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ARJ 21402.1-MS

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NONEQUILIBRIUM PHASE TRANSITIONS

Final Report

by
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JULY 1988

U. S. Army Research Office

DAAG 29-84-C-0022

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D905-10123-1

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 21402.1-MS	
6a. NAME OF PERFORMING ORGANIZATION Boeing Aerospace Co.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) P.O. Box 24969 Seattle, WA 98124-6269		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-84-C-0022	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Nonequilibrium Phase Transitions			
12. PERSONAL AUTHOR(S) Paul H. Lindenmeyer			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 10/1/84 TO 9/30/88	14. DATE OF REPORT (Year, Month, Day) July 1988	15. PAGE COUNT 66
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Nonequilibrium Phase Transitions, Polymeric Materials, Polymer Solidification, Thermodynamic Systems, Polymers, Phase Transitions	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A novel approach to a nonlinear nonequilibrium thermodynamics has been developed which predicts that the morphological structure and consequently the physical properties of polymeric materials might be controlled by dynamically fluctuating the external thermodynamic and/or pseudo-thermodynamic variables; measuring the response of the system to such fluctuations; and using this information to control the time evolution of the thermodynamic system. This report deals with the further development of the theoretical approach and with attempts to verify the basic concepts involved.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

Abstract

An experimentally based nonlinear thermodynamics is proposed in which time and distance are introduced in a novel way as experimentally measured quantities rather than assumed balance equations. A time scale is introduced experimentally as the period of one or more dynamically fluctuating environmental parameters. A distance scale is introduced experimentally as the distance between measuring sensors. Dynamic power is applied during the solidification phase transition as a means of independently controlling the elastic properties and the dissipative properties.

The elastic properties of solid materials are determined by the state variables (*i.e.*, temperature, pressure and composition). The inelastic or dissipative properties are determined by the integral over time and space of the rate variables (*i.e.*, the gradients and time rate of change of the state variables). Independent control of both the average state variables and the average rate variables by the application of controlled dynamic power should be possible. In other words one could use this means to independently control both the elastic properties (*e.g.*, moduli, hardness, *etc.*) and the dissipative properties (*e.g.*, toughness, damping, *etc.*). Since the elastic properties determine the force required to deform a material and the dissipative properties determine how much deformation can occur before catastrophic failure, the ultimate strength and deformation depend upon both. Independent control of the state and the rate variables during solidification should permit an optimum balance of properties seldom achieved without such control.

The theoretical development suggests replacing the concept of entropy with the concept of an excess energy. The excess energy of a nonequilibrium system — defined mathematically as the total Legendre transform of energy with respect to an independent set of extensive properties — plays the same role in nonequilibrium thermodynamics as do the free energy functions (*i.e.*, partial Legendre transforms) in equilibrium thermodynamics. The partial Legendre transforms are functions of the (average) thermodynamic parameters whereas the total Legendre transform or excess energy is a functional or integral over both time and space of the gradients and the time rate of change of the thermodynamic and pseudo-thermodynamic parameters. We note that at equilibrium there is no significant fluctuation about the average value of a thermodynamic parameter in either time or space so that the excess energy vanishes.

There exists an abundance of information that is qualitatively in agreement with the basic concepts expressed in this theoretical approach. However, there are as yet no quantitative data since the concept of an excess energy is still generally unknown in the field.

For	
GI	
Unpublished	☒
Justification	☐
Pv	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Forward

Polymeric materials are already important in the construction of equipment used by the Army. Such materials are almost certain to continue to play an increasingly important role as it becomes possible to substitute lighter weight, corrosion resistant polymer and polymer composite materials for more and more applications that presently require metals.

Theoretical calculations of the ultimate properties potentially available to polymer materials greatly exceed those which have been obtained in practice. Only in a few exceptional cases has the ultimate strength and modulus approached to within even an order of magnitude of the theoretical values. These exceptional cases serve to verify the correctness of the theoretical estimates and clearly indicate that substantial improvement in polymer properties is at least theoretically possible. How to achieve these theoretical possibilities in practice represents an important challenge.

We suggest that the principal difficulty lies in our lack of understanding of the basic thermodynamics of polymer solidification as well as other phase transitions. The time and distance scales applicable to phase transitions in polymer molecules are 3 to 6 orders of magnitude larger than those applicable to metals, ceramics and other common materials. *Thus, transitions in these materials occur very far from an equilibrium based upon the more usual time and distance scales.*

We have developed a novel approach to a nonlinear nonequilibrium thermodynamics which predicts that the morphological structure and consequently the physical properties of polymeric materials might be controlled by dynamically fluctuating the external thermodynamic and/or pseudo-thermodynamic variables; measuring the response of the system to such fluctuations; and using this information to control the time evolution of the thermodynamic system.

This report deals with the further development of the theoretical approach and with attempts to verify the basic concepts involved.

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Statement of Problem

The strength and modulus of polymeric materials falls far short of theoretical estimates of their ultimate potential. Realization of even a modest fraction of this potential would substantially increase the use of these materials and enhance the performance of the Army's mission.

The solidification process and other phase transitions in polymeric materials differs markedly from similar transitions in other materials. This difference is attributed to the fact that these transitions occur very far from the state of equilibrium as it is usually defined. Present theories of thermodynamics are based upon equilibrium where one can assume a linear or first order thermodynamics. Under these conditions the state of the system at any point in time is completely determined by its composition and the environmental conditions at that time. In other words, according to these theories, the state of the system at any point in time must be independent of the path or history of the way the system approached that state.

Even with the more usual metallic or ceramic materials such equilibrium thermodynamic theories are inadequate to completely describe materials properties. However, the behavior of these materials is usually "close enough" to equilibrium so that their properties differ from equilibrium properties by amounts that can easily be related to equilibrium properties. Carrying out the transition slower and slower causes these properties to approach the equilibrium properties along a single path that is experimentally possible to determine.

In contrast with this, the solidification of polymeric materials occurs so far from equilibrium that the approach to equilibrium may occur along multiple paths. Consequently, a theoretical description of such processes requires a nonlinear thermodynamics in which the state of the system is dependent upon the path by which it approaches that state.

That the properties of polymeric materials are dependent upon the history of their processing conditions is well known to every polymer technologist. What is not generally realized is that linear thermodynamic theory along with simple kinetics does not form an adequate basis for even qualitative reasoning. Experimental correlation of structure — processing — property relationships can only produce generalities because there exist no means of quantitatively determining which of several multiple paths the system may be following.

What is required is a new approach to a theory which introduces time and space into thermodynamics in a manner that is experimentally measurable. Such an approach should permit the development of a nonlinear thermodynamics which combines the usual

thermodynamics with kinetics and is truly dynamic. We believe we have discovered at least the basis for such a thermodynamics. This report covers both its theoretical development and attempts to experimentally confirm its basic concepts.

Summary of Results

We have developed an approach to an experimentally based nonlinear thermodynamics in which the time scale is introduced experimentally by dynamically fluctuating one or more environmental variables with a controlled frequency. The distance scale is introduced experimentally by the distance between measuring devices. Dynamic power is applied during solidification by fluctuating one or more thermodynamic variables (*e.g.*, temperature, pressure, *etc.*) or pseudo-thermodynamic variables (*e.g.*, stress, electrical fields, *etc.*). Modern microprocessor control of the amplitude and frequency of these fluctuations makes it possible to control independently both the average environmental parameter and its rate of change with both time and distance.

The theoretical development suggests replacing the concept of entropy with the concept of an excess energy. The excess energy of a system — defined mathematically as the total Legendre transform of energy with respect to an independent set of extensive properties — plays the same role in non equilibrium thermodynamics as the free energy functions (*i.e.*, partial Legendre transforms) do in equilibrium thermodynamics. The partial Legendre transforms are functions of the (average) thermodynamic parameters whereas the total Legendre transform or excess energy is a functional or integral over time and space of the gradients and time rate of change of the thermodynamic and pseudo-thermodynamic parameters. At an equilibrium state there is no significant fluctuation about the average values of a thermodynamic parameter in either time or space so that the excess energy vanishes.

The elastic properties of solid materials are determined by the state variables (*i.e.*, temperature, pressure and composition). The inelastic or dissipative properties are determined by the integral over time and space of the rate variables (*i.e.*, the gradients and time rate of change of the state variables). Independent control of both the average state variables and the average rate variables by the application of controlled dynamic power should be possible. In other words one could use this means to independently control both the elastic properties (*e.g.*, moduli, hardness, *etc.*) and the dissipative properties (*e.g.*, toughness, damping, *etc.*). Since the elastic properties determine the force required to deform a material and the dissipative properties determine how much deformation can occur before catastrophic failure, the ultimate strength and deformation depend upon both. Independent control of the state and the rate variables during solidification should permit an

optimum balance of properties seldom achieved without such control.

There exists an abundance of information that is qualitatively in agreement with the basic concepts expressed in this theoretical approach. However, there are as yet no quantitative data. Cyclic fluctuation of temperature and or pressure have been used to empirically modify physical properties but no one has attempted to use these fluctuations to quantitatively measure a change in excess energy. (This is not surprising since the concept of an excess energy is still generally unknown in the field).

In an attempt to provide such quantitative verification, the Dynamic Differential Calorimeter (DDC), described in the experimental section of this report, was designed and constructed. Unfortunately, unexpected difficulties encountered in programming the operation of this instrument so delayed its testing that quantitative verification of this theory is still not available.

Theoretical Development

All other approaches to nonequilibrium thermodynamics are based upon the assumption of local equilibrium in order to preserve the concept of entropy that can only be rigorously defined at equilibrium. The single except to this is the approach of Lavenda⁵ which is based upon a macroscopic balance of power and assumes that the concept of entropy is (*sec*) "not in need of definition or existence of proof". The second law is then introduced as an inequality, that is to say the change in entropy in an isolated system, is always positive. Time and distance are introduced into thermodynamics by means of balance equations containing both a flow and a source term for non conservative quantities such as entropy. Since entropy change must always be positive this source term is called entropy production.

The difficulty with the assumption of local equilibrium is not that it isn't valid and thus useful in many cases, but that there exists no way to determine the limits of its validity and find the cases where it doesn't apply. In nonequilibrium thermodynamics the problem is not so much with the concept of entropy as with its time rate of change or entropy production. Entropy production has the dimensions of power (i.e. force times velocity) and is given by the sum of the product of all the forces times their conjugate flows or fluxes.

In our earlier work we followed Glansdorff and Prigogine's universal evolution criterion which requires the system to always evolve in a manner that minimizes the forces and leads to the well known principle of "minimum entropy production". Since that time we have become acquainted with the work of Ziegler⁶ who reached what at first appears to be the

opposite conclusion - namely the principle of "maximal rate of entropy production" (*sec.*). After considerable effort in attempting to unravel this apparent contradiction and to determine the difference between entropy production and rate of entropy production, we have concluded that this is not the source of the apparent contradiction.

The situation is analogous to that which occurs in defining equilibrium. If the energy of a system is held constant it evolves to a state of maximum entropy. If the entropy is held constant (never mind how this might be accomplished) the system evolves to a state of minimum energy. In practice what is required, is to define the appropriate partial Legendre transform or free energy function whose minimization provides the optimal balance between minimizing energy and maximizing entropy.

In the evolution of a system to a steady state one has the possibility of holding the fluxes constant, in which case the forces take on their minimum value and the system evolves to a steady state of minimum entropy production *a la* Prigogine. Alternatively, one can hold the forces constant in which case the fluxes take on their maximum values and one has a maximal rate of entropy production *a la* Ziegler. Both cases are equally correct. In actual practice one has neither constant forces or constant fluxes and the entropy concept becomes inadequate to describe a dynamically changing situation. Where both the forces and the fluxes are allowed to vary one requires an appropriate function, in this case a functional, that maintains the proper balance between forces and fluxes. Just as evolution to equilibrium is controlled by the minimization of the appropriate free energy function or partial Legendre transform, we propose to show that evolution to a steady state involves the minimization of the total Legendre transform or free energy functional of a nonequilibrium system. We have called this total Legendre transform the excess energy.^{3,4}

The Mythical State of Equilibrium

Equilibrium represent the only condition under which entropy can be rigorously defined. But the state of equilibrium itself has considerably more ambiguity that is generally recognized. A system at equilibrium is both time independent and homogeneous (or at least is composed of a limited number of homogeneous phases). However, the definition of both time independence and homogeneity are relative to the time and distance scales of the observer³. Consequently, equilibrium is a mythical state that can only be operationally defined in terms of the time and distance scales of a particular observer. This is the reason that equilibrium concepts can be used by both particle physicists and cosmologists whose time and distance scales can differ by as much as 30 orders of magnitude.

In all other approaches to a nonequilibrium thermodynamics the assumption is made that there exists a region surrounding every point in space that is both large enough so that it contains sufficient particles to suppress the statistical fluctuations and thus permit one to apply thermodynamics, yet at the same time small enough to permit one to neglect any gradients or spacial fluctuations across this region.

In any truly dynamic theory one must also make the assumption, although it is almost never stated explicitly, that there exists an interval of time surrounding each point in time that is long enough to permit sufficient interaction between the particles to reach their equilibrium configuration, yet short enough to make any changes in the overall properties of the system negligible.

Only when both of these assumptions are valid can one make the assumption of local equilibrium and express the thermodynamic properties of the system as continuous functions of space and time.

The principal weakness of theories based upon local equilibrium is that they have no possibility of defining the limit of their applicability⁵. As long as one makes only implicit assumptions about the existence of regions large enough to meet one criterion yet small enough to meet another it becomes impossible to determine when the system no longer meet these criteria.

In many materials, subjected to sufficiently mild external forces, these assumptions have been shown to be valid⁶. When they are, one has the very successful linear nonequilibrium thermodynamics. However, we have shown, see appendix A, that for all polymeric materials and for many extreme external conditions the assumption of local equilibrium is not valid, at least not for the time and distance scales that are usually implicitly assumed. It is our contention that the way out of this dilemma is make explicit rather than implicit definition of the time and distance scales. The region in space and the interval of time can be made explicit by making measurements which actually average over both a volume in space determined by the distance scale and an interval of time defined by a time scale.

The definition of explicit time and distance scales has another practical advantage. It serves to clearly and explicitly define the state of equilibrium which can only be defined operationally for a given set of time and distance scales. A system is at equilibrium for a given time scale when it does not change by a measurable amount over that interval of time and for a given distance scale when it is homogeneous over that distance.

Averaging over space is equivalent to an old technique called "coarse graining" although

one seldom actually carries out any averaging. The question of "coarse graining " time has apparently never been considered since everyone seems to be looking only for a steady state or a time independent solution. But the measurement of time is several orders of magnitude more sensitive than the measurement of distance and one can easily carry out the averaging techniques that might be required. By explicitly defining time and distance scales over which we, the observers, choose to average, we can pin down once and for all the ambiguity of this mythical state of equilibrium.

Mathematical Development

In order to develop a concept which can adequately describe the situation in many processes sufficiently far from equilibrium, we begin by expressing the internal energy of the system as a function, in general a nonlinear function, of a set of independent extensive variables, α_i .

$$E = E (\alpha_i) \quad (1)$$

We next take the total Legendre transform of this energy.

$$\mathcal{E} = E - \sum_i^N \frac{\partial E}{\partial \alpha_i} \alpha_i$$

This transformation has the effect of a change of variables from the extensive variables, α_i , which all have the dimensions of volume, to the intensive variables which have the dimensions of stress or specific energy density. It can be shown that this change in variables can always be accomplished unless (1) energy is a linear function of the α_i , or (2) the $\partial E / \partial \alpha_i$ do not constitute an independent set of variables.

We next rearrange the right hand side of this equation by including the total internal energy under the summation sign. This requires what amounts to an equipartition of the energy between each of the i components associated with the α_i extensive variables.

$$\mathcal{E} = \sum_i^N \left(\frac{E}{N\alpha_i} - \frac{\partial E}{\partial \alpha_i} \right) \alpha_i = \sum_i^N \xi_i \alpha_i \quad (3)$$

This in effect gives us a compound intensive variable,

$$\xi_i = \left(\frac{E}{N\alpha_i} - \frac{\partial E}{\partial \alpha_i} \right)$$

which is composed of the difference between an integral and a differentially defined intensive variable or stress.

$$E/N\alpha_i = \text{Integral stress (space averaged)} \quad (5)$$

$$\partial E/\partial \alpha_i = \text{Differential stress (time averaged)} \quad (6)$$

The first or integral stress represents a stress averaged over the volume used to define E and the α_i at some instant of time. The second or differential stress represents a stress averaged over the interval of time used to define the $\partial E/\partial \alpha_i$ at some point in space within the system. By specifying the distance scale used to determine the volume necessary to define E and α_i and the time interval over which the $\partial E/\partial \alpha_i$ are taken we have effectively introduced time and space into our thermodynamics.

We note that if the system is sufficiently homogeneous over the volume determined by the distance scale and sufficiently independent of time over the interval of time represented by the time scale, then the compound intensive variables, ξ_i , become negligible small and the total Legendre transform, $\mathcal{E}$, vanishes. Since this condition represents the operationally defined equilibrium for the given time and distance scales, it follows that,

$$\xi = \sum_i^N \xi_i = \text{Local displacement from equilibrium} \quad (7)$$

That is to say "local" with respect to the volume defined by the distance scale and over the

time interval defined by the time scale. Integrating this local displacement over the total volume of the system yields

$$\mathcal{E} = \int_0^{V_0} \xi \, dV = \text{Global displacement from equilibrium} \quad (8)$$

Thus, our excess energy represents the displacement of the total system from the state of equilibrium defined by an explicitly assumed time and distance scales.

In order to obtain a more general expression of the change in excess energy of the total system as a function of time we must differentiate equation (8) with respect to time and then integrate over some arbitrary period of time to obtain the desired functional

$$\Delta \mathcal{E} = \int_0^{V_0} \int_{t_0}^t \dot{\xi} \, dV dt = \int_0^{V_0} \int_{t_0}^t \left[\frac{\partial \xi}{\partial t} + \nabla \xi \cdot \mathbf{v} \right] dv dt \quad (9)$$

Where $\mathbf{v}$ is the barycentric velocity of the net motion of mass. We suggest that the system will always evolve in a manner that tends to minimize the change in this displacement from equilibrium subject only to the requirement that it must always maintain a balance of power with the environment. That is to say the first law of thermodynamics must always be obeyed at any instant of time.

The Second Law of Thermodynamics

In the preceding section we pointed out that the α_i must be an independent set. This precludes the use of entropy as one of the extensive properties since the partial of energy with respect to entropy, that is to say temperature, is not independent of the pressure and the chemical potential.

The principle reason for retaining the concept of entropy, in spite of all its short comings, is in order to enunciate the second law of thermodynamics. Science has held onto this concept of entropy even though it has required extending the boundaries of a thermodynamic system to the point where accurate measurements can no longer be made (i.e., to include the environment or the whole Universe if necessary). We suggest that:

"It is the dissipation of energy within the system of interest — not the increase in entropy in the whole Universe — that represents the practical embodiment of the second law".

Energy is dissipated whenever energy is flowing into, out of, or through a system as well as whenever it is transformed from one form to another. The time evolution of a system will depend only upon the energy dissipated within the system that is not compensated by work done or energy flow to or from the environment as required by conditions on the boundaries of the system. That is to say by the power balance requirement of the first law. In other words it is only the uncompensated dissipation of energy within the system that determines its evolution.

We now define the dissipation of energy as the change in excess energy or total Legendre transform which allows us to reformulate the second law of thermodynamics as the following variational principle:

"Any system, arbitrarily far from equilibrium, whether open, closed or isolated, will evolve with time in a manner that minimizes its change in excess energy integrated over any time and any volume"

Mathematically, this requires the minimization of the excess energy functional as given in equation (9).

Formulation of the second law of thermodynamics as the minimization of a functional has the added advantage of providing the stability criteria for a nonequilibrium system. The calculus of variations tell us that in order for the excess energy to be a minimum it is necessary that its first variation vanish,

$$\delta \mathcal{E} = 0$$

and its second variation be positive or zero

$$\delta^2 \mathcal{E} \geq 0$$

If the second variation becomes negative

$$\delta^2 \mathcal{E} < 0$$

the system becomes unstable and can bifurcate into two or more subsystems that do not exchange mass or energy with each other and thus will evolve independently.

The expression of the second law as a variational principle can have a very practical consequence if one considers nonequilibrium thermodynamics as an experimental science rather than a theoretical one.

Experimental Nonequilibrium Thermodynamics

In experimental equilibrium thermodynamics one makes static measurements on the surface of two thermodynamic systems presumed to be at equilibrium. From these measurements one can calculate the thermodynamic properties of the two systems when they are brought in contact with each other and allowed time to again reach equilibrium. In practice, one of these systems, called the environment is presumed to be so much larger than the other so that any changes in its properties are negligible.

In an exactly analogous manner we suggest that one can develop an experimentally based nonequilibrium thermodynamics, actually a true thermodynamics, in contrast to the description in the preceding paragraph which is really thermostatics. In this thermodynamics the properties of the environment are driven to fluctuate about their average values in either or both time and location in space. The response of the system of interest to this fluctuation of the environment or boundary conditions can be measured both as a function of time and location in space. The time and distance scales are explicitly defined by the frequency of the fluctuation and the distance between the measuring sensors.

One can experimentally measure the variation of a functional in much the same way that one experimentally measures the differential of a function. With a function one increments the variables by a sufficient amount to cause a measurable change in the function. In a functional the variables are integrated between fixed limits. Consequently, it is necessary to cycle the variables rather than increment them. The excess energy functional, equation (9), is integrated over both time and space. If we cycle the environmental variables over a range of values in either or both time and space, we can measure the response of the system to this variation and obtain both a time and a space average.

The difference between these averages is a measure of the displacement of the system from the equilibrium operationally defined by the time and distance scales used in taking these averages. If there is no measurable difference between the space average and the time average, we must increase the amplitude of the fluctuation (i.e., increase the power) until one detects such a difference. Clearly, this will not occur unless or until one reaches a

power level where the response is sufficiently nonlinear. A linear response to the application of dynamic power will produce no difference between the time and the space averages.

Dynamic Power

Both entropy production and the dissipation of energy have the dimensions of power. In fact in an isolated system they are essentially identical. Entropy production decreases to zero as entropy reaches its maximum at equilibrium whereas the dissipation of energy goes to zero as the excess energy vanishes at equilibrium. In a system that is not isolated the dissipation of energy always approaches the minimum value required to satisfy the first law which requires a balance of power at the boundaries of the system. On the other hand, as we have already shown, entropy production can approach either a maximum or a minimum or any value in between, depending upon the nature of the boundary conditions.

Clearly, the time evolution of a nonisolated thermodynamic system is dependent upon exactly how power is applied to the boundaries of the system. Thus, power is the *sine quo non* of nonequilibrium thermodynamics and one must recognize that alternating or dynamic power can be applied without changing the average value of the usual thermodynamic parameters.

Experimental

The initial effort on this program was directed toward improving the mechanical properties of composite materials by the application of dynamic mechanical power. This was considered a reasonable choice since it is the mechanical properties of polymeric materials that, at least theoretically, offer the greatest potential for improvement. In addition commercial apparatus in the form of the hydraulic MTS tester and the Dynastat dynamic mechanical spectrometer were available for the application of dynamic stress.

This turned out to be a poor choice for at least two reasons. First, the scope of this program was too small to demand the dedicated use of either of these instruments. Second, the application of sufficient dynamic power to reach the region of nonlinear response required for this program, brings the system very close to the point of catastrophic failure. Thus, it proved to be impractical to apply sufficient dynamic power without at the same time having available the necessary real time analytical equipment and feedback control to prevent catastrophic failure. For these and other reasons it was decided, after the first year and one half of effort, to abandon dynamic mechanical power and to concentrate on thermodynamics even though the ultimate goal is still to use mechanical fluctuations when

sufficient controls are possible. See, for example, the schematic proposal in Figure 1 of Appendix B .

Consequently, it was decided to build the world's first Dynamic Differential Calorimeter as initially conceived by the principal investigator⁸. This instrument was designed and constructed by Dr. H. Weber-Annler of Bionik in Switzerland in conjunction with the principal investigator. It's design and construction are described in the report by Dr. Weber in appendix E.

The Dynamic Differential Calorimeter

The dynamic differential calorimeter (DDC), differs from the usual differential scanning calorimeter (DSC) in a number of ways. First, the specimen is not limited to a few milligrams of material as in the DSC. Secondly the thermal gradient across the specimen is subject to direct control of the experimenter. We note that even in the DSC there must always be a thermal gradient across the specimen in order to provide the flow of heat necessary to measure a differential temperature. This is the reason that the sample is restricted to a few milligrams so that this gradient will be negligible small. The gradient determines the rate of flow of heat through the specimen and consequently the sensitivity of the measurement. In the DSC, the gradient is determined indirectly by the scanning rate as the temperature of the environment is changed. In the DDC the gradient is independently controlled by means of the environmental temperature on either side of the specimen and the gradient is directly measured by the difference in temperature across the specimen. Using the difference between the average environmental temperature and the average sample temperature one can operate the DDC in exactly the same manner as the DSC with the advantage of having independent control of the sensitivity by means of both the sample size and the gradient across it.

However, the most important difference between the DDC and the DSC is the provision for reversing the temperature gradient imposed on the specimen with a controlled frequency without changing the average environmental temperature. This makes it possible to hold the space averaged environmental temperature constant and to measure the specimen temperature averaged over the period of the reversing frequency. The difference between the space averaged temperature and the time averaged temperature of the specimen is a measure of the change in the deviation of the system from equilibrium measured by an explicitly defined time and distance scale. The time scale is the period of the reversing frequency and the distance scale is the thickness of the specimen.

Unfortunately, a series of experimental difficulties and the unexpected difficulty in programming the microprocessor delayed the obtaining of more than a single preliminary

experimental run. The software written for the DDC is detailed in Appendix F.

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POLYMERIC PHASE TRANSITIONS UNDER EQUILIBRIUM CONDITIONS

or
(The myth of the infinite polymer chain)

by
Paul H. Lindenmeyer

Equilibrium thermodynamics has long provided the theoretical basis for understanding the behavior of polymer molecules in solution and to a lesser extent also in melts. However, the wide variety of polymer morphologies observable in crystallizable polymer solids have made strict thermodynamic explanations almost completely untenable. Nevertheless, the tacit assumption is still generally made that the transition to the solid state follows a single path from liquid to equilibrium solid and that progress along this path is interrupted and frozen at various "metastable" equilibrium states by the kinetics of solidification. If this were indeed the case then it should be possible to arrange all the observed polymer morphologies on a straight line with the random frozen liquid or glassy polymer at one end and the perfect equilibrium extended chain crystal at the other. After having spent many years attempting to do just that, I have been forced to the conclusion that this is not possible. The solidification process can follow a number of possible paths from liquid to solid. This by itself will not be surprising to most investigators. What may be surprising is the conclusion that equilibrium crystallization or even a "quasi-static" process is not one of the possible paths that polymer solidification may take.

Experimentally, it is well known that the solidification of polymeric materials cannot be observed to occur reversibly in the time frame of ordinary laboratory operations. For example, Flory and Chiang¹ crystallized a polyethylene fraction for over 3 weeks at 131.3°C, only to find that the last crystalline portion to melt required heating to 137.7°C, which is still significantly below the theoretical melting point of an infinite chain, (*i.e.*, 145°C). This effect is usually attributed to the kinetics of nucleation, and kinetic models have been proposed that fit the observed data (*e.g.*, Hoffman *et al.*²). However, kinetic models are not unique³, and alternate assumptions concerning the nature of the fold surface (*e.g.*, Mandelkern *et al.*⁴) also can be made to fit the kinetic data. Thus, it is unlikely that kinetics by itself can either resolve the nature of the fold surface or provide a satisfactory theoretical reason why solidification is always observed as an irreversible process so far from equilibrium.

The purpose of this paper is to provide a theoretical reason why polymeric phase transitions always occur by an irreversible process significantly far from equilibrium. Clearly, such processes will require a nonequilibrium thermodynamics for their complete explanation. Such theories are still controversial⁵ and our own approach to this subject is not yet complete and will not be described here. What we shall attempt is to provide a clear reason for the requirement of a nonequilibrium thermodynamics in explaining all kinds of polymeric phase transitions. As we shall see, this reason not only provides specific information about the behavior of polymer molecules but also may lead to important advances in nonequilibrium thermodynamics in general.

The conformational entropy of a single polymer molecule is a nonlinear function of the number of segments that are free to assume different conformations. In the language of solid state physics a polymer molecule may be said to have a very highly degenerate ground state in the liquid. In order to transform to a solid under equilibrium conditions it must lose this

conformational entropy at a temperature which makes it the exact equivalent of the loss in enthalpy (i.e., the latent heat of crystallization). But the conformational entropy of a polymer molecule undergoing a phase transition is a nonlinear function of the number of segments that have already undergone the transition, whereas the enthalpy change is a linear function. Consequently, a polymer molecule cannot undergo a phase transition with zero change in free energy unless it does so with no change in conformation. This is the fundamental reason why polymer molecules fold⁶. Phase transitions in polymers must occur at temperatures which provide a significant decrease in free energy. Consequently, they are not reversible^{7,8} regardless of how slowly they may be carried out. To be specific, we shall discuss only the liquid - solid transition, but the theoretical reasons that we shall use are more generally applicable.

The fact that conformational entropy is a nonlinear function of chain length has long been recognized, but its significance with regard to phase transitions has been missed, probably because the remarkable success of linear (i.e., Gibbsian) thermodynamics has blurred the assumptions upon which this thermodynamics is based. The Gibbs equation is based upon the assumption that the energy of a system is a linear homogeneous function of size and is independent of time. But both homogeneity and time independence are relative terms which depend upon the time and distance scales adopted by a particular observer⁹. Thus, whether or not the Gibbs equation is valid depends at least to some extent upon the needs of a particular observer and the time and distance scales which he has adopted.

If the Gibbs assumptions are valid, (for a particular observers time and distance scales), the total Legendre transform of energy vanishes. This yields the Gibbs-Duhem equation which provides a relationship between the extensive variables that makes it possible to solve for one of them (usually volume or mass) and to use it as a scale factor for expressing the thermodynamic potentials as densities or specific quantities¹⁰. When energy cannot be assumed to be a linear homogeneous function of size, the total Legendre transform does not vanish and consequently there is no Gibbs-Duhem relationship to provide a scale factor. Thus, expressing the thermodynamic potentials as densities or specific quantities is not theoretically justifiable. This has not stopped their use since one can simply assume the existence of a suitable region (the ubiquitous "unit volume" or "unit mass") without ever defining it. Now as long as such units are not defined their use amounts to an additional assumption that in those units energy is indeed a linear homogeneous function and independent of time.

However, in the case of a polymer molecule the "unit segment" is a defined unit and it is in the use of this unit that one encounters difficulties. The free energy change per segment for the solidification of an infinite chain is frequently expressed as:

$$\Delta F(\infty) = \Delta H_c^\circ (T_m^\circ - T)/T_m^\circ \quad \text{eqn 1}$$

This equation is based upon the assumption that "sufficiently" close to equilibrium, the entropy change upon crystallization is approximately equal to its value at equilibrium. (i.e., $\Delta S^\circ = \Delta H_c^\circ / T_m^\circ$) where T_m° is the equilibrium melting point of an infinite chain and ΔH_c° is minus the equilibrium enthalpy of fusion. If we wish to obtain an expression for the free energy change of a finite molecule with X segments, we must multiply equation (1) by X and add a term to correct for the increase in entropy of a finite length chain.

$$X \Delta F(\infty) = X H_c^\circ (T_m^\circ - T)/T_m^\circ + kT \ln X \quad \text{eqn 2}$$

The additional term may be justified by picturing the infinite chain to be joined at + and - infinity and evenly divisible by X. Then for each conformation of the infinite chain, there are exactly X different ways of dividing it into finite molecules of length X. The $kT \ln X$ term represents a nonlinear contribution to the conformational entropy of a polymer molecule with X segments over that of an infinite chain.

There are a number of other factors that can contribute to the nonlinearity of conformational entropy of polymer chains. For example, if a polymer molecule is in the neighborhood of a surface that it cannot penetrate, its conformational entropy is decreased and this decrease is also a nonlinear function of the number of segments. This effect, first pointed out by Zachmann¹¹, has more recently been extensively investigated in a number of other cases that have become collectively known as the "confined chain" problem¹².

At this point, most authors make the tacit assumption that linear (i.e., Gibbsian) thermodynamics is applicable and they divide equation (2) by X to obtain the specific free energy change or the free energy per segment of a finite chain of length X.

$$\Delta F(X) = H^{\circ}_c (T^{\circ}_m - T)/T^{\circ}_m + (kT \ln X)/X \quad \text{eqn 3}$$

Now the second term can easily be seen to become negligibly small as soon as the length of the molecule exceeds a few hundred segments. Consequently, the fact that conformational entropy is a nonlinear function of chain length -- although long recognized -- has generally been assumed to be of negligible importance because most polymers molecules are long enough to be considered infinite by equation (3). This is the origin of what I now call the "myth" of the infinite polymer chain so often used by polymer theorists.

The division of equation (2) is not justifiable because it cannot be assumed that the nonlinear conformational entropy can be uniformly distributed among all the segments of the molecule. In other words, the linear thermodynamics of Gibbs is not applicable to a single polymer molecule, as has been amply demonstrated by Hill¹³. One must take explicit account of the fact that the total Legendre transform of energy (which Hill represents as $\mathcal{E}$) does not vanish, there is no Gibbs-Duhem relationship to provide a scale factor, and the change in the nonlinear contribution, $\mathcal{E}$, which we have called excess energy, must be added to the change in the appropriate free energy function.

Even if one has an extremely long molecule one cannot consider it infinite when it is involved in a phase transition. Physically, this is easy to see if one recognizes that a polymer molecule, except under very unusual conditions, cannot undergo a phase transition as a single unit but must do so one segment at a time. Thus, the time must come when the number of segments free to assume various conformations is clearly finite. Since the conformational entropy is a nonlinear function of the number of these segments and enthalpy is a linear function, it follows that solidification can never occur with a zero change in free energy. Only when the polymer molecule has a reasonable probability of occupying the same conformation in both phases can the transition occur with no change in free energy, that is to say under equilibrium conditions.

Imagine a perfect, extended chain crystal in contact with a solution or melt at the equilibrium solidification temperature. How long would one expect to wait before a liquid molecule would happen to assume a completely extended chain conformation? Even assuming a perfect "hole" in the crystal so that no additional surface energy would be required, the probability is so low as to be impossible in any reasonable time. Thus, equilibrium (i.e., reversible) transitions

are essentially forbidden to all polymer molecules in the time frame of ordinary laboratory operations because of the nonlinearity of conformational entropy change with the number of segments that have undergone the transition.

By assuming that all polymer molecules with more than a few hundred segments may be treated as infinite, we perpetuate this "myth" of an infinite chain and ignore the necessity of developing and applying the nonlinear thermodynamics of small systems¹³. As long as we deal only with linear thermodynamics, it is possible to clearly separate kinetics and thermodynamics. By this separation, we have reduced thermodynamics to a science that is properly called "thermostatistics" and we have relegated kinetics to a empirical science.

In our first paragraph we concluded that polymer solidification can follow many different paths. Which path it follows will depend upon the nature of both the external physical and thermodynamic forces applied to the system. Any theory which attempts to predict these paths must go beyond both equilibrium thermodynamics and linear nonequilibrium thermodynamics since these theories are path independent. No successful nonlinear thermodynamic theories have yet been proposed⁵. We believe that the reason for this lack of success lies with the concept of entropy.

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THE THERMODYNAMICS OF FIBER FORMATION

by
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This paper is a sequel to a paper presented before the Fiber Society at the New Orleans meeting and published¹ in the Textile Research Journal in 1980. In that paper we described the fiber formation process as a dissipative process using the Glansdorff and Prigogine² theory of nonequilibrium thermodynamics. In this paper we propose to reaffirm essentially all the verbal description of the fiber formation process but to provide a modified theoretical approach which we have developed in the interim.^{3,4}

Basic Fiber Formation Process

The fiber formation process is basically a steady state process that occurs very far from equilibrium or from the "quasi-static" processes that can be adequately treated with the linear thermodynamic theories that are taught in school. The situation is not unlike the one that exists in the mechanics of fluid flow beyond the point where turbulence begins. Linear thermodynamics is directly analogous to what is called potential flow in fluid mechanics. In effect, a nonlinear thermodynamic theory in which the final state of the system is dependent upon the path followed by the system in reaching that state, is clearly required in order to describe the process of fiber formation.

Glansdorff and Prigogine attempted the development of such a theory but their effort has met with both limited success and notoriety in many different fields as well as controversy among other thermodynamists.⁵ Even they describe their "Universal Evolution Criterion" as the best obtainable rather than a completely satisfactory theory. We believe that it may very well be the best obtainable criterion so long as thermodynamists retain the concept of entropy. We suggest that it is the concept of entropy that is proving to be inadequate to describe the time evolution of thermodynamic systems so far from the state of equilibrium.

In our earlier work we followed Glansdorff and Prigogine which requires the system to always evolve in a manner that minimizes the forces and leads to the well known principle of "minimum entropy production". Since that

time we have become acquainted with the work of Ziegler⁶ who reached what at first appears to be the opposite conclusion - namely the principle of "(sec.) maximal rate of entropy production". After considerable effort in attempting to unravel this apparent contradiction and to determine the difference between entropy production and rate of entropy production, we have concluded that this is not the source of the apparent contradiction.

The situation is analogous to that which occurs in defining equilibrium. If the energy of a system is held constant it evolves to a state of maximum entropy. If the entropy is held constant (never mind how this might be accomplished) the system evolves to a state of minimum energy. In practice what is required, is to define the appropriate partial Legendre transform or free energy function whose minimization provides the optimal balance between minimizing energy and maximizing entropy.

In the evolution of a system to a steady state one has the possibility of holding the fluxes constant, in which case the forces take on their minimum value and the system evolves to a steady state of minimum entropy production *a la* Prigogine. Alternatively, one can hold the forces constant in which case the fluxes take on their maximum values and one has a maximal rate of entropy production *a la* Ziegler. Both cases are equally correct. However, in the general case, where both the forces and the fluxes are allowed to vary one requires an appropriate function, in this case a functional, that maintains the proper balance between forces and fluxes. Just as evolution to equilibrium is controlled by the minimization of the appropriate free energy function or partial Legendre transform, we propose to show that evolution to a steady state involves the minimization of the total Legendre transform or free energy functional of a nonequilibrium system. We have called this total Legendre transform the excess energy.^{3,4}

In fiber spinning, mechanisms exist, in principle, for controlling either the forces or the fluxes. Usually, spinning is carried out at a fixed spinning rate in which pump speeds, windup speed and cooling or precipitating fluid flow rates are fixed. Under these conditions the fluxes are essentially constant and the forces evolve to some minimum value yielding Prigogine's minimum entropy production. However, it is possible to install constant tension windup devices and constant force pumps in which case the evolution is towards Zeigler's maximal rate of entropy production. In actual practice one has

neither perfectly constant forces or fluxes and the entropy production concept becomes an inadequate means of describing the evolution of a thermodynamic system in general and a fiber spinning process in particular.

The Mythical State of Equilibrium

Equilibrium represents the only condition under which entropy can be rigorously defined. But the state of equilibrium itself has considerably more ambiguity that is generally recognized. A system at equilibrium is both time independent and homogeneous (or at least is composed of a limited number of homogeneous phases). However, the definition of both time independence and homogeneity are relative to the time and distance scales of the observer³. Consequently, equilibrium is a mythical state that can only be operationally defined in terms of the time and distance scales of a particular observer. This is the reason that equilibrium concepts can be used by both particle physicists and cosmologists whose time and distance scales can differ by as much as 30 orders of magnitude.

In all other approaches to a nonequilibrium thermodynamics the assumption is made that there exists a region surrounding every point in space that is both large enough so that it contains sufficient particles to suppress the statistical fluctuations and thus permit one to apply thermodynamics, yet at the same time small enough to permit one to neglect any gradients or spacial fluctuations across this region.

In any truly dynamic theory one must also make the assumption, although it is almost never stated explicitly, that there exists an interval of time surrounding each point in time that is long enough to permit sufficient interaction between the particles to reach their equilibrium configuration, yet short enough to make any changes in the overall properties of the system negligible.

Only when both of these assumptions are valid can one make the assumption of local equilibrium and express the thermodynamic properties of the system as continuous functions of space and time.

The principle weakness of theories based upon local equilibrium is that they have no possibility of defining the limit of their applicability⁵. As long as one makes only implicit assumptions about the existence of regions large enough

to meet one criterion yet small enough to meet another it becomes impossible to determine when the system no longer meet these criteria.

In many materials, subjected to sufficiently mild external forces, these assumptions have been shown to be valid⁷. When they are, one has the very successful linear nonequilibrium thermodynamics. However, we have shown^{3,4} that for all polymeric materials and for many extreme external conditions the assumption of local equilibrium is not valid, at least not for the time and distance scales that are usually implicitly assumed. It is our contention that the way out of this dilemma is make explicit rather than implicit definition of the time and distance scales. The region in space and the interval of time can be made explicit by making measurements which actually average over both a volume in space determined by the distance scale and an interval of time defined by a time scale.

The definition of explicit time and distance scales has another practical advantage. It serves to clearly and explicitly define the state of equilibrium which can only be defined operationally for a given set of time and distance scales. A system is at equilibrium for a given time scale when it does not change by a measurable amount over that interval of time and for a given distance scale when it is homogeneous over that distance.

Averaging over space is equivalent to an old technique called "coarse graining" although one seldom actually carries out any averaging. The question of "coarse graining" time has apparently never been considered since everyone seems to be looking only for a steady state or a time independent solution. But the measurement of time is several orders of magnitude more sensitive than the measurement of distance and one can easily carry out the averaging techniques that might be required. By explicitly defining time and distance scales over which we, the observers, choose to average, we can pin down once and for all the ambiguity of this mythical state of equilibrium.

Theoretical Development

In order to develop a concept which can adequately describe the situation encountered in the fiber formation process and in similar processes sufficiently far from equilibrium, we begin by expressing the internal energy of the system as a function, in general a nonlinear function, of a set of

independent extensive variables, α_i .

$$E = E(\alpha_i) \quad (1)$$

We next take the total Legendre transform of this energy.

$$\mathcal{E} = E - \sum_i^N \frac{\partial E}{\partial \alpha_i} \alpha_i$$

This transformation has the effect of a change of variables from the extensive variables α_i , which all have the dimensions of volume, to the intensive variables, $\partial E / \partial \alpha_i$ which have the dimensions of stress or specific energy density. It can be shown that this change in variables can always be accomplished unless (1) energy is a strictly linear function of the α_i , or (2) the $\partial E / \partial \alpha_i$ do not constitute an independent set of variables.

We next rearrange the right hand side of this equation by including the total internal energy under the summation sign. This assumes what amounts to an equipartition of the energy between each of the i th components associated with the α_i extensive variables.

$$\mathcal{E} = \sum_i^N \left(\frac{E}{N\alpha_i} - \frac{\partial E}{\partial \alpha_i} \right) \alpha_i = \sum_i^N \xi_i \alpha_i \quad (3)$$

This, in effect, gives us a compound intensive variable,

$$\xi_i = \left(\frac{E}{N\alpha_i} - \frac{\partial E}{\partial \alpha_i} \right)$$

which is composed of the difference between an integral and a differential

intensive variable or stress.

$$E/N\alpha_i = \text{Integral stress (space averaged)} \quad (5)$$

$$\partial E/\partial \alpha_i = \text{Differential stress (time averaged)} \quad (6)$$

The first or integral stress represents the stress averaged over the volume used to define E and the α_i at some instant of time. The second or differential stress represents the stress averaged over the interval of time used to define the $\partial E/\partial \alpha_i$ at some point in space within the system. By specifying the distance scale used to determine the volume necessary to define E and α_i and the time interval over which the $\partial E/\partial \alpha_i$ are taken, we have effectively introduced time and space into our thermodynamics .

We note that if the system is sufficiently homogeneous over the volume determined by the distance scale and sufficiently independent of time over the interval of time represented by the time scale, then the compound intensive variables, ξ_i , become negligible small and the total Legendre transform, $\mathcal{E}$, vanishes. Since this condition represents the operationally defined equilibrium for the given time and distance scales, it follows that,

$$\xi = \sum_i^N \xi_i = \text{Local displacement from equilibrium} \quad (7)$$

That is to say "local" with respect to the volume defined by the distance scale and over the time interval defined by the time scale. Integrating this local displacement over the total volume of the system yields

$$\mathcal{E} = \int_0^{V_0} \xi dV = \text{Global displacement from equilibrium} \quad (8)$$

Thus, our excess energy represents the displacement of the total system from

the state of equilibrium defined by explicitly assumed time and distance scales.

In order to obtain a more general expression of the change in excess energy of the total system as a function of time we must differentiate equation (8) with respect to time and then integrate over some arbitrary period of time to obtain the desired functional.

$$\Delta \mathcal{E} = \int_0^{V_0} \int_0^t \dot{\xi} dV dt = \int_0^{V_0} \int_0^t \left[\frac{\partial \xi}{\partial t} + \nabla \xi \cdot \bar{v} \right] dV dt \quad (9)$$

Where $\bar{v}$ is the barycentric velocity of the net motion of mass. We suggest that the system will always evolve in a manner that tends to minimize this displacement from equilibrium subject only to the requirement that it must always maintain a balance of power with the environment. That is to say the first law of thermodynamics must always be obeyed at any instant of time.

The Second Law of Thermodynamics

In the preceding section we pointed out that the α_i must be an independent set. This precludes the use of entropy as one of the extensive properties since the partial of energy with respect to entropy, that is to say temperature, is not independent of the pressure and the chemical potential.

The principle reason for retaining the concept of entropy, in spite of all its short comings, is in order to enunciate the second law of thermodynamics. Science has held onto this concept even though it has required extending the boundaries of a thermodynamic system to the point where accurate measurements can no longer be made (*i.e.*, to include the environment or the whole Universe if necessary). We suggest that:

it is the dissipation of energy within the system of interest
 -- not the increase in entropy in the whole Universe -- that

represents the practical embodiment of the second law.

Energy is dissipated whenever energy is flowing into, out of, or through a system as well as whenever it is transformed from one form to another. The time evolution of a system will depend only upon the energy dissipated within the system that is not compensated by work done or energy flow to or from the environment as required by conditions on the boundaries of the system. That is to say by the power balance requirement of the first law. In other words it is only the uncompensated dissipation of energy within the system that determines its evolution.

We now define the dissipation of energy as the change in excess energy or total Legendre transform which allows us to reformulate the second law of thermodynamics as the following variational principle:

"Any system, arbitrarily far from equilibrium, whether open, closed or isolated, will evolve with time in a manner that minimizes its change in excess energy integrated over any time and any volume"

Mathematically, this requires the minimization of the excess energy functional as given in equation (9).

Formulation of the second law of thermodynamics as the minimization of a functional has the added advantage of providing the stability criteria for a nonequilibrium system. The calculus of variations tell us that in order for the excess energy to be a minimum it is necessary that its first variation vanish,

$$\delta \mathcal{E} = 0$$

and its second variation be positive or zero

$$\delta^2 \mathcal{E} \geq 0$$

If the second variation becomes negative

$$\delta^2 \mathcal{E} < 0$$

the system becomes unstable and can bifurcate into two or more subsystems that do not exchange mass or energy with each other and thus will evolve independently.

The expression of the second law as a variational principle can have a very practical consequence if one considers nonequilibrium thermodynamics as an experimental science rather than a theoretical one.

Experimental Nonequilibrium Thermodynamics

In experimental equilibrium thermodynamics one makes static measurements on the surface of two thermodynamic systems presumed to be at equilibrium. From these measurements one can calculate the thermodynamic properties of the two systems when they are brought in contact with each other and allowed time to again reach equilibrium. In practice, one of these systems, called the environment is presumed to be so much larger than the other that its change in properties are negligible.

In an exactly analogous manner we suggest that one can develop an experimentally based nonequilibrium thermodynamics, actually a true thermodynamics, in contrast to the description in the preceding paragraph which is really thermostatics. In this thermodynamics the properties of the environment are driven to fluctuate about their average values in either or both time and location in space. The response of the system of interest to this fluctuation of the environment or boundary conditions can be measured both as a function of time and location in space. The time and distance scales are explicitly defined by the frequency of the fluctuation and the distance between the measuring sensors.

One can experimentally measure the variation of a functional in much the same way that one experimentally measures the differential of a function. With a function, one increments the variables by a sufficient amount to cause a measurable change in the function. In a functional the variables are integrated between fixed limits. Consequently, it is necessary to cycle the variables rather than increment them. The excess energy functional, equation (9), is integrated over both time and space. If we cycle the environmental variables over a range of values in either or both time and space, we can measure the response of the system to this variation and obtain both a time and a space average.

The difference between these averages is a measure of the change in displacement of the system from the equilibrium operationally defined by the time and distance scales used in taking these averages. If there is no measurable difference between the space average and the time average, we must increase the amplitude of the fluctuation (*i.e.*, increase the power) until one detects such a difference. Clearly, this will not occur unless or until one reaches a power level where the response is sufficiently nonlinear. A linear response to the application of dynamic power will produce no difference between the time and the space averages.

Dynamic Power

Both entropy production and the dissipation of energy have the dimensions of power. In fact in an isolated system entropy production is equivalent to the rate of decrease in excess energy. Entropy production decreases to zero as entropy reaches its maximum at equilibrium whereas the dissipation of energy goes to zero as the excess energy vanishes at equilibrium. In a system that is not isolated the dissipation of energy always approaches the minimum value required to satisfy the first law which requires a balance of power at the boundaries of the system. On the other hand, as we have already shown, entropy production can approach either a maximum or a minimum or any value in between, depending upon the nature of the boundary conditions.

Clearly, the time evolution of a nonisolated thermodynamic system is dependent upon exactly how power is applied to the boundaries of the system. Thus, power is the *sine quo non* of nonequilibrium thermodynamics and one must recognize that alternating or dynamic power can be applied without changing the average value of the usual thermodynamic parameters.

In order to make this clear let us consider the fiber spinning process as an example. The tension (*i.e.*, force) on the threadline is intimately related to the spinning rate (*i.e.*, flux). One cannot change one without changing the other unless one changes some other variable, for example the cooling rate. Yet it is well known empirically that this ratio of force to flux will impart properties to the fiber that limit how the fiber can be further processed (*e.g.*, drawing, texturizing, *etc.*). Fiber spinning operators have long ago empirically established the balance of spinning variables that optimize the processes they are using in the production of fiber. But these operators have been restricted in the total number of variables at their command.

Once it is realized that both tension and spinning rate, like all thermodynamic or pseudo-thermodynamic parameters, are averages, it becomes possible to independently control the average tension without changing the average spinning rate. This is possible by the application of dynamic power which brings at least two and perhaps more new variables into play. First, the frequency of the dynamic power which fixes the time scale and second the amplitude of the fluctuation which determines the dynamic power. Both of these variables can be subject to adaptive control mechanisms using modern microprocessor technology. The distance scale is not as readily controlled since it is fixed by the distance between the spinnerette and the tension measured device(s).

These principles are illustrated schematically in Figure 1 which consists of a pair of tension measuring devices and a means of fluctuating the distance between them. The first of these measures the tension between the oscillating roller and the constant speed windup device, whereas the second measures the tension between the roller and the spinnerette. The thread line is the first case is solid and will respond nearly elastically to changes in tension whereas that in the second is partially molten and of variable thickness and will have a quite different response. Time and distance averages can be obtained from these two sensors and the change in excess energy calculated and fed back in real time to control both the amplitude (*i.e.*, power) and the frequency (*i.e.*, time scale).

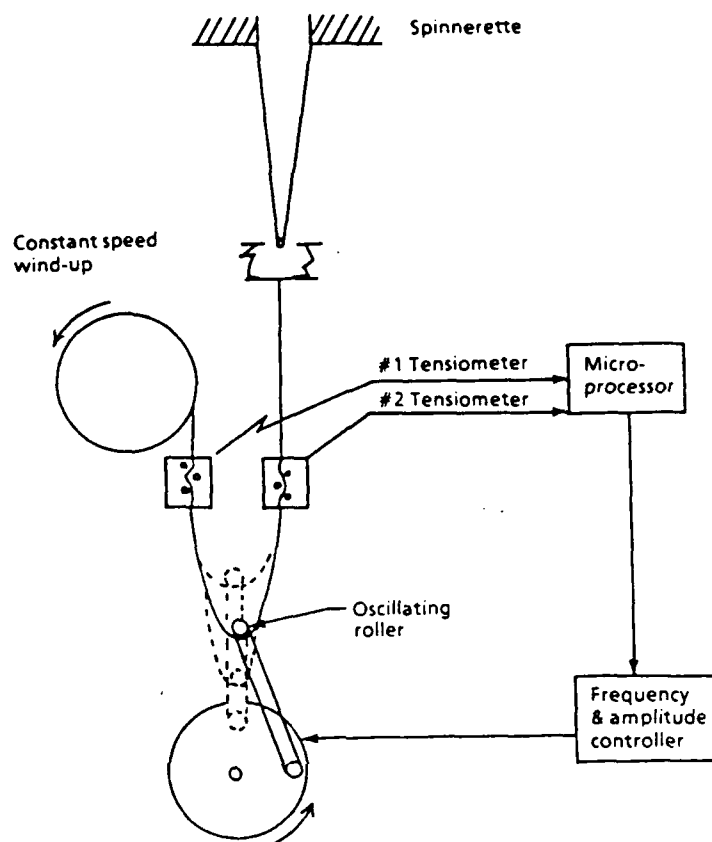
Summary and Conclusions

We have outlined an approach to a truly dynamic thermodynamics that is applicable to open, closed or isolated systems regardless of their distance from equilibrium and have illustrated this approach by the spinning of synthetic fibers. However, we suggest that it is applicable not only to any fiber forming process but also provides the overall physical thermodynamics which describes how living organisms function. The key to this thermodynamics lies in understanding how dynamic fluctuations, whether generated internally or externally, can effect the time evolution of thermodynamic systems. All higher forms of life have evolved their own internal circulating systems. It is not by chance that this system is a fluctuating system that provides the environment of each cell with a dynamically fluctuating chemical potential. Lower forms of life must make due with diurnal or seasonal fluctuations or those of some host organism.

When mankind has learned to understand and apply this thermodynamics to its manufacturing processes we predict that it will be possible to not only substantially improve fiber production but also to produce a wide variety of complex multiphase solid materials that can greatly improve their energy conversions processes.

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April 14, 1988 9:45 AM HTC/DOR 88 002s

THE EFFICIENCY OF ENERGY CONVERSION PROCESSES

By

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All living creatures are able to extract energy from their environment and to use this energy to produce useful work. The energy conversion processes used are far more efficient than anything man has yet produced. They are able to accomplish this by means of complex chemical reactions, only the most basic of which are understood and this understanding is only partial at best. The difficulty in gaining complete understanding of the chemistry involved in these energy conversion processes has prevented their use as a guide in helping man to improve the efficiency of his own commercial energy conversion processes.

The physical thermodynamic principles by which these processes are accomplished, are even less well understood since they would appear to violate the second law of thermodynamics as it is usually formulated. Only by extending the boundaries of what one calls the thermodynamic system to include enough of the environment (the entire Universe if necessary) so as to make precise measurements impossible, have Scientists been able to salvage the concept of entropy and avoid invalidating this law.

The only way that man has found to increase the efficiency of an energy transport or conversion process using the concept of entropy is to increase both the size of the system and the intensity of the driving force, (*i.e.*, the difference between the source and the sink). This, in spite of the fact that living systems clearly operate very efficiently with only modest or essentially no difference between source and sink and actually depend upon very small units, the cells, that function nearly independently.

We suggest that it is the concept of entropy that has outlived its usefulness which is preventing mankind from understanding and therefore emulating the way nature has evolved efficient energy conversion processes.

The entropy of a thermodynamic system can only be rigorously defined for an isolated system at equilibrium. This is a condition that can never be equally rigorously obtained experimentally. There will always be some temperature fluctuation and hence some heat flow, at least locally. It is true that textbooks on statistical thermodynamics can clearly show that fluctuations about the average value due to the inherent atomic and molecular motion at ordinary temperatures are negligibly small. However, this conclusion is only true when the system is "large enough" and "close enough" to being at equilibrium. But

equilibrium itself can only be defined operationally in terms of the time and distance scales adopted by a particular observer, either implicitly or explicitly. Thus, it is equally true that if the system is small enough and/or is subjected to sufficiently large changing or nonuniform boundary conditions, such fluctuations cannot be neglected, but actually provide the means of driving the system to new and quite different states.

All living systems make use of fluctuations, either those generated by their own internal circulating system, those provided by some host organism, or simply the diurnal and seasonal fluctuations of their environment.

Subjecting a system to boundary conditions that vary in both time and space can cause energy and/or mass to flow into or out of the system. According to our formulation of the second law of thermodynamics^{1,2}, the system will respond to this flow of mass and energy in a manner that always minimizes the uncompensated dissipation of energy. As long as the flow of energy (e.g., heat) is sufficiently close to being parallel to the net motion of mass (i.e., the barycentric velocity) the time evolution of the system can be described by a scalar potential. That is to say there is only one single state of motion compatible with these boundary conditions and we have a linear or first order thermodynamics. However when the direction of the flow of heat and the net motion of mass are not parallel, it becomes possible for the system to dissipate energy by the *formation of vortices*. The system will then break up into subsystems which do not exchange mass or energy with each other.

A subsystem has all the properties of a system except that it has a smaller volume and consequently dissipates less energy. It can exchange mass or energy with the original system or with its environment, but not with other subsystems of the same size. Consequently, the time evolution of a subsystem will proceed independently from all of its sister subsystems. In effect, the separation of the system into independent subsystems decreases the dissipation of energy even though the same amount or more mass and energy flows through what was originally the total system. This is true because if the environmental forces on the original system remain constant, the mass and energy will flow at a faster rate after this separation into subsystems. On the other hand if the flow of mass and energy remains constant the external force required will decrease. The first case yields the maximal rate of entropy production as found by Zeigler³ who carried out the variation of rates at constant forces. The second case is the one treated by Prigogine⁴ who varied the forces at constant fluxes and obtained the better known principle of minimum entropy production. This illustrates the confusion that exists whenever one attempts to use the concept of entropy production in a dynamic situation where entropy itself cannot be rigorously defined. In the general case both forces and fluxes should be allowed to vary and the concept of entropy is not capable of describing the result until and unless the

system approaches close enough to a time independent state where neither the forces or the fluxes are changing by a significant amount.

Until this occurs, the situation is complicated since the state of the system at any instant of time does not depend solely upon the boundary conditions at that time, but rather it also depends upon the past history. That is to say it depends upon the way in which the boundary conditions were changed and the path followed by the evolution of the system from the time that it could last be described by a scalar potential. The situation is exactly analogous to hydrodynamic or aerodynamic flow problems. The difference being only one of scale. Vortex formation in a thermodynamic system is usually on a time and distance scale that makes its observation very unlikely.

Only when there exists a steady-state that provides a balance between the forces and the fluxes in a dynamic situation can the concept of entropy be expected to be of some value. In exactly the same manner it is only at the time independent state of equilibrium that one finds a balance that both minimizes the energy and maximizes the entropy. A thermodynamics that is truly dynamic, requires a new concept to replace that of entropy which can only be rigorously defined for a nonexistent isolated system and is only useful for static or "quasi-static" situations. We suggest that the dissipation of energy, defined as the change in excess energy or total Legendre transform of energy, is such a concept^{1,2}. The change in excess energy is expressed as a functional integrated over both volume and time. Thus, the separation of a thermodynamic system into independent subsystems, reduces the volume and decreases the change in excess energy or dissipation.

In the usual equilibrium thermodynamics it is the minimization of the appropriate partial Legendre transform or free energy function that provides the criteria for minimizing energy and maximizing entropy. We propose that it is the minimization of the total Legendre transform or excess energy that provides the dynamic balance between the forces and the fluxes of a nonequilibrium system.

It is important to note that increasing the environmental forces on the system serves to increase both the dissipation of energy and the entropy production up until a maximum excess energy is reached. When this occurs, the system becomes unstable and separates into subsystems. This always decreases the dissipation of energy, but it can either increase or decrease the entropy production, depending upon whether the external forces are held constant or are allowed to decrease.

We are proposing that the change in excess energy, represented by the excess energy functional, can be experimentally measured. This measurement first requires the explicit selection of both the time and distance scales, which in turn determine the volume and

period of time over which the excess energy functional is evaluated. The distance scale is experimentally determined by the separation of the measuring devices. The time scale is determined by the period of dynamic fluctuation of one or more environmental variables. The amplitude of this dynamic fluctuation must be at least enough so that there is a measurable difference between the measured average over volume and the measured average over the dynamic period.

The criteria for the onset of instability that causes the system to break up into subsystems is that the first variation of the excess energy functional vanish and the second variation become positive. In other words when the excess energy functional reaches a maximum. This will occur when the gradient of the local deviation from equilibrium, $\nabla \xi$, is no longer parallel to the net mass flow or barycentric velocity. That is to say their cross product does not vanish when integrated over both the time and the distance scales adopted by a particular observer.

We emphasize the importance of the fact that the time and distance scales are, at least within certain limits, under the control of the observer. This is the practical significance of this approach to nonequilibrium thermodynamics. By controlling the time and distance scales it becomes possible for the observer to not just measure the time evolution of the system, but to actually control this evolution and to drive it either towards a *more perfect homogeneous* "equilibrium" state or into the *terra incognita* of multiphase "nonequilibrium" systems. The quotation marks in the previous sentence are there to indicate that these words refer to the conventionally used terminology where the time and distance scales are not defined but are assumed to be those which "everyone" understands. In other words, the system is at equilibrium if it doesn't change (during the period of observation) and it is homogeneous (with respect to the resolution of the observer).

We must again point out that the control indicated in the above paragraph is not simply a fiction accomplished by changing definitions, although such a change is involved. The change in the time scale is accomplished by changing the frequency of the applied dynamic force and the amplitude or power of this external force is increased sufficiently to make possible a measurement of the excess energy using the distance scale determined by the separation of the measuring sensors. If this measurement of excess energy is accomplished in real time, this information can be fed back and used to control the amplitude and frequency of the applied power. Consequently, it becomes possible to use this procedure to either accelerate the systems approach to what is conventionally called equilibrium, to decelerate this process (*i.e.*, control its rate), or even reverse it and drive the system away from conventional equilibrium. It is this latter possibility that opens the way to the production of new solid materials having complex multiphase structures. The properties of

these materials cannot be theoretically predicted with any reasonable accuracy.

However, the potential is truly enormous! What one would be doing in experimentally following this procedure would be emulating (at least physically) the way all living organisms produce the complex materials they use to perpetuate their existence and to maintain the efficiency of their energy conversion processes. Since the physical principle involved is the minimization of the dissipation of energy, it follows that the solid materials resulting from the application of this principle will have the primary property of minimizing the dissipation of energy. By using this approach it will be possible for man to manufacture complex materials and to use these materials for energy conversion processes that minimize the dissipation of energy. We note in closing that a material that minimizes the dissipation of electrical energy is known as a superconductor.

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NONEQUILIBRIUM THERMODYNAMICS AND MATERIALS PROCESSING

By Paul H. Lindenmeyer

We have developed a unique theoretical approach to materials processing based upon recent developments in nonequilibrium thermodynamics. This approach involves a reformulation of the second law of thermodynamics in which the concept of entropy is replaced by the concept of an excess energy. The principal advantage of this reformulation is that the change in excess energy can be measured experimentally, in real time, by the application of dynamic power and the use of modern microprocessor technology.

The excess energy of a system — defined mathematically as the total Legendre transform with respect to an independent set of extensive properties — plays the same role in nonequilibrium thermodynamics as do the various free energy functions (*i.e.*, partial Legendre transforms) in equilibrium thermodynamics. The partial Legendre transforms are functions of the average thermodynamic parameters whereas the total Legendre transform or excess energy is a functional or an integral over the gradients and the time rate of change of the thermodynamic and pseudo-thermodynamic parameters. At an equilibrium state there is no significant fluctuation about the average values of a thermodynamic parameter in either time or distance so that the excess energy vanishes.

Just as the various free energy functions can only be measured as the change or difference between two equilibrium states, the excess energy can only be measured as an integral over an explicitly defined time and volume. In order to measure a change in excess energy one must cause the excess energy to change by a measurable amount. This means that one must apply a dynamic power by fluctuating one or more of the environmental variables by an amount sufficient to cause a measurable change in the excess energy of the

system.

Since a dynamic fluctuation need not change the average value of the parameter being fluctuated, one can *independently* control the average value and the time rate of change and thus the gradients of the thermodynamic and pseudo-thermodynamic parameters. It well known that the solid state structure, and consequently the physical properties of many materials, are dramatically changed by their rate of solidification. However, the time that a system can be exposed to a high cooling rate is not independent of the change in average temperature. Energy is dissipated whether it flows into or out of the system. Dissipation has the dimensions of power and this power can become very high even when the average value of the environmental parameters are constant or changing slowly. If we define the rate of change of excess energy as the dissipation of energy the second law of thermodynamics can be reformulated as the following variational principle:

"A thermodynamic system, arbitrarily far from equilibrium, whether open, closed or isolated, will evolve with time in a manner that minimizes the change in excess energy integrated over any period of time and any volume".

The practical consequences of formulating the second law in terms of a measurable change in excess energy rather than a change in entropy, is that the excess energy can be measured experimentally and used as a control function to monitor and control the time evolution of a thermodynamic system. This provides the basic principle for automating materials processing using modern microprocessor technology.

The same technology that now guides a missile at high speeds over very uneven terrain can be adopted to control the reaction path over a multi-dimensional nonequilibrium free energy surface. The concept of excess energy defines the nonequilibrium free energy surface and the application of dynamic power provides the control of this surface. Location on the surface is given by the average value of the environmental parameters while the frequency and amplitude of fluctuation about these averages controls the height of the surface.

DYNAMIC DIFFERENTIAL CALORIMETER DESIGN AND CONSTRUCTION OF BREADBOARD MODEL

Autor(en) Dr. H. Weber and Dr. R.O. Brunner

Bericht Nr. F-3E-3

Klassifizierung ---

Zusammenfassung This report shows the basic principles of an active thermal system producing both large spatial temperature gradients and rapid temperature changes using a thermal switching technique. The principles of construction are elucidated and it is shown that attractive specifications of a Dynamic Differential Calorimeter (DDC) can be reached useful for both dynamic measurement and thermal treatment of samples. The construction plans of the first DDC and the schematics are included in the appendix.

Deskriptoren

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Glossary of Terms:

A : area for heat transfer
 α : heat transfer coefficients
 CH_i : heat capacity of heating element i
 $CWHi$: " of heating element coatings
 CT_i : " of hose and/or diffusers
 CiA : " of outer walls of channels
 CiE : " of inner walls of channels
 CiS : " of the cover sapphires of the sample
 $\dot{C}_i$: heat capacity current of working fluid in channel i
 D_h : hydraulic diameter of channels
 Δ : thickness of insulation
 H_i : heater of channel 1 or 2
 λ : thermal conductivity
 MV : magnet valve for temperature switch
 ν : dynamic viscosity of working fluid
 Nu : Nusselt number in the channels
 Re : Reynolds number of channel flow
 R_{0i} : thermal resistance from heater coating to ambient
 R_{1i} : " from diffuser i to ambient (incl. hose)
 R_{2i} : " from outer walls to jacket
 R_i : " from heater i to fluid
 R_c : " from inner walls upper to lower channel
 R_{iA} : " from fluid to outer walls
 R_{iE} : " from fluid to inner walls
 R_{iS} : " from fluid to cover sapphires
 RS : " of sample (thermal waveguide see A-82-2)
 RT_i : " from fluid to hose and/or diffusers
 RW_i : " from heater i to coating
 $R_{//}$: " of parallel circuit
 T_i : temperature of heater i
 T_{iFI} : " of fluid at entrance
 T_{iFO} : " of fluid at exit
 T_{iE} : " of channel inner walls (measured and controlled)
 T_{iS} : " of sample outer & cover sapphire inner surfaces
 Tw_i : " of heater coatings
 τ : thermal time constant of calorimeter
 v : velocity of working fluid in the channels
 $\dot{V}_i$: volume flow in Nl/s in the channels
 ω : thermal angular frequency

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1. Principle of Construction of the DDC:

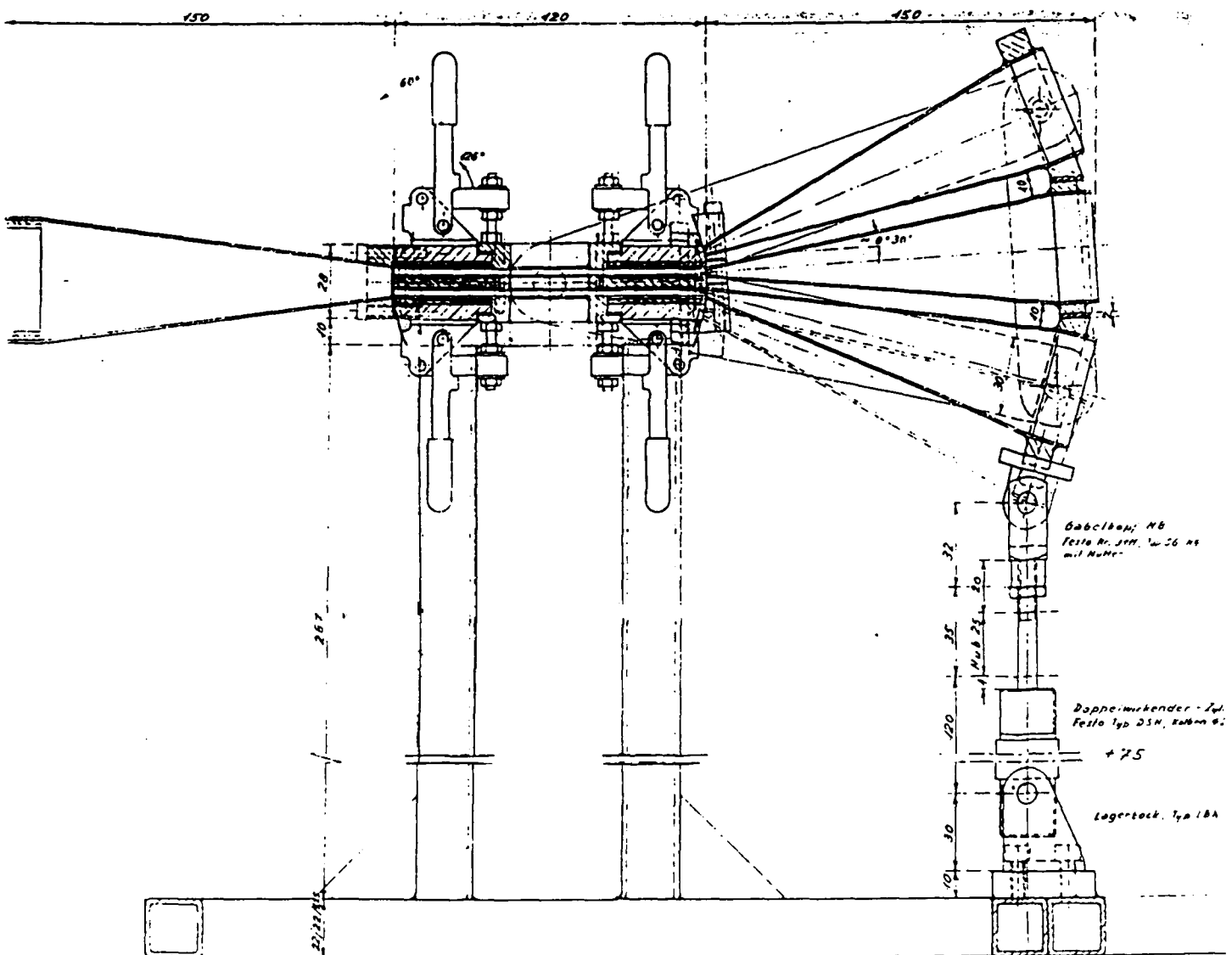
The heart of the dynamic differential calorimeter is a calorimeter proper with two rectangular channels only two millimeters high. The wall separating the upper from the lower channel is well insulated and carries a ceramic sample holder with two sapphire covers. The circular sample with 30 mm diameter and 4 mm thickness can be observed through two sapphire windows mounted in a stainless steel frame. These windows can easily be removed in order to insert or replace the sample holder carrying the sample.

The sample can be thermally treated by two currents of air, nitrogen, helium or other suitable gases properly blown into the calorimeter channels through three diffusors (see fig.1). The central diffusor is connected directly to a first heater (H1), the two peripheral diffusors through a flexible hose made from stainless steel to a second heater (H2). The wall-temperatures of the two channels can individually be measured and controlled by a DDC processor and rapid temperature fluctuations in the upper and lower channels are forced by a small rotary motion of the diffusors around the center of the calorimeter.

This temperature switch is essential for the proper operation of the DDC and has been evaluated from a set of four possible solutions (see appendix). The temperature switch (Tswitch) is operated through a pneumatic system and controlled by the DDC processor (magnetic valve MV).

Apart from the channel wall temperatures T1E and T2E, the processor measures the two sample temperatures T1S and T2S on both sides of the sample. These signals are evaluated together with the channel wall temperatures by a dynamic calorimetric technique.

When helium or some other noble gas is used, the exhaust gases can be collected again by a 1 1/2 inch gas connection. The whole calorimeter is mounted on a stainless steel frame (see appendix). Figure 1 shows an overview of the mechanical part of the dynamic differential calorimeter.



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2. Thermal Circuit of the DDC:

The thermal behaviour of the DDC can be represented by a lumped element thermal circuit as shown in figure 2.

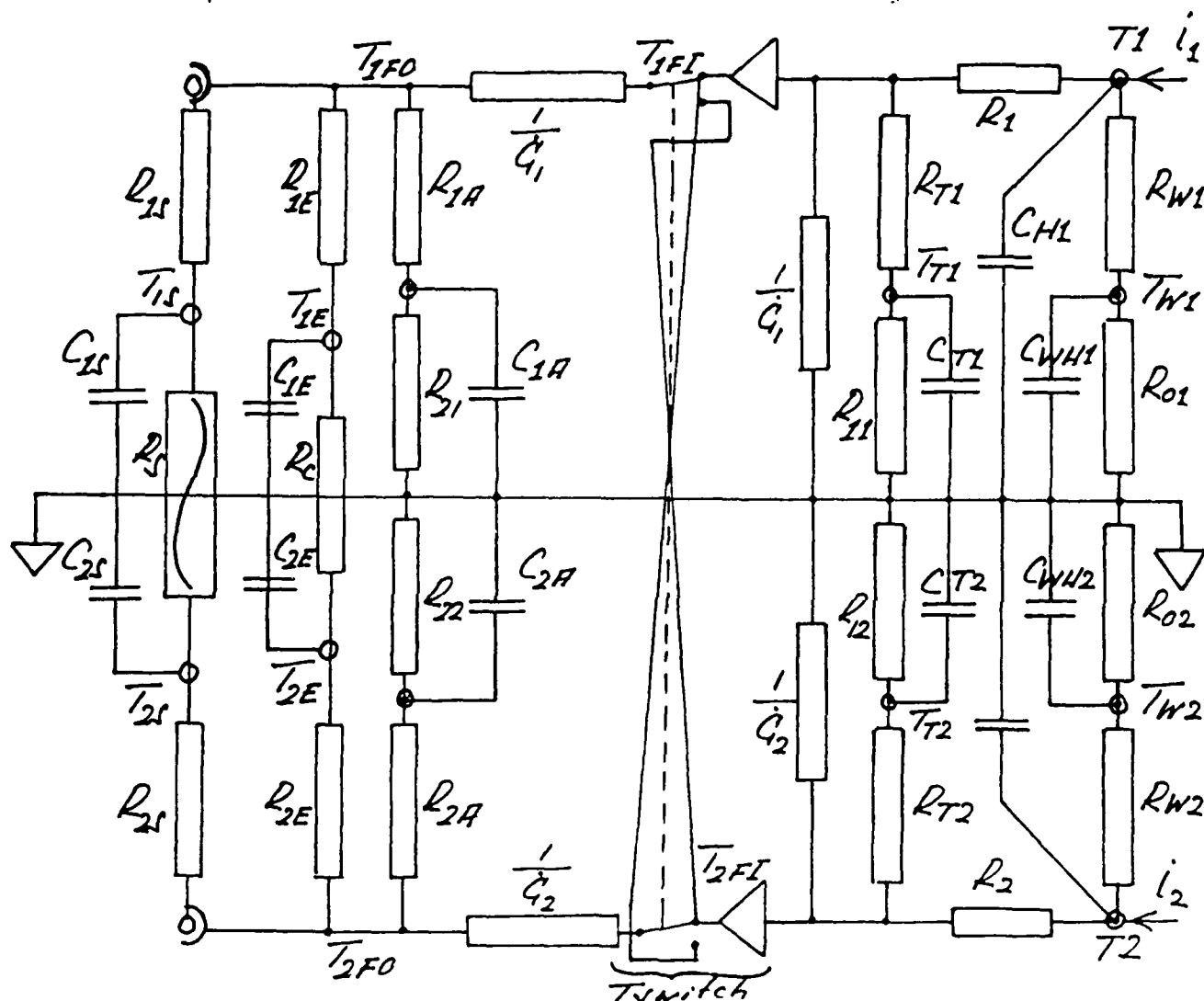


Figure 2: Lumped element representation of the DDC

The notation is as follows:

Heat capacities:

- Chi : Heating element 1 or 2
- CWHi : Coating of heating element 1 or 2 including hose
- CTi : Diffuser and/or hose of channel 1 or 2
- CiA : Outer walls of channel 1 or 2
- CiE : Inner walls of channel 1 or 2
- CiS : Cover sapphires of sample

Thermal resistances: (from ... to)

- RWi : Heater i to coating
- ROi : Coating to ambient
- Ri : Heater i to fluid

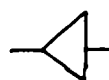
R1i : Hose and/or diffuser to ambient
 RTi : Fluid to hose and/or diffuser
 RiA : Fluid to outer walls
 R2i : Outer walls to jacket
 RiE : Fluid to inner walls
 Rc : Inner walls upper to lower channel
 RiS : Fluid to cover sapphires
 RS : Sample (thermal wave guide, see A-82-2)

Temperatures: of ...

Ti : Heaters
 TWi : Heater coatings
 TTi : Hose or Diffuser of channel 2 or 1
 TiFO: Fluid at exit
 TiFI: Fluid at entrance
 TiE : Channel inner wall (measured and controlled)
 TiS : Sample outer = cover sapphire inner (measured)
 Ci : Heat capacity current of fluids
 i1/i2: heater power



: thermal ambient conditions



: thermal impedance converter

The heat capacities have been estimated from the geometry and material properties as follows:

CHi = 200 J/K
 CWHi = 20 J/K
 CT1 = 70 J/K
 CT2 = 200 J/K
 CiA = 25 J/K
 CiE = 25 J/K
 CiS = 1.5 J/K

The thermal resistances have been obtained from the geometry and the $\mathcal{L}$ or λ - values either by estimation, by measurement or from the literature as follows: (all calculations done for air as working fluid at initial temperature of 0 °C)

$$RWi = \frac{1}{\mathcal{L} \cdot A} = 5 \text{ K/W}$$

from $A = 0.01 \text{ m}^2$ and
 $\mathcal{L} = 20 \text{ W/m}^2/\text{K}$ (estimate
 for forced convection)

$$Roi = \frac{1}{\mathcal{L} \cdot A} + \frac{\Delta}{\lambda \cdot A} = 14 \text{ W/K}$$

from $A = 0.01 \text{ m}^2$ and
 $\mathcal{L} = 10 \text{ W/m}^2/\text{K}$ (estimate
 for free convection)
 and $\lambda = 0.0475 \text{ W/m/K}$
 measured for glass
 fibre insulation of
 thickness $\Delta = 4 \text{ mm}$

$$R1 = \frac{1}{\mathcal{L} \cdot A} = 1 \text{ K/W}$$

from $A = 0.02 \text{ m}^2$
 $\mathcal{L} = 50 \text{ W/m}^2/\text{K}$
 (estimate for forced
 convection)

$$RT1 = \frac{1}{\alpha \cdot A} = 2.5 \text{ K/W}$$

From $A = 0.02 \text{ m}^2$ and
 $\alpha = 20 \text{ W/m}^2/\text{K}$ (estimate for forced conv.)

$$R11 = \frac{1}{\alpha \cdot A} + \frac{\Delta}{j \cdot A} = 9 \text{ K/W}$$

from $A = 0.02 \text{ m}^2$
 $\alpha = 10 \text{ W/m}^2/\text{K}$
 (estimate for free convection) and j measured

$$RT2 = 1/4 \cdot RT1 = 0.6 \text{ K/W}$$

$$R12 = 1/4 \cdot R11 = 2.3 \text{ K/W}$$

} total length four times
 length of channel 1

$$RiA = RiE = \frac{1}{\alpha \cdot A} = 0.77 \text{ K/W}$$

from $A = 0.0078 \text{ m}^2$
 α calculated from

$$Re = vDh/\nu, v = 13.3 \text{ m/s at } 200^\circ\text{C and } \dot{V} = 1 \text{ Nl/s,}$$

$$Dh = 0.001 \text{ m, } \nu = 34.6 \cdot 10^{-6} \text{ m}^2/\text{s, } \alpha = j/Dh \cdot Nu,$$

$$Nu = 0.037 \cdot Re^{0.8}, j = 0.0385 \text{ W/m/K, } Re = 384, \alpha = 166 \text{ W/m}^2/\text{K.}$$

$$R2i = \frac{\Delta}{j \cdot A} = 2 \text{ K/W}$$

from $A = 0.0078 \text{ m}^2$
 $\Delta = 0.002 \text{ m}$
 $j = 0.13 \text{ W/m/K}$
 (estimated)

$$Rc = 2 \cdot R2i = 4 \text{ K/W}$$

$$R1S = \frac{1}{\alpha \cdot A} = 8.5 \text{ K/W}$$

from $A = 7.70 \cdot 10^{-4} \text{ m}^2$
 $\alpha = 166 \text{ W/m}^2/\text{K}$ as
 above.

Channel 2 has higher losses due to the 0.5 m long hose. The calculation for the temperatures will therefore be done for channel 2. At a power of $i2 = 800 \text{ Watts}$, the temperature of the fluid entering the calorimeter proper is found for $C2 = 1.33 \text{ W/K}$, $\dot{V}2 = 1 \text{ Nl/s}$ of air (total air consumption is $7.2 \text{ Nm}^3/\text{h}$) as follows:

$$T2FI = \frac{R_{//} \cdot (RW2 + R02) \cdot i2}{R_{//} + R2 + RW2 + R02} = 443^\circ\text{C, } R_{//} = \frac{RT2 + R12}{1 + (RT2 + R12) \cdot C2} = 0.60 \text{ K/W}$$

The temperatures of the heating element, its coating and the hose will be as:

$$T2 = 1181^\circ\text{C, } Tw2 = 870^\circ\text{C, } T12 = 351^\circ\text{C.}$$

The excessively high value of the heater coating temperature $Tw2$ will be lowered by a leaking air current not shown in the circuit of figure 2.

The temperature leaving the calorimeter proper when channel 1 is cooled to 20°C is obtained from:

$$RI = \frac{(R_{2A}+R_{22}) \cdot (R_{2E}+R_c)}{(R_{2A}+R_{22}+R_{2E}+R_c)} = 1.752 \text{ K/W}, \quad T_{2F0}=T_{2FI} \cdot \frac{RI}{RI+1/C_2} = 310 \text{ }^{\circ}\text{C}$$

RI is the internal thermal resistance of channel 2 of the calorimeter proper when channel 1 is at $T_0 = 0 \text{ }^{\circ}\text{C}$. The mean temperature of channel 2 will therefore reach $T = 377 \text{ }^{\circ}\text{C}$ at $i_2 = 800 \text{ W/K}$. The large temperature drop of nearly $140 \text{ }^{\circ}\text{C}$ results from the low current of fluid V. At a larger fluid current the temperature drop is reduced accordingly.

When the DDC is operated with helium, C can be increased by a factor of four at a power of twice 3000 W (220 Volt option). The temperature drop in the channels will correspondingly be reduced to about $35 \text{ }^{\circ}\text{C}$. Another means of reducing the temperature drop would be to improve the thermal insulation of the channels.

The jacket of the calorimeter is cooled by the ambient air, through thermal radiation, free convection and partly through thermal conduction of the support. Its temperature will rise to a maximum when both channels are operating at the maximum temperature of $400 \text{ }^{\circ}\text{C}$. This temperature is given by:

$$T_{J\max} = 400 \text{ }^{\circ}\text{C} \cdot \frac{R_{\text{amb}}}{R_{\text{amb}}+R_{1A}+R_{2A}} = 200 \text{ }^{\circ}\text{C}.$$

R_{amb} is the thermal resistance of the jacket to the surroundings and has been estimated to about 2.8 K/W . This elevated jacket temperature will rise the mean maximum channel temperature to above $400 \text{ }^{\circ}\text{C}$ at 800 W .

The time-constant of the heater system (right part of figure 2) is of the order of several minutes because of the large value of the heat capacities CH_1 and CT_2 . The time-constant of the calorimeter proper (left part of figure 2) is much lower. This time-constant is dependent on the sample and is of the order of 20 seconds. At maximum amplitude of the channel temperatures T_{1E} and T_{2E} of about $280 \text{ }^{\circ}\text{C}$, the amplitude of the sample will be damped by a factor of

$$\frac{1}{1 + (\omega\tau)^2} \quad \text{and is independent of the large}$$

time-constant of the heaters. This is the result of the thermal switching-technique, that decouples the calorimeter from the heaters. For $\tau = 20 \text{ s}$ and a frequency of $\omega = 0.05 \text{ Hz}$, a thermal amplitude in the sample of about $44 \text{ }^{\circ}\text{C}$ can be reached with air as working fluid. With helium, the time-constants can even be reduced by a factor of about four.

Thermal treatment of samples in the DDC allow simultaneous optical and thermal observations of its changes. The control unit described below controls mean temperatures, temperature amplitudes and frequencies independently. The operating and test procedures are introduced in the form of computer programs. The description of these programs will be found in the next chapter and operation manual of the DDC.

3. Control of the Dynamic Differential Calorimeter:

The DDC is controlled by an electronic control unit that consists of a processor and a power interface. The processor reads the four temperatures T1E, T2E, T1S and T2S, calculates the mean and differential temperatures and stores them. It controls both heaters H1 and H2 and the magnet valve MV in order to establish the thermal treatment of the sample as wanted during an experiment. All the data and programs can be transferred between the processor and the personal computer in both directions. All the experiments can be performed from the processor (frontend) and data can be stored for one hour without using the personal computer. Evaluation and collection of experiments however must be done with the personal computer. Figure 3 shows a block circuit of the whole system. A more detailed description of the control unit is given below.

For normal operation with air, nitrogen or helium the system operates at the 110 Volt mains at 2x800 Watt. For improved properties a 220 Volt option can be implemented at 2x3000 Watts (four times the power and fluid flow).

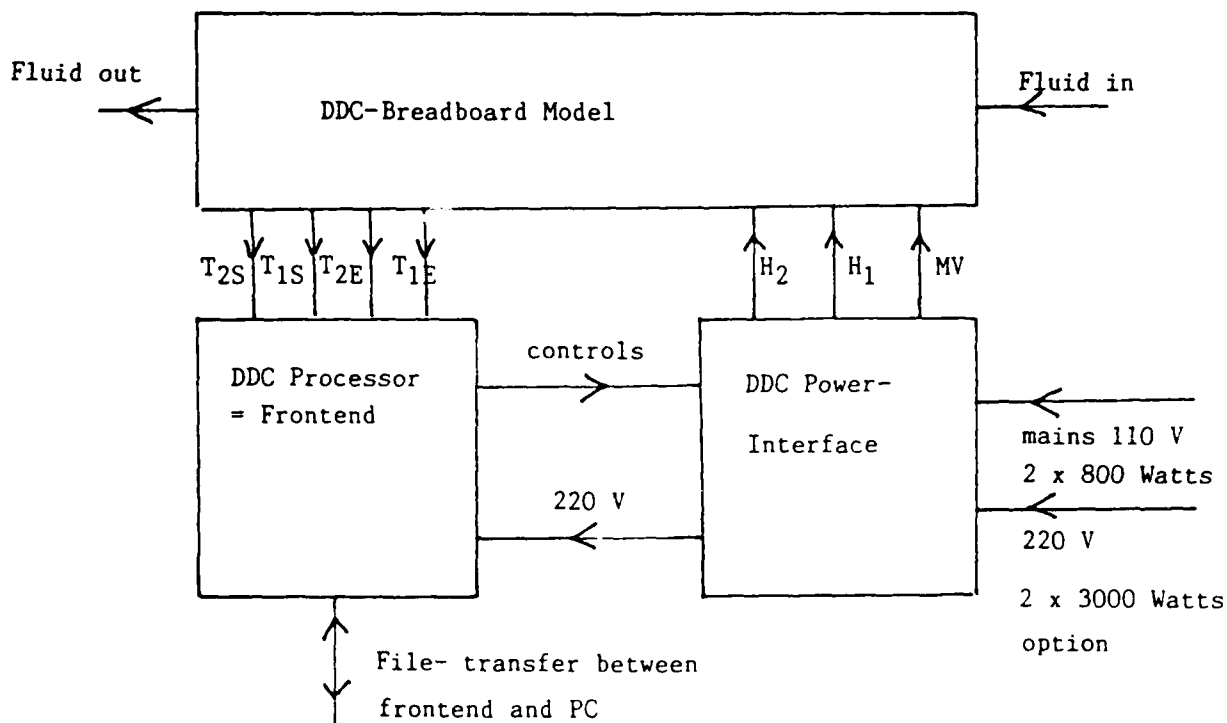


Figure 3: Block Circuit of the DDC

3.1 Description of the DDC Control Unit

The control-unit for the dynamic differential calorimeter consists of 6 plugins.

The mainunit UMC-51-001 is a single-board-computer, equipped with Intel's 8052 CPU. MCS-BASIC-52 is the programming language. The user-program resides in a EEPROM or UVEPROM. Datas are stored in a 16 KByte CMOS-Memory with battery-backup.

The LCD and keyboard unit UKD-51-001 allows stand alone operation.

The analog-digital-converter ADC-12-002 has 12 bit resolution and is multiplexed for multichannel use. Analog-section and digital-section are separated by opto-isolaters.

The DC-DC-converter- and Pt-100-unit signal conditions and linearizes the RTD's. The power-isolation by the DC-DC-converter provides maximum noise immunity.

The necessary voltages are delivered by the power supply unit SNT-01-001.

The OPTOUT-24-1 Module allows the separation between the control unit and the power circuits.

Communications with the hostcomputer occurs via RS 232 serial port.

The power interface consists of three sections, two for the heaters and one for the magnetic valve. Zero-voltage-controllers drive the heater-triacs by variable burst length for minimizing radio frequency interference.

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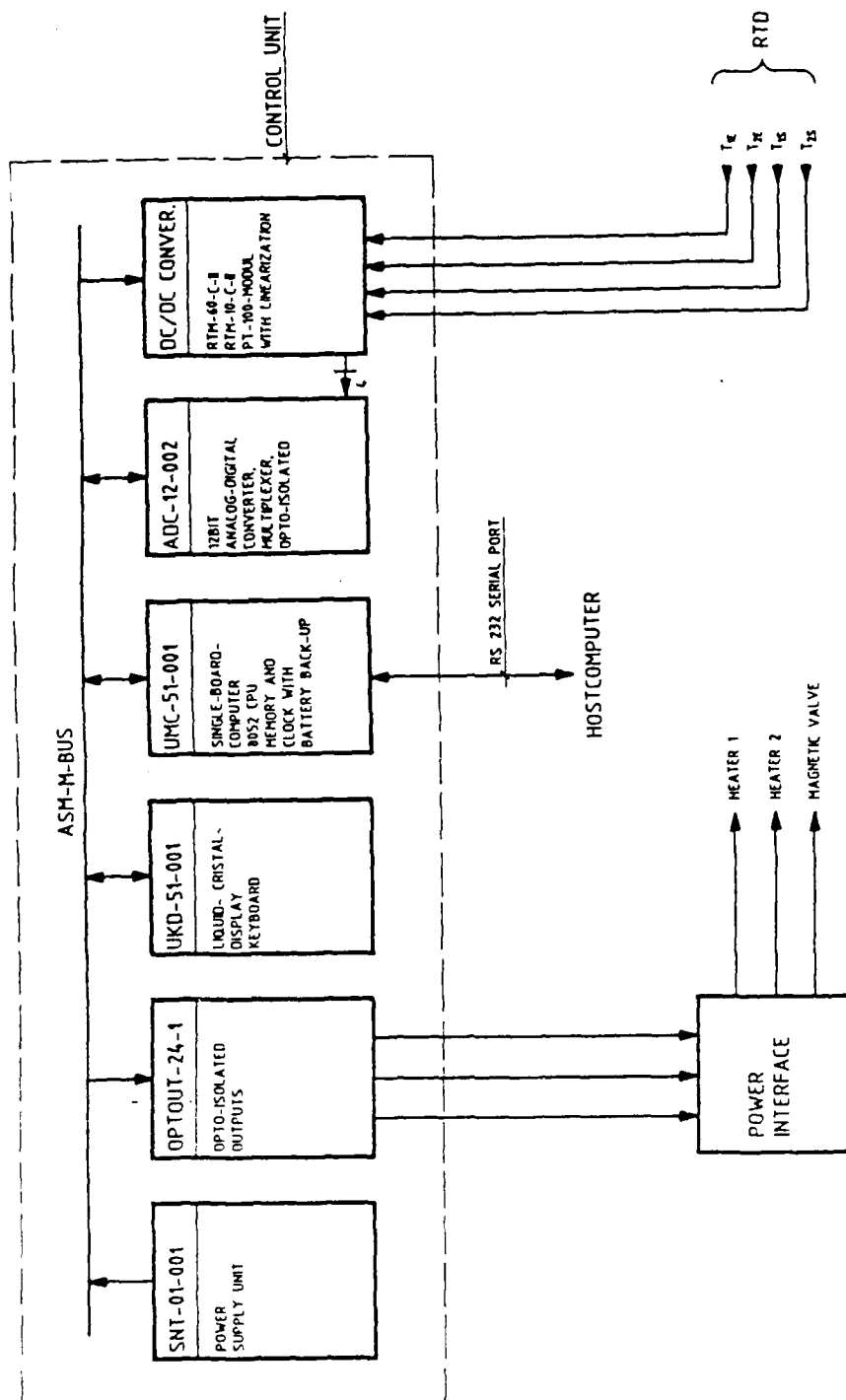
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Communications with the hostcomputer occurs via RS 232 serial port.

The power interface consists of three sections , two for the heaters and one for the magnetic valve. Zero-voltage-controllers drive the heater-triacs by variable burst length for minimizing radio frequency interference.

CONTROL UNIT FOR DYNAMIC DIFFERENTIAL CALORI-METER DDC



Dr. Brunner & Partner AG	DRAWN	DL
	DATE	28 OCT 1986
DDC - CONTROL - UNIT		PLAN-Nº
		21 4703-001

DDC-CONTROL-UNIT

Control-Unit
for the
Dynamic Differential Calorimeter

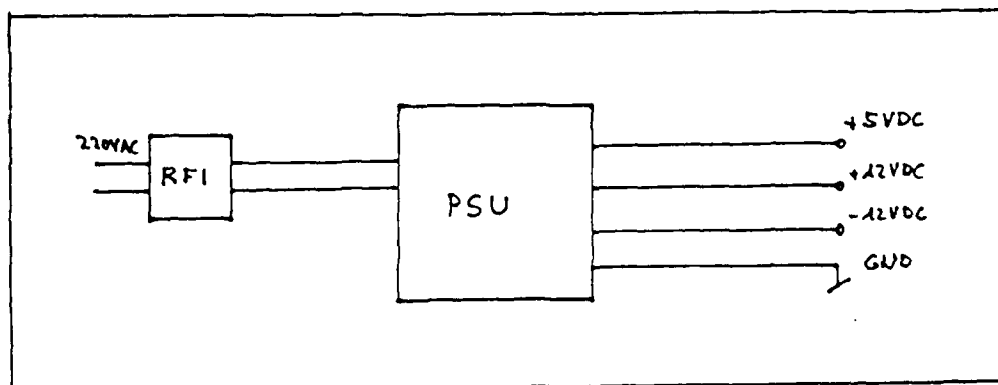
CONTENTS :

1. Power-Supply-Unit
2. Optocoupler Power Output
3. Keyboard & Display
4. Single-Board-Computer
5. Analog to Digital Converter
6. Pt-100-Amplifiers
7. Power Interface

DDC-CONTROL-UNIT

1. Power-Supply-Unit

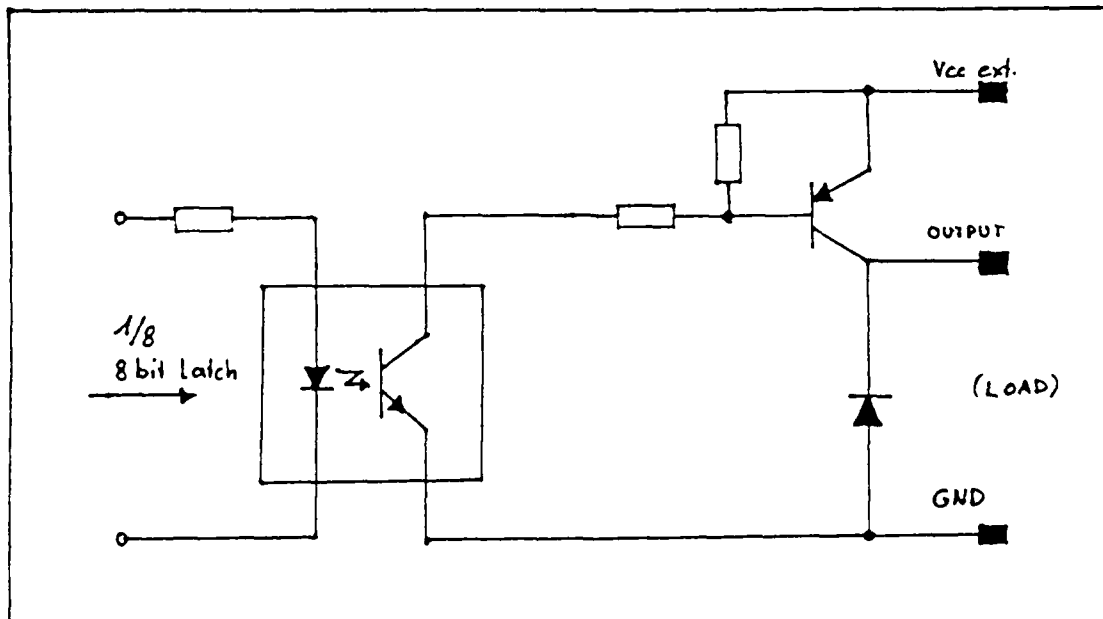
- * AC-DC-switching power supply
- * input voltage : 230 VAC
-25%.....+15% nominal voltage
45.....440 Hz
- * output voltage : 5 VDC /4.0 A
12 VDC /0.2 A
-12 VDC /0.2 A
LED indicators
- * regulation : mains : $\pm 15\%$ output : 0.1%
load : $\pm 10\%$ output : 0.2%
- * efficiency : 88%
- * switching frequency : ca 100 kHz
- * mounted on EUROCARD
- * equipped with radio frequency interference filter
- * AMS-M-BUS-interface

Power Supply Unit

DDC-CONTROL-UNIT

2. Optocoupler Power Output

- * latched 24 channel parallel output
3 port organization
4th port for individual release of the 3 output-ports
via software
each channel with source-driver
- * output stage
optocoupler isolation voltage :3000 VDC
medium power transistor (max. ratings): 45VDC/0.5A
overvoltage protection
load between ground and transistor
power separation with additional power-supply

Output Stage (24x)

DDC-CONTROL-UNIT

3. Keyboard & Display

- * unit interfaced to system via PPI (8255)
works with SYSLIB -monitorprogram
- * keyboard : 21 keys
4 characters/key
(normal-cntrl-shift-cntrl*shift)
ASCII-code
- * display :Liquid-Crystal-Display with backlight
2 lines
24 characters/line
- * loudspeaker
- * power consumption : 5.0 VDC $\pm 5\%$ /0.05A

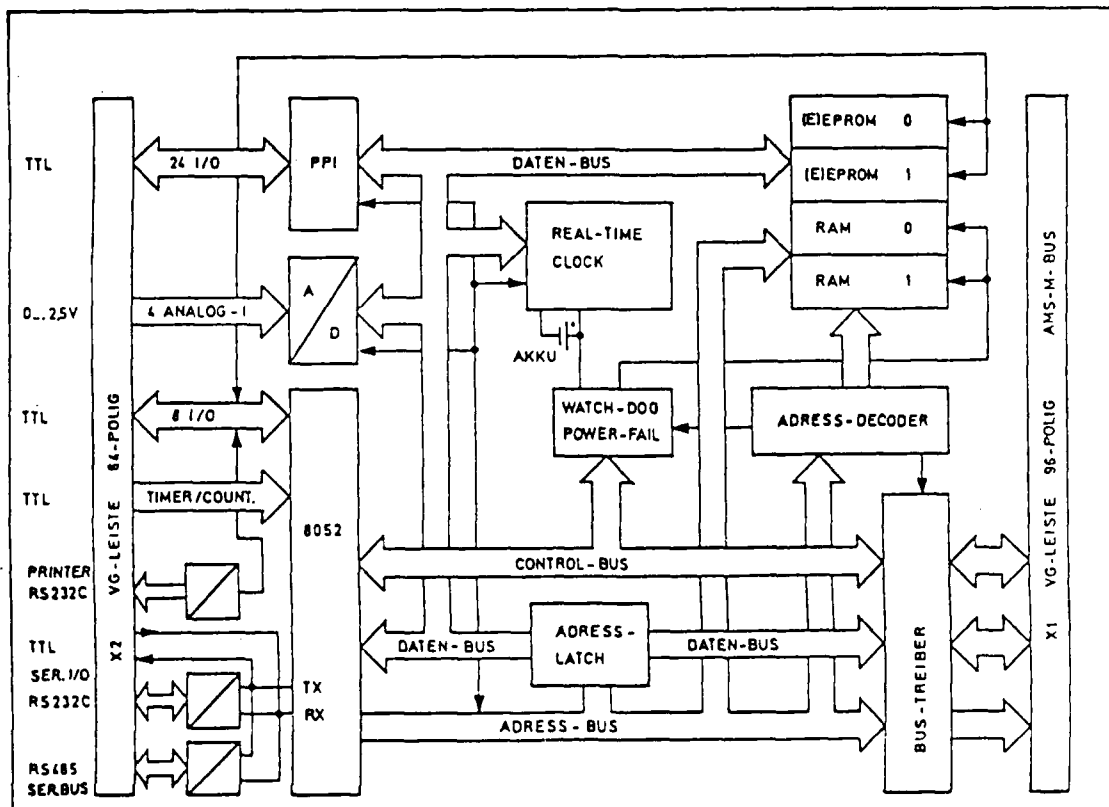
5 S	6 T	7 U	8 V	9 W	ESC X	KEY
A !	B #	C \$	D %	E &	F ;	
Ø Y	1 Z	2 +	3 -	4 *	LF /	CTRL
G ?	H	I [	J]	K \	L ^	
SPC (	,)	. "	: =	DEL >	CR <	SHIFT
M {	N }	O	P ~	Q '	R ~X	

Keyboard Layout

DDC-CONTROL-UNIT

4. Single-Board-Computer

- * single board computer with CPU 8052 on EUROCARD
- * on-board 4 channel analog to digital converter (not used)
- * 24 TTL input/output lines via programmable peripheral interface (partially used by the display unit)
- * memory : 16 kByte static RAM (opt. battery backup)
 - 8 kByte EEPROM (user BASIC-program)
 - 8 kByte EPROM (SYSLIB-monitorprogram)
 - 8 kByte ROM (BASIC-interpreter)
- * clock and calendar with battery backup generation of interrupt-signals
- * watchdog-circuit and reset-generator
- * 3 timer/counter 16 bit max.
- * RS 423/V24 interface console or hostcomputer baudrate up to 19'200 baud, compatible with RS 232C possibility of AUTOBAUD-search-routine (works with the spacebar-signal of the host)
- * expansion with AMS-M-bus interface
- * power requirements: 5 VDC / 0.45 A, $\pm 5\%$
 12 VDC / 0.02 A, $\pm 10\%$
 -12 VDC / 0.02 A, $\pm 10\%$
- * ambient temperature : 0°C + 55°C



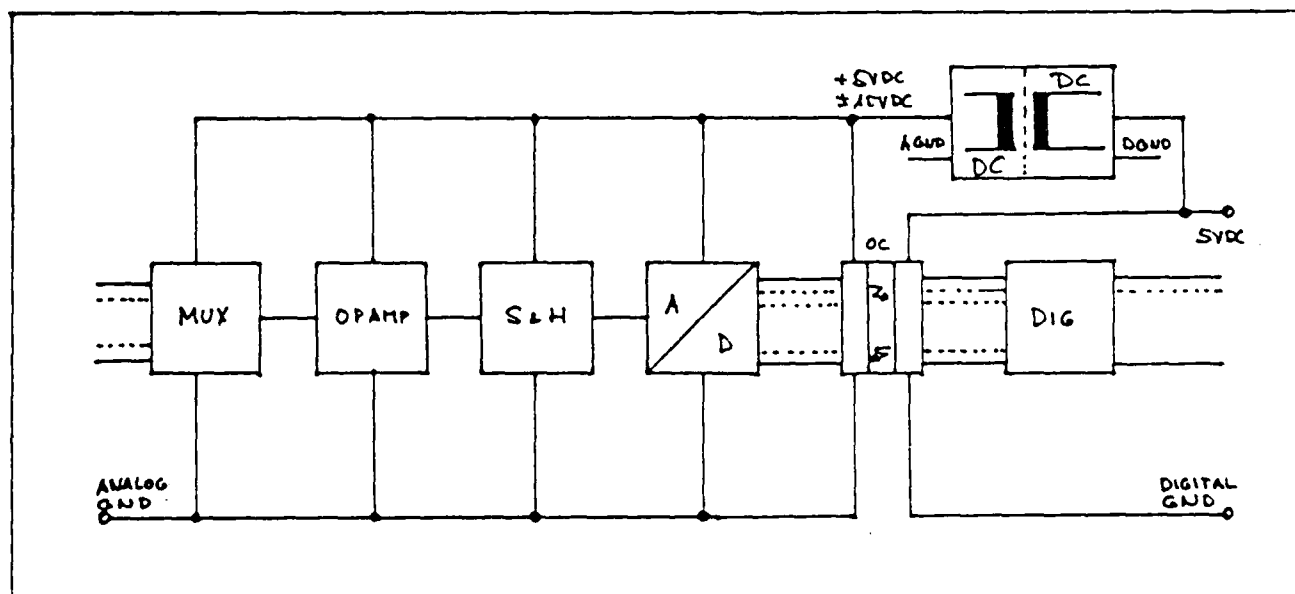
Blockdiagram Single Board Computer

D905-10123-1

DDC-CONTROL-UNIT

5. Analog to Digital Converter

- * analog to digital converter with operational- and sample & hold-amplifier
- * 16 channels unipolar
- * 8 channels bipolar
- * 4 input voltage ranges :± 5 V
 ±10 V
 10 V
 20 V
- * settable gainfactor with jumpers (1x,10x,100x,1000x)
individual gain with additional resistor
- * 12 bit resolution
- * 25 µs conversion time/channel
end-of-conversion signal : status signal
 : interrupt signal
- * start-of-conversion possible with external triggersignal
- * 8 bit or 16 bit output data
- * analog ground and digital ground separated
by mean of DC-DC-converters and optocouplers

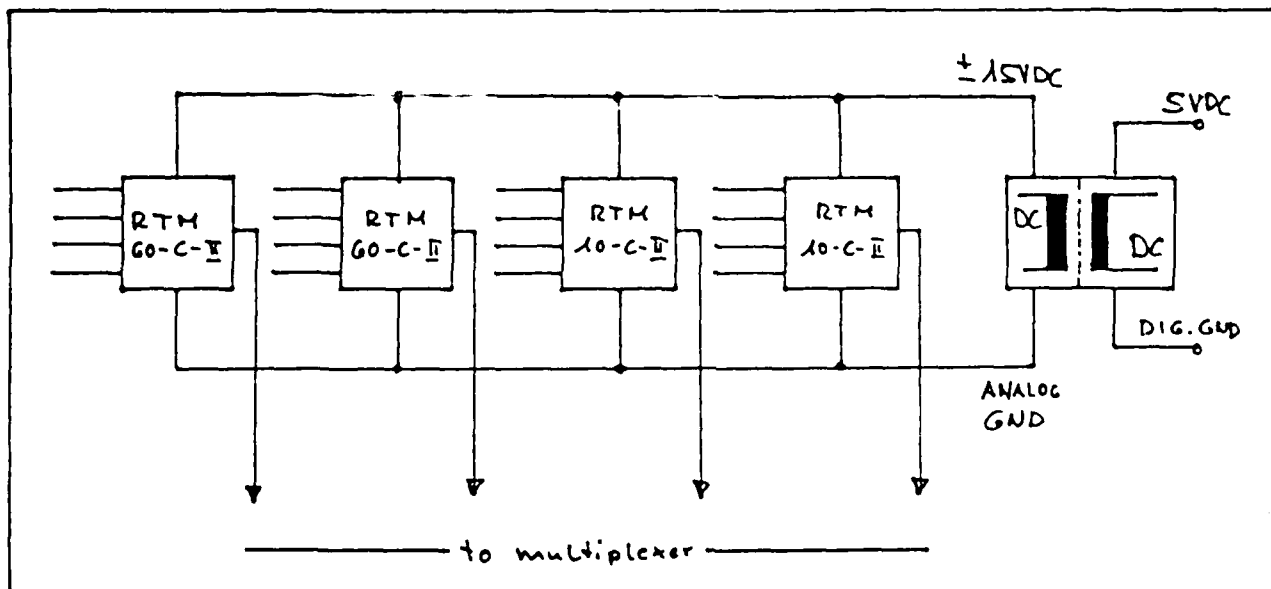


ADC with analog-digital-separation

DDC-CONTROL-UNIT

6. Pt-100-Amplifiers

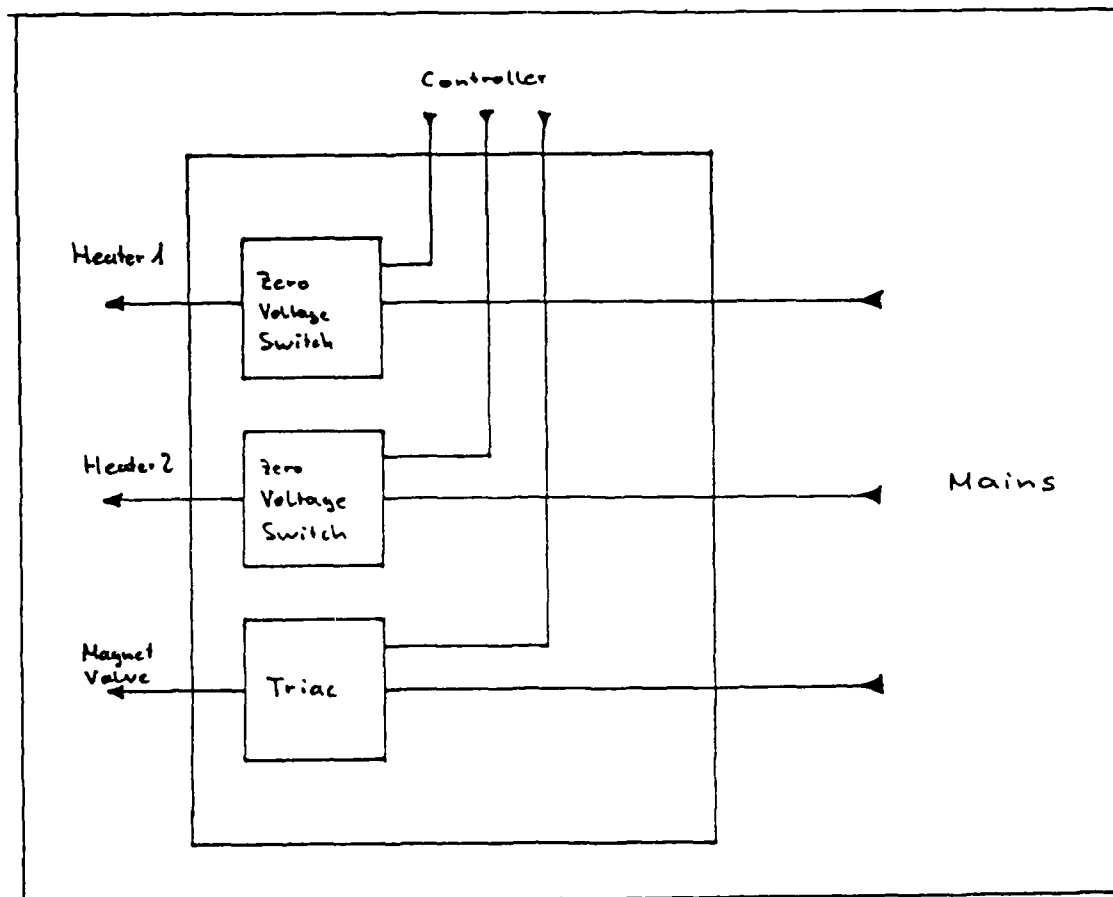
- * Pt-100-moduls: precision RTD-signal-amplifiers for grounded RTDs (RTM-60-C-II) and for floating RTDs (RTM-10-C-II)
- * gain- and offset-trimmers for better accuracy
- * 4-wire-technique
- * temperature-measuring range : -50°C to 500°C (Pt-100)
- * output linearized : $10 \text{ mV}/^{\circ}\text{C}$
- * accuracy : typ. 0.2°C
- * power consumption : $\pm 15 \text{ VDC}/0.005 \text{ A}$ /modul
- * DC-DC-converter: galvanic separation input/output, high isolation voltage between input and output (3000 VDC)
- * equipped with low-pass filter to minimise feedback
- * MTBF > 350000 hours at 40°C (calculated)
- * operating temperature range : 0°C to 70°C
- * input voltage : $5 \text{ VDC} \pm 5\%$
- * efficiency : 58%
- * output power : 1 W
- * output voltage : $\pm 15 \text{ VDC} / 0.033 \text{ A}$ ($\pm 5\%$)

Blockdiagram Pt-100-Amplifier & DC-DC-Converter

DDC-CONTROL-UNIT

7. Power Interface

- * *heater control: the power of the heater is controlled by a triac by variable burst length. The burst length is calculated by the computer and fed to the electronics via the optocoupled power output. A bimetallic thermostat built in the heater-housing protects the heater in case of failure*
- * *magnetic valve control: the pos1/pos2 signal is routed to the magnetic valve triac via the optocoupled power output. The switching-period is set by the computer.*

Blockdiagram Power Interface

Evaluation of different Concepts for the Construction of the Tswitch:

Function: to switch from hot to cold in a manner to disturb the flows as little as possible. The path from the temperature switch to the calorimeter channels must be as small as possible. Axial temperature gradients as small as possible.

Requirements:	Solutions:			
	I	II	III	IV
Flow disturbance	u	v	g	g
Path length	v	s	v	v
Axial gradients	u	g	u	g
effort to get func. g	g	a	u	g

Solutions:

I	Mr. Hess' design with balancing system
II	Dr. Lindenmeyers rotary valve
III	Weber's proposal with integrated tungsten heaters
IV	three diffusers on one side

Evaluation:

v	very good
g	good
s	satisfactory
a	acceptable
u	unacceptable

The table shows that solution IV must be chosen

Control Program for the Dynamic Differential Calorimeter

This temperature control program controls the sum of the two environmental temperatures by calculating a pulse length for the on-time of the heater, H1, for each second. The pulse length is determined by the sum of a proportional, an integral and a differential contribution. Temperatures are measured as often as the computer speed permits (approximately four times a second) and the temperatures are fed into a circular buffer in order to obtain a sufficiently smoothed signal for calculating the derivative contribution. A circular buffer with five positions was found to provide sufficient smoothing.

In addition to controlling the average environmental temperature this program also controls the frequency of alternating the temperature in the upper and lower channels by counting the number of "one second" pulses. Time between pulses is somewhat greater than one second so that the true frequency requires calibration.

Finally this program measures the two sample temperatures and prints out all data for each pulse. In addition both the environmental and the sample temperatures are averaged over each half cycle.

A1	Proportional contribution to pulse
A2	Integral contribution to pulse
A3	Differential contribution to pulse
B1	Pulse length
W1	Average Environmental Temperature
T1	Temperature in upper channel
T2	Temperature in lower channel
T3	Temperature in upper surface of sample
T4	Temperature in lower surface of sample
20-100	Subroutine to address 12 bit ADC
100-1050	Initialize and set parameters
1050-2000	Start program
2000-3000	Set interrupts and turn on and off heater
3000-4000	Measure temperatures
4000-5000	Measure temperatures with heater off
5000-6000	Change set temperature
9000-9999	Shut-down sequence

```

LIST
10 REM *** DDC TEMPERATURE CONTROL TEST PROGRAM TEST4.DDC ***
15 REM **** CIRCULAR BUFFER WITH P I D CONTROL ****
20 GOTO 100
40 REM ***SUBROUTINE TO ADDRESS 12 BIT ADC ****
45 POP TI
47 A=7E00H
50 XBY(A)=TI
60 XBY(A+1)=0H
70 B=128.AND.XBY(A+1) : IF B=128 THEN 60
80 TH=XBY(A+1).AND.15
90 TL=XBY(A)
95 WB=TL+256*TH
97 PUSH WB
98 RETURN
100 REM ***INITIALIZE ***
102 C6=5
105 DIM CB(C6) : REM **DEFINE CIRCULAR BUFFER **
110 INPUT "ENTER HIGH TEMPERATURE TARGET: "H1
115 G1=20
250 INPUT "ENTER NUMBER OF 1 SECOND INTERVALS IN VALVE FREQUENCY:"V
260 IF V<1 THEN PRINT "INVALID INPUT, V < 1" : GOTO 250
270 HZ=.5/V : PRINT "FREQUENCY =", : PRINT USING(###.###),HZ
330 F1=H1/G1
335 F2=.025
340 F3=-3
370 XBY(7E42H)=00H : XBY(7E43H)=00H : I=00H : REM * INITIALIZE HEATERS
400 PRINT " P I D DUTY CT T1 T2 T3 T4"
440 GOSUB 3000 : REM *** GET TEMPERATURES AND PULSES ***
510 TIME=0 : CLOCK 1 : REM * INITIALIZE TIME *
1050 K=0 : Z=0 : N=0 : S1=0.0 : S2=0.0 : REM * * * START * * *
1055 ONTIME 1,2600 : IDLE
1060 GOSUB 3000 : REM *** GET TEMPERATURES AND PULSES ***
1070 GOTO 1060
2000 I=I.AND.0FDH : XBY(7E42H)=I : REM *TURN OFF H1 *
2020 DBY(71)=B1 : ONTIME TIME+1,2600 : REM ***SET INTERRUPT FOR NEW**
2050 RETI
2600 REM **** START NEW CYCLE ****
2601 A=GET : IF A<0 THEN GOTO 5000
2602 C4=0
2603 FOR I2=1 TO C6
2604 IF CB(I2)<(C5-2) THEN CB(I2)=C5
2605 C4=C4+CB(I2) : NEXT I2
2607 W1=C4/C6
2609 O=O+(H1-W1)
2610 A1=(H1-W1)*F1 : A2=O*F2 : A3=(W1-D1)*F3 : D1=W1
2615 P=INT(A1+A2+A3)
2618 PRINT USING(###.#), CR ,A1,A2,A3,B1,W1,T1,T2,T3,T4
2620 K=K+1
2630 IF K=V THEN P=1 : I=I.XOR.01H : XBY(7E42H)=I : Z=Z+1
2636 DBY(71)=0 : TIME=0
2640 IF P=0 THEN B1=0 : GOTO 2650
2645 IF P=199 THEN B1=199 ELSE D1=P
2648 I=I.OR.02H : XBY(7E42H)=I : REM *TURN ON H1 *
2650 DBY(71)=(199-B1) : ONTIME TIME+1,2000
2700 RETI

```

```

3000  REM **** SUB 3000 **** TAKE TEMPERATURE SAMPLES ****
3430  PUSH 0 : GOSUB 40 : POP W
3440  PUSH 1 : GOSUB 40 : POP W2
3450  PUSH 2 : GOSUB 40 : POP W3
3460  PUSH 3 : GOSUB 40 : POP W4
3465  W=W/4096*400 : W2=W2/4096*400 : W3=W3/4096*400 : W4=W4/4096*400
3466  W=W-.5 : W2=W2-.8 : W4=W4-.4
3467  T1=W : T2=W2 : T3=W3 : T4=W4
3468  E4=(W+W2)/2 : S4=(W3+W4)/2
3469  C5=E4
3470  I3=I3+1 : IF I3>C6 THEN I3=1
3475  CB(I3)=C5
3490  IF Z<=0 THEN N=N+1 : S1=S1+W+W2 : S2=S2+W3+W4 : GOTO 3999
3495  M1=S1/(N*2) : M2=S2/(N*2) : PRINT M1,M2
3500  N=1 : S1=W+W2 : S2=W3+W4 : Z=0
3999  RETURN : REM *** END SUB 3000 ****
4000  REM***TAKE TEMPERATURES WITH CONTROLS OFF**
4010  PUSH 0 : GOSUB 40 : POP W
4020  PUSH 1 : GOSUB 40 : POP W2
4030  PUSH 2 : GOSUB 40 : POP W3
4040  PUSH 3 : GOSUB 40 : POP W4
4050  W=W/4096*400 : W2=W2/4096*400 : W3=W3/4096*400 : W4=W4/4096*400
4055  E4=(W+W2)/2 : S4=(W3+W4)/2
4060  PRINT USING(###.##), CR ,W," ",W2," ",W3," ",W4," ",E4," ",S4.
4070  RETURN
5000  REM *** CHANGE SET TEMPERATURE***
5010  INPUT "ENTER NEW TEMPERATURE TARGET: "H1
5012  IF H1<=0 GOTO 9000
5036  F1=H1/G1
5040  TIME=0 : DTIME 1,2600 : RETI
5050  GOTO 1060
9000  CLOCK 0 : XBY(7E42H)=01H : REM *** BOMB OUT SEQUENCE ***
9003  PRINT "HEATERS OFF "
9007  GOSUB 4000
9008  A=GET : IF A<=0 THEN GOTO 9010
9009  GOTO 9007
9010  PRINT "JOB DONE"
9999  END

```

END

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