legender transforms of internal energy, known as thermodynamic potentials, as well as for the entropy known as Massieu functions.

3. Conclusion

In this study, the fundamental concept of thermodynamic stability for closed equilibrium systems has been examined in details from both algebraic and graphical viewpoints of concavity and convexity of functions. The study demonstrates that a graphical representation markedly improves the understanding of the concepts of concavity and convexity, as well as their applications within the field of thermodynamics. Moreover, this methodology proposes a graphical technique that offers a conceptual framework for transforming entropy representation into internal energy representation. It has been shown, that a counterclockwise rotation of ninety degrees in the entropy-internal energy graph, which exemplifies a concave function, will result in a transformation of internal energy-entropy as a convex function. Within the context of entropy-internal energy representation, as well as internal energy-entropy representation, it seems that rotation acts as a transformation operator relevant to the concept of thermodynamic stability.

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