Levy defects in fluctuating pattern of liquids. A quasi thermodynamic approach to the dynamic glass transition in classical molecular liquids.

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This theoretical paper is to advance a phenomenological, quasi thermodynamic approach to the dynamics of classical liquids which uses the Levy distribution of probability theory. Doubts from the chemical physics community about the application of its unusual properties to this field are tried to be removed. In particular, to understand the preponderant component of the Levy sum for Glarum Levy defects and Fischer speckles, the classical mathematical proof [D. A. Darling, Trans. Amer. Math. Soc. 73, 95 (1952)] for the existence and the influence of this component is accompanied by addition of physical arguments related to these defects. It is tried to explain an underlying fluctuating spatial pattern of free volume with weak contrast and a pattern of mobility with strong contrast, and to explain the characteristic lengths for the main transition and the Fischer modes. The structure of the relaxation chart (dynamic glass transition) and several properties of, and relations between, the slower dispersion zones therein, are reviewed for classical glassforming liquids of moderate complexity. For the main transition, the preponderant component is pushed in the midst of the defect and induces the molecule to its diffusion step across the cage door of the next neighbors. An Experimentum Crucis for an indirect proof of the existence of defects – via characteristic lengths – is also described.
I. INTRODUCTION

The Levy sum for stable distributions with Levy exponent $\alpha < 1$ has a preponderant component. An example of its physical relevance was recently published for Laser cooling. The reviews for dynamics in classical molecular liquids are sometimes accompanied by catalogs of open questions. The relevance of Levy distributions for this dynamics may be discussed in a thermodynamic frame of fluctuating space-time pattern for free volume, where islands of mobility from temporary concentrations of free volume can be formed by using a general length/mobility scaling. Such spots in the pattern are called Levy defects, if they can be explained by an appropriate Levy sum, in particular with a preponderant component. A well known model is Glarum’s defect diffusion model, which was later reviewed by means of Levy flights, cf. also Ref.13. The more later variant of Bendler, Fontanella, and Shlesinger is aimed to interaction of several or many defects forming clusters as basis for the glass transition. On the contrary, our variant is aimed to an explanation of molecular cooperativity of the dynamic glass transition from one defect alone. An experimental indication for defects in larger spatial scales are Fischer’s speckles.

If confirmed, the Levy defect pattern would be a surprising phenomenon: Upon some ”primary democratic” conditions, Levy statistics can promote shaping. The basic physical assumption of our approach is that the Levy sum components can be related to spatially separable, dynamically independent subsystems or partial systems. (Such a relation is not necessary, which means that there are Levy situations where spatial aspects play a minor role. An example is the treatment of Laser cooling in Ref.4, where a trap in the momentum space is considered, and the Levy distribution is related to lifetimes such as trapping or escaping times.) Our assumption is completed by a general space vs. mobility scaling of fluctuation modes to treat the spatial structure of the defects. Our approach is supported by a Representativeness Theorem, showing inversely that the distribution of representative subsystems corresponds to a Levy sum. An Experimentum Crucis for Levy defects of the main transition in classical liquids is suggested that uses the relevant characteristic lengths.

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As a rule, experimental retardation in glass forming liquids can well be adjusted by a Kohlrausch function in the time $t$ domain,

$$\text{retardation} \sim \text{correlation function} \sim \exp(-at^\alpha), \quad a > 0, \quad \alpha = 0.4...1.0.$$  

(1)

The proportionality to a correlation function is a consequence of the classical fluctuation dissipation theorem, FDT.

On the other hand, such ”stretched exponentials” are important in probability theory: They are characteristic functions (Fourier transforms) for stable (Levy) distributions with exponents $\alpha \leq 1$. If the stretched exponentials Eq.11 are really indications for a Levy distribution, then the latter is some kind of (inverse) Fourier transform of such exponentials. Graphs for $\alpha \leq 1$ are in Ref.9, pp.305-311.

Since the Fourier transform of the above correlation function from the FDT is a spectral density $x^2(\omega)$ for an extensive variable $x$ corresponding to the concrete retardation, the relevant Levy distribution density is proportional to $x^2(\omega) \ d\omega$,

$$f(\omega) \ d\omega \sim x^2(\omega) \ d\omega.$$  

(2)

This density is fractal at high frequencies,

$$\text{spectral density } x^2(\omega) \sim \omega^{-1-\alpha},$$

$$\text{susceptibility } \alpha''(\omega) \sim \omega x^2(\omega) \sim \omega^{-\alpha},$$  

(3)
with the same exponent $\alpha$; $\varepsilon''(\omega)$ is the loss part of the susceptibility (dynamic compliance) corresponding to $x$, $\omega$ the frequency; $\log \omega$ is called the mobility. The general concept of fractality is restricted here to a power law expressing selfsimilarity.

A Levy distribution with exponent $\alpha < 1$ has neither a finite variance $D$ nor a finite expectation $E$,

$$D(\omega) = \text{Var}(\omega) \to \infty \text{ for } 0 < \alpha < 2,$$

$$E(\omega) \sim \int_{\omega>0} \omega x^2(\omega) d\omega \to \infty \text{ for } 0 < \alpha < 1.$$  (4)

The second equation (4) leads to a preponderant component in the Levy sum for a Levy distribution considered as a stable limit distribution. One term of the sum retains a finite influence of order the “tilt” $(1 - \alpha)$ on the sum, irrespective that the number of its components tends to infinity.

Are all these properties a direct consequence of the experimental Kohlrausch function (1), especially for short times? Are additional arguments necessary that cannot simply be concluded from the existence of a Kohlrausch function or from present experiments at short times $t$ or, correspondingly, at large frequencies $\omega$?

As indicated above, we try here an answer via a defect pattern from free volume $V'(\omega)$, making higher mobility ($\log \omega$) at places where more local free room is available for molecular motion. We shall introduce a Levy sum via separated partial systems or thermodynamic subsystems and try to explain the property $\alpha < 1$ by some kind of instability.

It is a general difficulty in understanding liquid dynamics by an approach that represents the complicated motion of molecules with ”strong interaction” between many of them by means of statistical independence, being one of the basic assumptions to get a Levy distribution.

The aim of this paper is a quasi thermodynamic approach to the dynamics of classical liquids starting from a robust mathematical and physical background for a fluctuating pattern with Levy defects. The mathematics used is based on the classical theorems of Darling and Feller. The mathematical development along their original proofs is accompanied by physical arguments, because the handling of a probability distribution with nonexistent expectation and variance (Eq. (4)) is strange for physicists which are educated and experienced by only distributions that have normal (Gauss) limit distributions with finite, existing variances and expectations, in particular with no preponderant components in the limit sum.

II. TERMINOLOGY FOR OUR LEVY SITUATION

Aim. A glossarial introduction of some verbal concepts seems useful for the ”thermodynamic” application of the Levy distribution in different fields. Calling $f(x) dx = p(x) dx$ the density of a stable Levy distribution, then examples for the $x$ coordinate of the sample space are: $x = \omega$ for the frequency of liquid dynamics, $x = k$ for the wave vector of cosmic density fluctuation, and $x = money$ for the economics of a Levy society (9, p.334-336). The discussion with the aid of Levy distribution is more suitable for the macroscopic, phenomenological thermodynamics (e.g., the state) and for susceptibilities near the equilibrium (modulus $m(\omega)$, compliance $j(\omega)$); the discussion with a Levy flight is more suitable for a molecular approach, e.g. the molecular diffusion leading to equilibrium values of a chemical potential. Warning: This Section is not a summary of the difficult probability theory of stable distributions.

Concepts. (1) Levy sum is defined by

$$S_n = X_1 + \ldots + X_n$$  (5)
where the Levy sum components $X_i$ are equivalent (cf. Point (2), below) independent random variables. The sum is suitable for the discussion of additive situations, e.g. for extensive thermodynamic variables, compliances, or for money in economics. (For the index $i$ cf. Point (4), below).

2) **Equivalence** of the Levy components means that their distributions $F_i(x)$ differ only by location ($\beta_i, b$) and scale or norming parameters ($a_i, a$), e.g. for $i = 1, 2$,

$$F_2(x) = F_1(x_\gamma + \beta_\gamma), \ a_1 > 0. \quad (6)$$

Mathematically it is said that they are "of the same type". Another notion for two distributions $U$ and $V$ is: $U \doteq aV + b$. Often, mathematically, it is said that ". . .there are constants $a_i$ and $\beta_i$ so that..". In the applications we need robust reasons for that: physical, cosmological, economical... The "same type" is used for general arguments, the "parameters" are used for individual properties, e.g. for subsystems

3) **Exclusiveness. Levy scaling.** The concept means that there are mathematically stable limit distributions ($n \to \infty$) only for Gauss ($\alpha = 2$) and Levy ($0 < \alpha < 2$), with $\alpha$ the Levy exponent (cf. Eq. 7 and Point (4), below). For variations of components (small $n$), there are domains of attraction to the limit only for this two cases. It is important for the applications, that there is a broad spectrum of possibilities which tend to only the two sharply defined limits: Gauss or Levy, for the free volume or dynamics of liquids, or for the invisible hand of economics. We have then, for the $n \to \infty$ limit distributions, only one behavior of norming constants. In the form of $S_n \doteq c_n x_n + \gamma_n$, we get $c_n = n^{1/\alpha}$ (Levy scaling). A useful concept is the scaled Levy sum,

$$S_n = n^{1/\alpha}. \quad (7)$$

This sum is existent for $n \to \infty$; the components $X_i$ are then equivalent to $S_n$. A norming factor $n^{-1/\alpha}$ is for "damping" the $n^{1/\alpha}$ "increase" of the original nonscaled Levy sum $S_n$. This damping is much stronger than for Gauss ($1/\sqrt{n}$ for $\alpha = 2$). Examples are the sharp hierarchy of the ordered Levy sum for $\alpha < 1$, Ref. 5, or the non-Arhenius behavior of the dynamic glass transition at low temperature (Section VI.D), cf. also Theorem 1, below.

4) **Pluralism.** This concept describes the great variety of the Levy distribution for applications. Two Examples. A. According to Eqs. 4, the Levy exponent $\alpha$ distinguishes three general cases (apart from some special cases for $\alpha = 2$ and $\alpha = 1$): (a) Expectation $E$ and Variance $D$ both finite: Gauss, $\alpha = 2$; (b) $E$ finite ("existent"), but $D$ infinite ("nonexistent") for $1 < \alpha < 2$; and (c) both $E$ and $D$ infinite for $0 < \alpha < 1; 1 - \alpha > 0$ is called a "tilt". The (b) region is called hierarchy, the (c) region is called dictoriant (because we find a preponderant Levy component there) on the top of a sharper hierarchy. Example for (b): stock market with usually $\alpha \approx 1.5$. Further. The Gauss case may be called democracy. The general equivalence of the Levy sum components is called primary democracy. – B. The index $i$ of the components $X_i$ in Eq. 5 must be completed by further aspects: For the dynamics of liquids by temperature, pressure, kind of response after different disturbances; for the Levy society by the field (economics, politics, culture), and so on. The pluralism is a wide-ranging concept: Even for the same situation or the same defect, different response can have different exponents with different dependence on temperature, pressure, and so on. Such "individual" $\alpha$ exponents are not fixed by general arguments (cf. Section VI.C, below).

5) **Fractality** characterizes here the power laws of Eq. 3 and their selfsimilarity. Defining $F(x)$ or $F(x)$ as the distribution, $f(x)$ or $f(x)$ as the density with $F_i(x) = \int_0^x f_i(\xi) d\xi - f(x)$ is continuous for Levy distributions and $1 - F_i(x) = \int_0^\infty f_i(\xi) d\xi$ for large $x$ coordinates as tail, the fractality according to Eq. 3 holds for the large $x$, i.e. for the tail: $f(x) \sim x^{1-\alpha}$, with $\alpha$ the Levy exponent. Complementarily, for the characteristic function (e.g. for the simpler Laplace transform instead of Fourier, $\phi(\lambda) = \int_0^\infty e^{-\lambda t} f(x) dx = E(e^{-\lambda X})$, we get a stretched exponential according to Eq. 1 with $t = \lambda$ for Fourier and $x = \alpha$ frequency in a spectral density $p(\alpha) = f(\alpha)$. The stretched exponential is more suitable for large times (or for less money in economy), where fractality is more suitable for high frequency (or many money in economy). The input of a spatial aspect (Eq. 14, below) leads to a spatial unity, called "defect", with, for $\alpha < 1$, a preponderant component in the midst, a fractal (hierarchical) center, and a stretched, cooperative periphery, all with the same exponent $\alpha$. The size of the defect may be defined by a cooperativity $N$. 
(6) Levy instability. Mathematically, the term "stable" means that, whatever the deviations in a finite sum of independent random variables \( X_i \) in the domain of attraction are, the limit sum \( S_n \) stabilizes itself, i.e. \( S_n/n^{1/\alpha} \) converges to a definite limit distribution for \( n \to \infty \). Exclusiveness for \( \alpha < 2 \) leads then to a Levy distribution. In the applications, for illustrative or intuitive purposes, fractality for large \( x \) coordinate values, esp. with a preponderant component for \( \alpha < 1 \), can be associated with a very special kind of instability, called "Levy instability." Example for liquids: a local breakdown to high frequencies due to a center of lower particle density, i.e. a local concentration of free volume. In the applications, of course, the high frequencies (\( \Omega \)) are very large but finite. "Very large" means a comparison of the center with the periphery, and \( \Omega \to \infty \) means a tendency, e.g. \( \mathbf{D}(\omega) \sim \Omega^{2-\alpha} \) and \( \mathbf{E}(\omega) \sim \Omega^{1-\alpha} \), formally with \( \omega = \Omega \to \infty \). The liquid example is described in Section III.A.

(7) Levy situation is defined as an applicative situation (e.g. in physics, cosmology, economics) with a robust equivalence of the Levy components in the Levy sum and with robust reasons for a Levy instability for explanation of exponents \( \alpha < 2 \), in particular of \( \alpha < 1 \) when a preponderant component is to be expected.

**Examples.** A distribution is symmetrical, if \( f(x) = f(-x) \); its expectation is zero, \( \mathbf{E}(X) = 0 \). The spectral densities for classical (non-quantum mechanical) liquids are symmetrical, \( x^2(-\omega) = x^2(\omega) \). Positive variables \( X \geq 0 \) (i.e. the variables \( x \geq 0 \)) are often physically motivated. For our (and many general) considerations about Levy distribution, \( X \geq 0 \) is no serious restriction, because centering (selection of \( \gamma_i \), in Point (3) above) is relatively free in the frame of equivalence. [To find e.g. the general expression for Levy distributions, depending on \( \alpha \) and \( \gamma \) (Ref. \( \text{p.}580 \)), no centering procedure is required for \( \alpha < 1 \), while for \( \alpha > 1 \) the natural centering to zero expectation suffices. In Particular, the influence of preponderant component is independent of \( \gamma \) values. For construction of a concrete molecular structure of a defect, however, centering may be important.]

For the sum of two independent variables, \( X_1 + X_2 \), the joint probability density \( f_{x_1,x_2}(x_1,x_2) = f_1(x_1) \cdot f_2(x_2) \). A common variable may be defined by the sum \( x = x_1 + x_2 \). The common distribution \( F(x) \) for \( P(\xi < x) \) is obtained by integration over the \( x \) space region \( x < x_1 + x_2 \) with measure \( dx_1dx_2 \). We get then for the sum density the convolution

\[
f = f_1 * f_2, \quad \text{i.e.} \quad f(x) = \int f_1(z) \cdot f_2(x-z) \, dz.
\]

(8)

For the ratio of independent variables, \( X_1/X_2 \), we have e.g. a joint probability density \( f_{x_1,x_2}(x_1,x_2) \sim x_2 \cdot f_1(x_1x_2) \cdot f_2(x_2) \) for \( F(x) = P(\frac{\xi}{x_2} < x) \). The integration is more complicated than for the sum, because the ratio of the variables \( x_1/x_2 < x \) must be used. The result is

\[
f(x) = \int_{-\infty}^{\infty} |z| \cdot f_1(zx) \cdot f_2(z) \, dz
\]

(9)

with the possibility of a partial rescaling procedure that affects \( f_1 \) and \( f_2 \) differently: the product \( x_1x_2 \) vs. \( x_2 \) alone.

Be \( f_1 \) a symmetrical Gauss density (\( \alpha = 2 \)) with variance \( \mathbf{D}_1 = \sigma_1^2 \), and \( f_2 \) such a density with \( \mathbf{D}_2 = \sigma_2^2 \), then, for independent variables, the sum gives again a symmetrical Gauss density with variance \( \mathbf{D} = \sigma^2 = \sigma_1^2 + \sigma_2^2 \) (Gauss + Gauss = Gauss). Their ratio, however, gives a Cauchy distribution,

\[
f(x) = \frac{\sigma_1\sigma_2}{\pi(\sigma_1^2 + \sigma_2^2x^2)}.
\]

(10)

This is a symmetrical Levy distribution with exponent \( \alpha = 1 \), i.e. with no existing variance (\( \mathbf{D} = \infty \)), and applied for positive variables \( x \geq 0 \), also with no expectation (\( \mathbf{E} = \infty \)); (Gauss/Gauss = Cauchy). The ratio favours large variances, but a Gauss/Gauss ratio cannot generate preponderant components. The latter are restricted to Levy exponents \( \alpha < 1 \).

<ref>Ref. \( \text{p.}580 \)</ref>
III. FLUCTUATING PATTERN WITH LEVY DEFECTS

This section is to describe pictures for Levy instability and for equivalence of Levy sum components, i.e. a Levy situation for the fluctuating pattern of molecular liquids.

A. Free volume. Partial systems. Levy instability

To get a Levy instability, we consider a local breakthrough of molecular mobility (log $\omega$) as response to a virtual local concentration of free room for molecular movements. The aim of the concept of free volume ($V'$) for the pattern is that a local concentration of free volume, i.e. a low local particle density, pushes the mobility there to high frequencies, in the limit to $\omega$ of order $\Omega \approx 10^{12}$rad/s as for free rattling of particles in a sufficiently large molecular cage of next neighbors. Small local density reduction of order some percent is sufficient to rise $\omega$ from e.g. $10^{6}$rad/s in the main transition to cage rattling, because the repulsive inter (and relevant intra) molecular potentials are steep. Locality of the breakthrough follows from a given free volume of the total sample in equilibrium. Lower local density here demands higher local density somewhere else. Lower density everywhere would finally lead to negative pressure. As the degree of divergence in expectation $E$ and variance $D$ is larger for smaller Levy exponents $\alpha$, we may say that this exponent controls the Levy instability.

To get a large number of equivalent small systems as components of a Levy sum we partition the volume of a subsystem into small parts, called partial systems: The large numbers needed for a robust dynamic partition for the limit distribution of spectral density $x^2(\omega)$ are thought to be numbers of random attempts for rearranging the molecular situation in the nanometer range there. We have many high-frequency attempts for a relevant low-frequency ($\omega$) rearranging in the dispersion zone considered; the number of attempts (as used for the limit) in the time interval $1/\omega$ is much larger than the number of affected particles. We think about molecular collisions which may cause the emission of a quantum $\hbar \omega$ that can be catched by Nyquist’s transmission lines in a model for thermodynamic response, cf. also Ref.\(^9\), p. 270.

Be careful to distinguish the two possibilities. The large number $n$ for the spatial systems leads to a Gauss distribution for free volume with weak contrast in the pattern, the large number $n$ for the attempts leads to a Levy distribution with exponent $\alpha < 1$ for the spectral density with strong contrast. The relation between the two is explained in Step 2 of the Proof for the Representativeness Theorem in Section VI.D, below.

We now assume that the frequency of slow rearranging ($\omega$) is locally controlled by the local free volume ($V'$). For given independent partial systems (index $i$) we assume, therefore, the existence of functions $\omega_i(V_i)$ for each partial system,

$$\omega_i = \omega_i(V'_i) \quad \text{(11)}$$

(no sum convention; Fig. 1). This assumption is justified by the high attempt rate. If the partial system is not too small, i.e. if the attempt rate inside is still much larger than the rearranging frequency,

$$\omega \ll \text{attempt rate} \lesssim \Omega \approx 10^{12}\text{rad/s}, \quad \text{(12)}$$

then we find a limit distribution for each partial system. Robustness of equivalence and partition for the domain of attraction and exclusiveness of Levy distribution allows to find a local control (11) and to identify the partial systems $\{i, i = 1, \ldots, n\}$ with independent components of a Levy sum for free volume,

$$S'_n = V'_1(\omega_1) + \ldots + V'_n(\omega_n). \quad \text{(13)}$$

B. Cooperativity

A problem for intuition is whether the statistical independence of partial systems with infinitive expectation (4) due to high attempt rates is sufficient for explanation of a phenomenon that is usually described by cooperativity or cooperative
FIG. 1: Local control of mobility \( \log(\omega) \) by free volume \( V' \) of partial systems, or by free volume of representative subsystems (index \( i \), Eq. (11)).

In the limit, each component has an equivalent dynamic distribution \( x^2(\omega) \) [that is of the same type as all others, including the sum]. This is valid also for partial systems in the periphery \( (14) \) of the defect. Their contribution to the sum (general susceptibility \( (2) \) may be small, nevertheless the movements in these partial systems may become very lively because of the infinite expectation \( \mathbb{E} \rightarrow \infty \). Any partial system can profit from the possibilities. It can e.g. take the advantage to use the high frequencies for an effect on the rearrangement, e.g. to become preponderant and get the center: All particles may take part in diffusion.

Competition for cooperativity can so be simulated by independent attempts of partial systems. Expressed e.g. by the Gauss distribution for free volume, large fluctuation of one partial system \( i \) must be compensated by small fluctuation of some others, because the fluctuation of the sum becomes relatively small \( (1/\sqrt{n}) \). We get the chance to determine the extent of cooperativity \( (N_{mt}) \) from thermodynamic variables (Section VII.A, below). For the Levy distribution with exponent \( \alpha < 1 \) for dynamics, the competition of the interchangeable, equivalent Levy sum components leads to a preponderant component, probably connected with the diffusion step through the cage door, necessary for equilibrium in liquids.

How can cooperativity be distinguished from collectivity, sometimes also used\(^{20} \) for the glass transition? Two types of collectivity are used for glass transition: (I) A common treatment of the high frequency \( c \) and \( a \) processes\(^{20,27} \) (Fig. 3, below), and (II) A certain structure of thermodynamic phases (order parameter, clustering\(^{15,17} \)).

Let us here discuss type (I) collectivity. The separation of \( c \) and \( a \) process is related to two neighbored processes that both are at high frequencies and have direct mechanical relations. A Götze ansatz can, therefore, use one formula for both, e.g. \( m(t) = v_1\phi(t) + v_2\phi^2(t) \). where \( m(t) \) is a memory and \( \phi(t) \) is the relevant correlator, the mode of the mode coupling theory MCT. This leads to a cusp bifurcation into \( a \) and \( c \) and to several scaling properties around the bifurcation, with reasonable experimental confirmation. Collectivity is therefore a suitable concept for the \( a \) and \( c \) processes in the relaxation chart of dynamic glass transition.

What, however, about the crossover region from the \( a \) to the \( \beta \) and \( \alpha \) processes (Fig. 3, below)? This is no bifurcation (Section VI.E below), which was assumed by MCT at the beginning. The rare experimental information about the crossover\(^{28,29} \) shows two scenarios different from a bifurcation. It is discussed below (Section VI.E) that the defect pattern alone suffices to explain the existence and location of the Johari Goldstein \( \beta \) process. We see that collectivity is not needed for understanding the \( \alpha, \beta, \) and \( \phi \) processes of the dynamic glass transition.
Remark. The above “inside” argumentation via partial systems for obtaining a Levy distribution is consistent to an “outside” proof via minimal subsystems (Fig. 4, Representativeness theorem Section VI.D).

C. Johari’s islands of mobility

The concept of islands of mobilities is introduced by Johari\textsuperscript{10}. In our context, we argue as follows.

Since the free volume ($V'$) has finite variance and expectation, there is no preponderant component in its distribution: we find a Gauss distribution for $V'$. For a dynamic spectral density $x^2(\omega)$ of the “same” partition in partial systems we obtain, however, a preponderant component due to the Levy instability (Step 2 of Section VI.C). A spatial concentration of free volume is, however, possible, if the interchangeable free partial or sub systems can spatially be redistributed. Some shallow ”defect” in a free volume pattern (as basis for a mobility or frequency pattern from Eq. (11)) can then be constructed by means of a general length/time or length/mobility scaling\textsuperscript{11} for relevant modes (Fig. 2a and 2b),

![Defect pattern](image)

FIG. 2: (a + b). Defect pattern. If the white regions have more free volume, and the hatched regions less free volume, then (a) = islands of immobility that are not consistent with the general length/time scaling \textsuperscript{14}, but (b) = islands of mobility are consistent with the general length/time scaling \textsuperscript{14} (dynamic heterogeneity). (c). Sketch of the spatial defect structure. Calling the spatially separable contributions to the susceptibility $\alpha''(\omega) \sim \omega x^2(\omega)$ the "responsibility" [with $x^2(\omega)$ the spectral density via the FDT], we obtain from the above scaling and the Levy distribution a sharpened spatial picture for one defect. The one Levy distribution corresponds to the three parts of the defect: the influence of the preponderant component (for $\alpha < 1$), the fractality of the center, and the cooperativity of the periphery. (d). The size of the defect in the pattern is determined by the average distance (Section VI.B): The statistical independence of minimal representative subsystems for the $mt$ dispersion zone determines a characteristic length $\xi_{mt}$ via von Laue thermodynamics (Section VII.A).

\begin{align}
\text{defect periphery: large mode length } &\sim \text{ low mobility} \\
\text{defect center: small mode length } &\sim \text{ large mobility} \\
\end{align}

This means that the $\omega(V')$ function of (11) increases very sharply at the upper boundary for local free volume fluctuations. We get the picture of Fig. 2c. In the center of the defect we find the partial systems with much free volume, in the periphery those with less free volume. Transformation to the frequency (11) means that the preponderant component related to the spectral
density is near or in the midst of the center for this island of mobility. In summary, we find more free volume in the center of the defect.

Let us underline again, that the density differences across the defect are small, since the repulsive intermolecular potentials are steep. We get a dynamic heterogeneity with large mobility differences (but no or a small "structural" heterogeneity): a fluctuating pattern with temporary mobility defects. In terms of point (4) of Section II, the Johari Goldstein $\beta$ process (Section VI.E) contributes to the dynamic dictatorship of the preponderant component.

D. Description of the defect

1. The defect embraces three properties of the Levy distribution (Fig. 2.c): (i) Fractality properties (3)-(4) that care for the influence of large frequencies in the spectral density. (ii) A stretched exponential (1) for the correlation function. (iii) The preponderant component of the Levy sum for spectral density.

Assuming the above space/time scaling (14), then the Levy distribution stabilizes the Levy instability by connecting the center of the defect (fractal divergencies at high frequencies, preponderant component in the midst of the center, collection of partial systems with more free volume) with its cooperative periphery (long-time tail of relaxation from the stretched exponential, collection of partial systems with less free volume). Embracing by one distribution with one exponent $\alpha$ results in the correspondence between center and periphery (without any freezing-in). The statistical independence and equivalence of the Levy sum components inside the defect describes spatial aspects of the competition for cooperativity, e.g. for being the preponderant component in the midst of the center or for belonging to the hierarchy around the midst.

2. We have three aspects of the preponderant component in the defect. (a) Induction of an extraordinary process for volume and entropy fluctuation. (b) The $n \to \infty$ limiting process for the Levy sum pushes the preponderant component in the midst of the center (Sections V.B-C). (c). The molecular picture is the diffusion step through the cage door and the promotion of the Johari Goldstein process.

3. The size of the defect results from the length/time scaling (14). We find an opposite behavior of responsibilities (Fig. 2c) on the way from a given defect to a neighbor defect. The responsibility in the periphery of the first defect decreases and becomes smaller than the increasing responsibility in the periphery of the second defect (Fig. 2d). We get an average distance in the pattern. The absolute length (in nanometers) can be determined by thermodynamics, if there are reasons to consider equivalent defects as some minimal representative units (Sections VI.C and VII.A, below).

The three points 1.-3. for the defects allow some visualization for the shaping power of Levy statistics in form of a fluctuating mobility or responsibility pattern in liquids.

IV. RELATIONSHIP BETWEEN KOHLRAUSCH FUNCTION, LEVY SUM, AND LEVY INSTABILITY. THEOREM 1

A Kohlrausch correlation function (1) can also, in principle, be imagined without a relationship to Levy distributions, e.g. as obtained from a dynamic differential equation or even from a Hamiltonian. As mentioned in Section II, additional things are necessary to relate Eq. (1) with a Levy distribution for spectral density ($x = \omega$). This is expressed by the "if" in the following (Ref. 3, p. 448).

**Theorem 1.** For fixed Levy exponent $\alpha$, $0 < \alpha < 1$, the function $\varphi^{(\alpha)}(\lambda) = \exp(-\lambda^\alpha)$ is the Laplace transform of a distribution $F^{(\alpha)}(x)$ with the following properties:
(1) $F^{(\alpha)}(x)$ is a Levy distribution; more precisely, if $X_1, \ldots, X_n$ are independent random variables with distribution $F^{(\alpha)}(x)$, then the normalized (scaled) Levy sum $(X_1 + \ldots + X_n)/n^{1/\alpha}$ has again the distribution $F^{(\alpha)}(x)$.

(2) Fractality is obtained that may be normed by

$$x^{\alpha}[1 - F^{(\alpha)}(x)] \to 1/A(1 - \alpha), x \to \infty.$$ \hspace{5cm} (15)

**Comment.** According to our basic assumption (Section I) we think here about spatially separable partial systems when components of a Levy sum are considered. For a physical Levy situation we need, for Theorem 1, a robust partition in the normalized (scaled) Levy sum

$$\text{Such functions may be used to describe the domain of attraction of a probability distribution. The limit of Eq. (16) is only fulfilled by power functions (the basis for our fractility) which is, after a special selection of the probability by the Gamma function of the tilt (1 above influence) is}$$

is completely monotone. Since $\phi^{(\alpha)}(0) = 1$, the measure $F^{(\alpha)}(x)$ with Laplace transform $\phi^{(\alpha)}(x)$ has a total mass 1.

The proof for part (2) is obtained along the following line. A positive function $L$ defined for $0 < x < \infty$ varies slowly at $\infty$, if for every fixed $x$

$$L(ax) \to L(a) \text{ for } a \to \infty.$$ \hspace{5cm} (16)

Such functions may be used to describe the domain of attraction of a probability distribution. The limit of Eq. (16) is only fulfilled by power functions (the basis for our fractility) which is, after a special selection of the probability by the Gamma function of the tilt $(1 - \alpha), \Gamma(1 - \alpha)$, expressed by (15). End of the Proof.

**V. PHYSICAL UNDERSTANDING OF THE PREPONDERANT COMPONENT FOR LEVY DEFECTS**

Let us recall Feller’s (Ref. p. 172) mathematical heuristic. "Consider, for example, a stable distribution ... with $\alpha < 1$... The average $(X_1 + \ldots + X_n)/n$ has the same distribution as $X_1 n^{1 - 1/\alpha}$, and the last factor tends to $\infty$. Roughly speaking we can say that the average of $n$ variables is likely to be considerably larger than any given component $X_i$. This is possible only if the maximal term $M_n = \max[X_1, \ldots, X_n]$ is likely to grow exceedingly large and to receive a preponderating influence on the sum $S_n$". Section V is firstly to bring some analysis used and is secondly to describe the preponderant component in Levy defects more precisely than in Section III.

**A. Darling Lemma**

To calculate the influence of a preponderant component as expressed by the Levy exponent $\alpha < 1$ we need a method for handling the maximal component $(M_n)$ in a Levy sum $(S_n)$. This is demonstrated along the original Proof for following (Darling).

**Lemma.** The Laplace transform $\varphi_{S_n}(\lambda) \equiv \xi_{S_n}(\lambda)$ of the random variable $Z_n = S_n/M_n$ (which ratio should characterize the above influence) is

$$\xi_{S_n}(\lambda) = n \exp(-\lambda) \int_0^1 (\beta \int_0^1 e^{-\lambda \gamma} f(\gamma \beta) d\gamma)^{n-1} f(\beta) d\beta$$ \hspace{5cm} (17)
with \((\beta, \gamma)\) dummy variables for the probability density \(f\) of equivalent components \(\{X_i\}\).

**Proof.** We start from the equivalence of the Levy components. There is no loss in generality by assuming \(X_1 = M_n\), since each \(X_i\) has a probability of \(1/n\) of being the largest term (and \(P\{x_i = x_j\} = 0\) for \(i \neq j\) since the distribution is presumed to be continuous). The joint density \(f_g\) (index \(g\)) is then

\[
f_g(\beta_1, \beta_2, \ldots, \beta_n) = \begin{cases} \frac{n}{\beta_1} f(\beta_1) f(\beta_2) \cdots f(\beta_n) & \text{if } \beta_1 = \max\{\beta_i\} \\ 0 & \text{otherwise} \end{cases}
\]  

Then the relevant expectation \(E_{\gamma}\) =

\[
E(e^{-\gamma Z_n}) &= \int_0^\infty \cdots \int_0^{x_1} e^{-\lambda(x_1+x_2+\ldots+x_n)/x_1} \\
& \times f_g(x_1, x_2, \ldots, x_n) \, dx_1 \, dx_2 \cdots dx_n \\
&= ne^{-\lambda} \int_0^\infty \cdots \int_0^\infty e^{-\lambda(y_2+\ldots+y_n)/\beta} \\
& \times f(\gamma_2) \cdots f(\gamma_n) \cdot f(\beta) \cdot d\gamma_2 \cdots d\gamma_n \, d\beta \\
&= ne^{-\lambda} \int_0^\infty \left( \int_0^\infty e^{-\lambda y/\beta} f(\gamma) \, d\gamma \right)^{n-1} f(\beta) \, d\beta. \quad (19)
\]

The Lemma follows from rescaling of the dummy variables: \(\beta d\gamma \rightarrow d(\gamma \beta)\). The upper limit 1 in the inner integral comes from \(\gamma \leq \beta\), i.e. from the maximality of the component for \(\beta\). Note the different variables, \(\beta\) and \(\gamma \beta\), for the densities \(f\) in the Lemma (17), typical for ratios of random variables (9).

**B. Influence of the preponderant component. Theorem 2**

This subsection is to calculate the expectation of the random ratio: Levy sum over its maximal component, \(Z_n = S_n/M_n\) with variable (observable) \(E_{\gamma}\), for \(n \rightarrow \infty\).

**Theorem 2** (Darling\(_\beta\)). The expectation of \(Z_n\) for the limit \(n \rightarrow \infty\) with a Levy exponent \(0 < \alpha < 1\) is

\[
E(S_n/M_n) \rightarrow 1/(1-\alpha). \quad (20)
\]

The Proof is divided in two parts: The limit is first explicitly calculated for the limit distribution itself, and in a Comment the participation of the domain of attraction is discussed. We put for the inner integral of the Laplace transform \(\varphi_{(n)}(\lambda) = E_{\gamma}(\lambda) = E(e^{-\lambda Z_n})\) from the Lemma, Eq. (17).

\[
\psi(\beta) \overset{\text{def}}{=} \beta \int_0^1 e^{-\lambda y} f(\gamma \beta) \, d\gamma. \quad (21)
\]

Note the different variables in exponent and density. In the limit \((n \rightarrow \infty)\), only the tails of the Levy distribution are important (cf. the Comment). Hence we put for their fractility

\[
1 - F'(x) = \tilde{c}/x^\alpha. \quad (22)
\]

with a constant \(\tilde{c} = \tilde{c}(\alpha, \tilde{\gamma})\) where \(\tilde{\gamma}\) is ascribed to centering. There are no further parameters beyond \((\alpha, \tilde{\gamma})\) in the general Levy density. Eq. (22) is a consequence of Eqs. (16) and (17). Then, from arithmetic manipulation in direction of the tails, such as
we get

$$\psi(\beta) = 1 - (1 - F(\beta)) - \lambda \int_0^1 e^{-\lambda \gamma} [(1 - F(\gamma \beta)) - (1 - F(\beta))] \, d\gamma.$$  \hspace{1cm} (24)

The integral yields

$$\int_0^1 e^{-\lambda \gamma} [\ldots] \, d\gamma = \frac{\tilde{c}}{\beta} \alpha \int_0^1 (e^{-\lambda \gamma} - 1) \frac{d\gamma}{\gamma^{\alpha-1}}.$$  \hspace{1cm} (25)

Defining the number

$$\phi_1 \equiv \alpha \int_0^1 (e^{-\lambda \gamma} - 1) \frac{d\gamma}{\gamma^{\alpha-1}}.$$  \hspace{1cm} (26)

we obtain

$$\psi(\beta) = 1 - (1 - \phi_1) \tilde{c}/\beta^\alpha.$$  \hspace{1cm} (27)

Rescaling now with the variable

$$v \equiv \frac{\tilde{c}}{\beta} \alpha,$$  \hspace{1cm} (28)

(which eliminates \(\tilde{c}\) and therefore any centering \(\gamma\) in \(\tilde{c}\)), gives in our limit

$$\tilde{\xi}(\lambda) = \frac{e^{-\lambda}}{1 - \alpha \int_0^1 (e^{-\lambda \gamma} - 1) \gamma^{1-\alpha} \, d\gamma}.$$  \hspace{1cm} (29)

The wanted expectation value follows as

$$E(\tilde{\xi}(\lambda)) = -\tilde{\xi}'(0) = -d\tilde{\xi}/d\lambda (\lambda = 0) =$$

$$= -\lim_{\lambda \to 0} \frac{d}{d\lambda} \left(1 - \lambda + \frac{\lambda \alpha}{\alpha - 1}\right) = \frac{1}{1 - \alpha}.$$  \hspace{1cm} (30)

The influence of the maximal term on the limit Levy sum is calculated as \(1/(1 - \alpha)\) in the ratio \(S_n/M_n\). The only remaining parameter is the Levy exponent \(\alpha\).

We may say, that the influence of the maximal term, the preponderant component, is of order \((1 - \alpha)\), (the tilt in cosmological terms). Compared with Gauss, where the influence of the maximal term remains infinitely small, we get e.g. for \(\alpha = 1/2\) the surprising result, that the maximal, the preponderant component has approximately the same influence as the rest of the infinitely many components.

**Comment.** The domain of attraction is handled by the deviation from Eq. (16), using the symbol \(o(1)\) which means of the order less than 1,
We pursue this symbol along the proof by the chain due to rescalings,

$$o(1) \to o(1 - F(\beta)) \to o(1/n).$$  \hfill (32)

From (21) we get for $1 - F(\gamma \beta)$ after $\gamma \beta \to \gamma$ rescaling

$$1 - F(\gamma \beta) = (1/\gamma^\alpha) \left(1 - F(\gamma)(1 + o(1))\right).$$  \hfill (33)

The integral (25) yields then the

$$\text{integral} = (1 - F(\beta)) \alpha \int_{0}^{1} (e^{-\lambda \gamma} - 1) \gamma^{-1-\alpha} d\gamma + o(1 - F(\beta)).$$  \hfill (34)

The shift into the tail is therefore

$$\psi(\beta) = 1 - (1 - \phi_1)(1 - F(\beta)) + o(1 - F(\beta))$$  \hfill (35)

with the same $\phi_1$ as before, Eq. (26). Since $|\psi(\beta)| < 1$ for bounded $\beta$, the early portion of the integral for $\xi_n(\lambda)$ is negligible for sufficiently large $n$. This can be seen after introduction of a new variable instead of (28), now

$$v = n(1 - F(\beta)).$$  \hfill (36)

Hence

$$\xi_n(\lambda) \sim e^{-\lambda} \int_{0}^{n} (1 - \frac{v}{n}(1 - \phi_1) + v o(1/n))^{n-1} dv,$$  \hfill (37)

and we get again $1/(1 - \alpha)$ in the limit. End of the Proof for Theorem 2.

We see from the Comment chain (32) that the preponderant component really pushes the play into the tail’s fractality asymptote. The large number of participants (attempts in our model) pushes the preponderant component into the midst of the defect center; Fig. 2c is a picture for the shaping power of the Levy statistics.

Remark. Absence of a preponderant component would mean $S_n/M_n \to \infty$. This is prevented by the $o(1/n)$ pushing into the defect center and the finiteness of the remaining integral due to the fractality $\gamma^{-1-\alpha}$ in the denominator of (34). This leads to the finiteness of $-\xi'(\alpha)$ in (30).

C. Verbal understanding of a preponderant component in a defect

This brings some comments to the Points (4) and (6) of Section II and continues the defect discussion of Section III. The Levy distribution is characterized by a large number $(n)$ of statistically independent equivalent random components in a sum (inside example: the partial systems of a subsystem; outside example: the subsystems of a larger subsystem) and a Levy exponent $\alpha$ that describes some Levy instability, larger for smaller $\alpha$. Let us remark, that the equivalence of the Levy sum components means that they are interchangeable near equilibrium. They can be interchanged between the periphery, the hierarchy, and the
In a spatial picture of a $\alpha < 1$ defect (Fig. 2c above), the preponderant component is in the midst of the fractal center of the defect. This component is pushed in the center by Eq. (32). The defect center collects the components with more influence around the preponderant component: the sharp "hierarchy" below the "dictator". The other components are in the cooperative periphery where the components with temporarily less influence on the sum are collected, although all components are equivalent by having infinite expectation ($E \to \infty$). The Levy distribution stabilizes the defect by connecting the fast fractal center with the slow cooperative periphery; there is a correspondence between center and periphery. The cooperativity is stimulated (encouraged) by the equivalence in expectation. For infinite expectation, the competition of the equivalent and independent components is stimulated by the property that a considerable part of influence, of order the tilt $(1 - \alpha)$, on the total sum is realized by only one, the preponderant component, interchangeable with the others in the equilibrium.

In other words, the "actual events" are pushed in the center with the preponderant component. This are therefore fast actions. In liquids, the preponderant component in dynamics may induce the diffusion step through the molecular cage door as basic process to maintain the equilibrium. In the midst of the center there is only action for one, the preponderant component. [The "dictator" can fill the midst because of his infinite "personal" expectation, $E \to \infty$.] This is mathematically complemented by the absence of (this) one component outside, which absence makes the integrals of Eq. (17) suitable.

Let us conclude with an example for nonequilibrium. If we have an underlying trend, in liquids e.g. a cooling rate $\dot{T} = dt/\dot{T} < 0$, then we may ask, which parts of the defect firstly cannot longer follow. Due to the general length/time scaling relevant for the spatial structure of the defect, it is the slow periphery that first falls out of equilibrium. The trend leads unavoidably to incrustation, to a frozen vault structure (Ref. 9, p. 386), while the center continues a time with responsibility to outer dynamic contacts.

VI. DYNAMIC GLASS TRANSITION IN MODERATE MOLECULAR LIQUIDS

A. Dispersion zones in a mobility -(reciprocal) temperature diagram

The term "dynamic glass transition" is synonymously used for the dynamics in liquids. For classical molecular liquids of moderate complexity ("moderate liquids") we find a surprisingly general relaxation chart, i.e. a log $\omega - 1/T$ diagram (Fig. 3). There is a characteristic arrangement of dispersion zones (zones of higher dissipation) with a typical width of one or a few frequency decades, if crystallization can be prevented. The symbols and names of these zones are listed in the figure caption. This picture can be discussed as a consequence of Levy defects for the main transition ($mt = a$ plus $\alpha$ process) and for the Fischer modes ($\phi$).

The concentration of mobility (log $\omega$) into zones can be explained by the defects. The width of the imaginary part of the susceptibility (dynamic compliance $\alpha''(\omega)$) is, because of $\alpha''(\omega) \sim \omega^{x^2(\omega)}$, determined by the embracing Levy distribution for $x^2(\omega)$. The corresponding $\alpha''(\omega)$ graphs for $\alpha \leq 1$ show (Ref. 3, p. 307 and p. 311) an approximate half width of one decade in frequency $\omega$, divided by the Levy exponent $\alpha$,

$$\Delta \log \omega = (1.05 \pm 0.05)/\alpha.$$

[This equation is valid independently on the spatial dimension of the defect model. The width of the $\alpha''(\log \omega)$ peak depends only from the Levy exponent $\alpha$.] Large mobility distances between the zones in the relaxation chart care for large attempt rates in partial systems as used for the above inside treatment.

The non-Arrhenius behavior of the main transition $mt$ is, in principle, connected with the increase of its cooperativity $N_{mt}$ at low temperature (Fig. 6, below) via a Levy scaling equation

$$d \log \omega / dT \sim N_{mt}^{1/\alpha}.$$

$$38$$

$$39$$
FIG. 3: Relaxation chart for moderate liquids; log $\omega$ the mobility, $T$ the temperature. Dispersion zones: $a$ the high-temperature process, $\alpha$ the cooperative process, $(mt = a + \alpha)$ the main transition or main process = The dynamic glass transition), $\beta$ the local Johari Goldstein process, $C$ the $a - \alpha$ crossover region, and $\phi$ the Fischer modes. [Boson peak $b$ and cage rattling $c$ are not further discussed.] The conventional glass temperature $T_g$ corresponds approximately to the intersection of the $\alpha$ process with the experimental 10 millihertz isochron. $T_c$ is the crossover temperature. More complicated substances such as polymers or liquid crystals may have additional dispersion zones.

where $N_{mt}$ is the number of molecular units in the $mt$ defect. This equation is related to the existence of a bulk modulus $m_f$ being the "reciprocal" of an invariant free volume $v_f \sim 1/m_f$,

$$v_f = dV'/d\log \omega,$$

invariant against the partition of a larger system into partial systems (Section VLD).

A Levy treatment of partial systems inside one minimal subsystem (Ref. 9, p. 327, see also Section VLD, below) is explicitly based on our main assumption to consider spatially separable components of a Levy sum. Further development leads to an extreme smallness of $m_f$ for small Levy exponents $\alpha$ at low temperature, $m_f (\alpha \lesssim 0.4) \approx m_f (T = T_c)$. The large curvature of the $mt$ in the relaxation chart follows from (39) with a thermodynamic equation along the $mt$, $dV' \sim dT$:

$$d\log \omega / dT \sim d\log \omega / dV' \sim 1/v_f \sim m_f$$

increases more than Arrhenius, $d\log \omega / dT \sim 1/T^2$. The equation

$$m_f \sim v_f^{-1} \sim N_{mt}^{-1/\alpha}$$

is called control equation. This actual operational freedom $m_f$ becomes narrow inside large units, irrespective of the dictatorial control by a preponderant component.

Remark. The extreme smallness of the operational freedom $m_f$ below $\alpha \lesssim 0.4$ implies an exhaustion of the $mt$ process at low temperature where, in the equilibrium, not enough free volume can be organized by increasing cooperativity of the defect periphery. The $mt$ process is then successfully "attacked" from distributed "accidental" loss effects (Ref. 9, p. 178), and the control by equation (41) is expected to be lost at a surprisingly sharp exhaustion transition.

**B. Gedankenexperiment for finding a minimal subsystem**

If external large heat reservoirs and the imagination of walls between subsystems are given up and if, for dynamics, the subsystems are defined by statistical independence in a given dispersion zone, then the larger subsystems are free in partition,
and all subsystems are freely fluctuating in all relevant thermodynamic variables. We obtain freely fluctuating subsystems.

The following gedankenexperiment is for the definition of representativeness. Consider a sufficiently large freely fluctuating subsystem having a certain spectral density $x^2(\omega)$ (e.g. for fluctuating (free) volume in the main transition and the following increments for thermodynamic variables across the $mt$). Divide this subsystem into two halves. If they also are sufficiently large, then both have the same non-extensive (e.g. density-like) variables. It is said that they are representative. Divide again, till the subsystems become too small for representativeness. We find finally a minimal representative freely fluctuating subsystem for the given dispersion zone: shortly a minimal subsystem.

Representative and minimal means that this subsystem contains one defect and has a size of order the defect size (Fig. 2d). The defect labels the minimal subsystem as a thermodynamic unit. The unit has three corresponding parts: preponderant component, center, and periphery, united by a Levy distribution. [Since the only true unity of the defect is the one preponderant component, we may say that this component makes the minimal subsystem to a thermodynamic unit: to “the molecule” of $mt$ fluctuation of the liquid.]

Representative subsystems have the same relevant thermodynamic variables as the macroscopic systems, with all its fluctuations. This means that also the minimal subsystem has a temperature $T$ that can completely be defined via Carnot and Kelvin, and has an entropy $S$ that can completely be defined via Clausius; both $T$ and $S$ fluctuate, $\delta T \neq 0$, $\delta S \neq 0$, also for the minimal subsystem when it is in the nanometer range. The systems from the gedankenexperiment plus arbitrary combinations of them are expected to be candidates for equivalent and robust components in an appropriate Levy sum for thermodynamics of liquids.

C. Representativeness Theorem. Pluralism

We conclude from the above gedankenexperiment that the shape of spectral density $x^2(\omega)$ in all representative subsystems is the same. We expect additionally from the equivalence of all partitions into a sum of representative subsystems that for additive, i.e. extensive variables the shape of $x^2(\omega)$ is fixed to be a density of a Levy distribution. We show, so to speak, that the bare existence of minimal subsystems in liquids implies the defect. As an example, we think firstly on $x^2(\omega) = \Delta V^2(\omega)$ as a density for free volume ($V'$) fluctuations in the main transition ($mt$).

Representativeness theorem. (Ref. 9, p. 237). Consider the classical (non-quantum mechanical = symmetrical) spectral density for stationary fluctuations of free volume, or a corresponding extensive caloric variable, in the slower part of the $mt$ dispersion zone ($\log \omega$ (rad/s) $< 11$) of a representative freely fluctuating subsystem. This spectral density is a Levy distribution density $f(x)dx$ with frequency measure $dx = d\omega$ and a Levy exponent $\alpha \leq 1$. The exponent $\alpha$ depends on temperature $T$, pressure $p$, substance, and kind of response.

Remark. The appropriate variables for measurement are susceptibilities, e.g. dynamic ones as function of frequencies $(\alpha^*(\omega)$ according to Eq. (3); i.e. moduli $m(\omega)$ for intensive and compliances $j(\omega)$ for extensive thermodynamic variables). The thermodynamic increments for e.g. the extensive (free) volume follow from integrals across the dispersion zone (DZ),

$$\Delta V = \int_{DZ} V^2(\omega) d\omega.$$  \hspace{1cm} (42)

Defining the volume compliance by $B = -\partial V/\partial p$, $[B] = m^3/Pa$, we get for the FDT (the "measuring equation" [9] p.269 ff.)

$$\overline{\Delta V^2} = k_B T B,$$  \hspace{1cm} (43)

with a correlation function $\Delta V^2(t)$ in the time domain.
\[ \Delta V^2(t) = k_B T (B(t) - B_{\text{eq}}), \]  

(44)
or with a spectral density \( \Delta V^2(\omega) \) in the frequency domain,

\[ \Delta V^2(\omega) = k_B T B'(\omega) / \pi \omega, \]  

(45)

with \( B'(\omega) = B'(\omega) - iB''(\omega) \), real part minus imaginary part.

**Proof.** The proof is divided in five steps.

1. Let us recall some terminological foundations of probability theory. Consider the random variable \( X_1 = V'_1 \). The observable, \( v_1 > 0 \) or \( v_1 > 0 \) for \( V'_1 \), means a coordinate in the sample space \( \mathbb{R}^1 \), i.e. a variable for a ”conceptual experiment” of probability. [For thermodynamics, this experiment is described by the FDT]. The distribution \( F_1(v_1) \) for the random variable is defined by the probability \( P \) to observe a value \( v_1 < v_1, F_1(v_1) = P[v_1 < v_1] \); the corresponding density is denoted by \( f(v) \),

\[ P[a < v < b] = \int_a^b f_1(v_1) dv_1. \]  

Analogous definitions are used for the other subsystems, \( \{V'_1, ...\}, V'_i, ...V'_n \} \).

For the sum of independent free volumes \( V'_i \) of two subsystems, \( S'_2 = V'_1 + V'_2 \), we have \( F_{S_2}(s_2) \) with a convolution (8) for the density,

\[ f_{S_2}(s_2) = \int f_1(s_2 - v) f_2(v) dv = f_1 * f_2(s_2). \]  

(46)
The variance and expectation for any free volume exist, e.g.

\[ E(s_2) = \int s_2 f_{S_2}(s_2) ds_2. \]  

(47)
The distribution for \( S'_n \) as function of the variable \( s_n \) tends, therefore, to a Gauss limit distribution. In general, we have a Gauss bell curve for \( f_V(v) = f(v) \).

2. Interested in dynamics of liquids, we must change the variables from volume to frequency, \( v \rightarrow v(\omega) \). Consider the representative inverse function \( \omega(v) \) of Fig. 1, e.g. via the inside treatment of the local breakthrough of mobility, our Levy instability for \( \alpha < 2 \). Practically, substituting \( \omega = \Omega \approx 10^3 \text{rad/s} \) by \( \omega = \infty \), we find a continuous function diverging at some finite, maximally accessible free volume inside the minimal subsystem, \( V'_{\text{max}} < \infty \):

\[ \omega(v) \rightarrow \infty \quad \text{for} \quad v = v_{\text{max}}. \]  

(48)
The expectation value of frequency may therefore diverge,

\[ E(\omega) = E(\omega(v)) = \int \omega(v) f(v) dv \rightarrow \infty, \]  

(49)
and we expect a new distribution, \( f_V(\omega) = f(\omega) \), different from Gauss.

One may ask, whether the general shape of the new, dynamic density \( f(\omega) \) depends on details of the \( \omega(v) \) function. The answer is no, since the convolution property (46) for many components \( v_i \) pushes the distribution for their sum into the domain of attraction of a limit distribution. Then from a divergence (49) we expect a Levy distribution with Levy exponent \( \alpha \leq 1 \), whatever the details of the continuous \( \omega(v) \) function beyond the property (49) are. The details of \( \omega(v) \) can, however, influence the particular value of \( \alpha \). It is interesting that changing the measure may imply a change of the exponent \( \alpha \) (cf. the Corollary).
3. What is the appropriate (physical) density function \( f(\omega) \) for the stationary fluctuation of an extensive variable? This is the spectral density, \( f(\omega) = x^2(\omega) \) (2), because the corresponding variable measures are equivalent as indicated by the integral Eq. (42),

\[
\int x^2(\omega) d\omega = \int f(v) dv = \Delta V'_m,
\]
where \( \Delta V'_m \) is the (free) volume step increment for crossing the main transition \((mt)\). The "additivity" of \( x^2(\omega) \) is also ensured by its equivalence to the compliance \( \partial V/\partial p \) or \( \partial V/\partial T \) via the FDT.

4. From (46) for free volume we get, after the substitution \( f(v) \to f(\omega) = x^2(\omega) \) for each component of the Levy sum,

\[
X^2_2(\omega) = (X^2_1 + X^2_2)(\omega).
\]
Hence, for general \( n \), we have for any sum of minimal subsystems

\[
X^2_m(\omega) = X^2_1 \ast \ldots \ast X^2_n(\omega).
\]
Physically, the general frequency variable \( \omega \) follows from the \( \omega \)-identity of the FDT, measuring a general frequency for any set of representative subsystems and the same frequency \( \omega \) for any activity,

\[
\{\omega_i\} \to \omega.
\]
Since (52) is a sufficient condition for a Levy distribution, we get such a distribution for \( x^2(\omega) \) with measure \( d\omega \).

In the Nyquist model (2,25) for the FDT (mentioned in Section III.A), the \( \omega \)-identity is related to the indistinguishability of the \( \hbar \omega \) quanta in the transmission lines between "sample" and "apparatus": different activities correspond to different selections of quanta from these lines.

5. A thermodynamic argument for exponent \( \alpha < 1 \) follows from the periphery of the defect. The Levy distribution connects the center of the defect (fractality) with the periphery (tail of stretched exponential, Fig. 2c). The long-time retardation is in the periphery. The simplest case for retardation is a "thermodynamic" or "quasi-stationary" one (in the terminology of Landau and Lifshitz, Ref.32, §118)

\[
dx/dt \sim -x, \quad x \to 0 \quad \text{for} \quad t \to \infty.
\]
This gives a Debye (exponential) decay corresponding to a Cauchy distribution (2) (\( \alpha = 1 \)) in the frequency domain.

The cooperativity of the periphery induces a spectrum of such thermodynamic decays. This means stretching the retardation. For Levy distribution we get necessarily the Kohlrausch function (1), i.e. a Levy exponent \( \alpha < 1 \), holding for the total defect because of the correspondence between center and periphery. This ends the Proof, if the question of variables wherefrom the exponent \( \alpha \) may depend (and physically depends) is delegated to the

**Corollary.** The only free parameter in the correlation function for fluctuations of extensive variables in the main transition of moderate classical liquids is the Levy exponent \( \alpha \leq 1 \). The exponent \( \alpha \) is representative, but remains non-fixed for minimal subsystems in the one-nanometer range. It is therefore expected to be influenced by the structure and the responsibility (Fig. 2c) of the molecules and of the molecular structure of the Levy defect. This includes the dependence on the thermodynamic state (temperature \( T \), pressure \( p \), composition \( x \),...). We have got

\[
\alpha = \alpha(\text{activity, substance, } T, p, x, ...).
\]
Activity means the different kind of response for extensive variables, e.g. volume, entropy, dielectric polarizability, incoherent or coherent dynamic neutron scattering, and so on.

Six Remarks. (1) The Representativeness Theorem shows that in moderate liquids the outside approach to the Levy distribution via representative subsystems is consistent with the inside approach via partial systems.

(2) The Gauss distribution for free volume from Eq. (39) excludes the picture, that there is a partial system with a preponderant contribution of the free volume itself. But this Gauss distribution does not exclude a spatial concentration of such partial systems that do have more free volume than others. The general space/time scaling (Fig. 2) can generate a defect with more free volume from these partial systems in the center.

(3) Does the correspondence between center and periphery mean that there is no diffusion step through the cage door in a Levy liquid without a preponderant component?

(4) Long range correlation as from lattices in solid state physics and long range quantum correlations in liquids may prevent a reasonable partition into smaller and smaller independent subsystems, so that representativeness does not longer remain a reasonable concept: No spatial Levy defects there.

(5) In other words, the Corollary expresses some kind of pluralism of different activities. Although the different activities are collected by the molecules, in a way, in the same dispersion zone, and although always the same molecules of the minimal subsystem are involved, the activities are different in shape and location across the zone. This is related not only to the value of the Levy exponent \(\alpha\), but also to modifications from molecular particularities in the center (e.g. proximity of NMR signals to mechanics) or in the periphery (e.g. nonlocal properties of shear response). Each activity for itself is related to Levy, but each has different Levy exponents and possible modifications, even in the same \((p, T)\) state. The shape of the limit distribution has different "faces". Although frequently confirmed by experiments, such a pluralism of a theoretical approach seems difficult to be accepted by the glass transition community.

(6) A drastic example for the pluralism is the above variable-change from free volume \(v'\) to frequency, \(\omega(v')\). For \(f(v) = f(v')\) we get a Gauss distribution \((\alpha = 2)\), and for the spectral density \(f(\omega) = \omega^2(\omega)\) we get a Levy distribution with \(\alpha < 1\). Such findings may have consequences on the statistical physics in liquids (Section VII, von Laue approach). The problem is hidden, because Gauss behaviour \((\alpha = 2)\) may be expected for all thermodynamic potentials that may be found in the nominator of Gibbs exponents, from similar arguments as for free volume.

D. Derivation of invariant free volume and control equation

The Levy treatment of Section VI.A is based on an inside treatment of cooperativity, inside one minimal subsystem i.e. inside one defect (Section VI.B). Consider independent partial systems with a fixed average volume. The size of the subsystem is then proportional to the number \(m\) of such partial systems, \(N_{me} \sim m\). Consider the frequency \(\omega_i, i = 1, ..., m\), as a transition probability. Statistical independence is then expressed by a common product,

\[
\omega_k = \text{const} \times \omega_1 \times \omega_2 \times ... \times \omega_m.
\]  

(56)

From (11) and Fig. 1, we have

\[
\omega_i = \omega_i(v'_i) , \text{ same } i ;
\]  

(57)

from additivity of free volume \(V'\) we have
\[ V'(\text{subsystem}) = V'_1 + V'_2 + \ldots + V'_m. \] (58)

These three equations define a functional equation yielding the general solution

\[ \omega(\text{subsystem}) = \omega_M \exp\left(\frac{V'_1 + V'_2 + \ldots + V'_m}{v_f}\right) \] (59)

with \(\omega_M\) a prefactor depending of the partition and \(v_f\) a scaling parameter of the minimal subsystem not depending on the partition. This \(v_f\) is called the invariant free volume. The cooperativity is now described by exchange of free volume between the independent partial systems balanced by the relatively small fractional volume fluctuation \(\delta V/V\) of the total minimal subsystem (“minimal coupling”).

Intuitively, the decrease of operational freedom \(m_f\) (Section VI.A) is connected with smaller free volume. Comparing directly the scaled Levy sum \(\sum X_i/n^{1/\alpha}\) (Eq. (7), cf. also Theorem 1, above) with the exponent in Eq. (59), we would get \(v_f \sim N_m^{1/\alpha}\), i.e. \(v_f\) would increase with the cooperativity. This means that \(v_f\) cannot be directly proportional to this freedom. To analyse the situation (free volumes \(V'_i\) also decrease with lower temperatures) we are led to susceptibilities near equilibrium, being the direct measures from the FDT (Section VI.C). We have then dynamic compliances \(j(\omega)\) that become larger for softer materials (high temperature, small cooperativity \(N\)), and moduli \(m(\omega)\) that become larger for harder materials (low temperature, large cooperativity). That is, the operational freedom, decreasing for low temperatures, increases with the modulus. Using the rheological equation \(j(\omega) \cdot m(\omega) = 1\), and putting \(j \sim v_f \sim N_m^{1/\alpha}\), we get for the operational freedom \(m_f \sim m(\omega) \sim 1/j \sim v_f^{-1}\), i.e. really Eq. (41). [In the book \(\text{and Re}^{34}\) this relation was used without any derivation.] Since the general Levy scaling by \(n^{1/\alpha}\) is for Gauss consistent with the fluctuation variance \(\alpha\), p.172), the scaled Levy sum seems to be the only possibility to get a general damping of the operational freedom with increasing cooperativity \(N\). Reducing with Gauss \((\alpha = 2, m_f \sim N^{-1/2})\), we get \(m_f = m_f/(\text{Gauss}) \sim N_m^{(\alpha-2)/2\alpha}\), e.g. \(m_r \sim N_m^{-3/2}\) for \(\alpha = 1/2\), i.e. a considerably stronger restriction of freedom than from Gauss.

E. Johari Goldstein \(\beta\) process

Consider falling temperatures. The \(\beta\) process “emerges” in the \(\alpha-\alpha\) process crossover region \(C\) of the relaxation chart Fig. 3. According to the idealized version of the mode coupling theory MCT\(^3\), the cage door of next molecular neighbors (for the \(\alpha\) process), necessary for the diffusion in liquids, is closed at the critical temperature \(T_c\) of this MCT. In our Levy defect approach, \(T_c\) is substituted with the crossover temperature: Because of the generality of defects, esp. some continuity of molecular motion in the cooperative periphery (see Fig. 6, below), Johari’s islands of mobility (Section III B,C) survive the crossover with a modification\(^3\). The increasing cooperativity of the \(\alpha\) process, located in the periphery of the defect, leaves the cage door open for diffusion. The position of the crossover region in the relaxation chart is then determined by crossing of the \(\alpha\) process with a virtual molecular-mechanical process for \(\beta\), finding free room enough in the center of the defect. From this point of view, the parameter change for the \(m_t\) at the crossover\(^3\) means a change from a defect without \((T > T_c)\) to a defect with the inside mechanical process \((T < T_c)\). [The parameters of the \(\alpha\) process and the mechanical core of the \(\beta\) process must suffice some relation to get a crossing. There are glass formers where no crossing is observed, i.e. with ”no \(\beta\) process”\(^3\)].

A \(\beta\) process is approximately of Arrhenius type and is accompanied by a “continuous” background from the periphery. The total formal variance of the \(\beta\) process can be affected (i.e. broadened) by a distribution of molecular activation-barrier properties. A concrete \(\beta\) activity can be rather small, if the mechanical process does not generate the corresponding fluctuations.

The main issue is the relation of the \(\beta\) process to the \(\alpha\) process below the crossover region. Wherefrom does the free volume concentration necessary for the above activation process come? Although the free volume of the bulk becomes extremely small at low temperatures, so that the \(\alpha\) process needs more and more cooperativity for perpetuating the diffusion steps through the cage door? A short answer is the phase continuity of the liquid state so that cooperativity must increase to ensure the fluidity of the liquid, even at the cost of long times (large viscosity) at low temperature, cf. Eq. (59). The longer answer from our approach
is that free volume enough can be collected in the center of Levy defects of the cooperative $\alpha$ process (with the preponderant component for dynamics in the midst). The correspondence between center and periphery then guarantees that increasing cooperativity of the periphery for falling temperatures (Fig. 6, below) ensures the continuous existence of the mechanical process by the preponderant component for $\alpha < 1$, also when the total free volume becomes shorter. [Let us repeat: In the idealizing MCT closing of the cage door is possible; in our approach the periphery cannot end its action to keep the cage door open.] The alternative\textsuperscript{25}, that the $\beta$ process is a precursor or local step of the $\alpha$ process which can occur anywhere, cannot answer the above wherefrom question. In our defect picture, the anywhere would only be right in the sense that the Levy defect can occur anywhere in the pattern, but anywhere outside the defect center would not be probable.

F. Fischer speckles

One of the greatest surprise in glass transition research was the discovery, that the Debye Bueche\textsuperscript{37} inhomogeneities in frozen glasses correspond to a slow dispersion zone $\phi$ in the relaxation chart Fig. 3. These Fischer modes have e.g. times about $10^7$ times longer and lengths about 50 times larger than those of the main transition process ($mt$)\textsuperscript{16}. It follows from the Representativeness Theorem that there must be also defects in the fluctuating pattern for the $\phi$ process zone. These defects are to be identified with the experimental\textsuperscript{12} Fischer speckles.

The volumes of partial systems for the inside approach to the Glarum defects of the main transition are smaller than the volumes of the $mt$ minimal subsystems, whereas for the Fischer speckles the partition into just such subsystems (as "partial systems" for $\phi$) is used (Fig. 4).

![Fischer speckles](image)

**FIG. 4:** Fischer speckles ($\phi$ speckles). Two Levy situations in moderate liquids. Left for the main transition $mt$, right for Fischer modes $\phi$. The small squares are the minimal subsystems for the main transition.

The Fischer modes $\phi$ are a direct consequence of the main transition $mt$. No structural thermodynamic assistance ("cluster") is necessary for the construction of the length and time ratios between $\phi$ and $mt$ processes (Fig. 5). These ratios can be estimated from alone the two-defect pattern of Fig. 4. We have to look for a physical $mt$ process in the liquid that eats its way through large space $\lambda$ and time $t$ ranges: diffusion process. How probes the fast $mt$ process the slow $\phi$ process speckles? What about the reliability of the short-range $mt$ process for the long-range $\phi$ process?

The $mt$ process defects are rather dense, their average distance is of order 1 nm (see Fig. 6, below). The molecular diffusion is therefore step by step, from one Glarum Levy defect to the next one along the "diffusion line". We expect locally, at any step, a modification of the "normal diffusion" by the Levy fractality at the cage doors: "Levy diffusion". This defines the local $\log t / \log \lambda$ slope, and an "analytical continuation", step by step along the line gives the required reliability of the defect behavior over the full distance between the speckles. The Representativeness Theorem includes also the large subsystems between the Fischer speckles. – Conversely, the fast $mt$ process should also be "probed" by components of the slow $\phi$ process. We have got two aspects:

Seen from the fast $mt$ process. For instance, dynamic neutron scattering\textsuperscript{38,39} shows that the $a$ process can be described by a sublinear diffusion whose exponent may be related to the Kohlrausch (Levy) exponent $\alpha$ of a certain $a$ process relaxation. In the
frame of pluralism (Section VI.C), this exponent may be different from a dielectric exponent (cf. Eq. (55)). The corresponding Levy diffusion is described by a slope from

$$\omega \rightarrow \omega^\alpha, \quad t \sim \lambda^{2/\alpha}. \quad (60)$$

Seen from the slow $\phi$ process. Consider the flaring up (1) and fading away (0) of the $\phi$ speckles at different space and time "points" as some kind of $(1,0)$ spin diffusion from virtual, spatially fixed spin carriers. Since different minimal subsystems for the $mt$ process are independent, this spin diffusion is normal:

$$t \sim \lambda^{2}. \quad (61)$$

We estimate the required $\phi/mt$ ratios from the triangle in Fig. 5. We find the nearest neighbors of $\phi$ process defects (speckles) at the upper $\phi$ corner of the triangle, since the Levy diffusion, to be effective, must be faster than the normal diffusion. The basis $\varepsilon$ is the log-time difference $\varepsilon$ between normal and Levy diffusion at the $mt$ process length scale, $\lambda \approx \xi_{mt}$. The Levy diffusion is at some time $\bar{t}$ in the short time tail (fractality) of the $mt$ process spectral density, i.e. in the molecular cage door being the center of the Glarum Levy defect. The normal diffusion is near the average time of the $mt$ process, $t_{av}$:

$$\varepsilon = \log(t_{av}/\bar{t}). \quad (62)$$

From Fig. 5 we see that the time and the length ratios ($\phi/mt$) are mainly determined by the tilt $(1 - \alpha)$. Defining $\tau_{mt} = t_{av}$, we get the slope difference as $(1 - \alpha)/\alpha$ and

$$\log \frac{\xi_{\phi}}{\xi_{mt}} = \frac{\alpha}{2(1 - \alpha)} \varepsilon, \quad \log \frac{\tau_{\phi}}{\tau_{mt}} = \frac{\alpha}{1 - \alpha} \varepsilon. \quad (63)$$

For small tilts, $1 - \alpha \ll 1$, we obtain the slope difference directly as the tilt $(1 - \alpha)$, and $\log(\xi_{\phi}/\xi_{mt}) \approx \varepsilon/(1 - \alpha)$ as well as $\log(\tau_{\phi}/\tau_{mt}) \approx \varepsilon/(1 - \alpha)$. Large values for the $\phi/mt$ ratios can easily be obtained, also in the experimental range for moderate
molecular liquids (Ref. 9, p. 349). A minimal subsystem for the φ process as claimed by the Fischer speckles contains a large number of Glarum Levy defects.

VII. VON LAUE THERMODYNAMICS FOR LIQUIDS?

A. Characteristic length of the main transition

The characteristic length is a concept for an estimation of the defect size from thermodynamic bulk measurements (Fig. 2(d), Sections III.D and VI.C). This length is decisive for an Experimentum Crucis of the defect pattern.

The usually applied molecular Gibbs statistics rests on a virtual transfer of the temperature $T$ from a macroscopic heat reservoir, transferred without temperature fluctuation to the subsystems, $\delta T \equiv 0$. This transfer does not seem reasonable, if one tries to eliminate external experiments (the conscious observer of the Copenhagen program) from thermodynamics or quantum theory of independent subsystems.

Statistical independence of Landau subsystems is rested on negligible potential energy between the foreign molecules according to the Boltzmann factor $\exp(-E_{pot}(p,q)/k_BT)$ in the Gibbs probability. This does not seem appropriate for dynamics that is based on large attempt rates allowing much smaller independent subsystems.

It seems more reliable to substantiate a thermodynamics of liquids by time or mobility integration of dynamic compliances and dynamic moduli from the fluctuation dissipation theorem (FDT) that can be derivated from quantum mechanics without external experiments (Ref. 9, p. 227ff, 25,31, cf. the Remark in Sec. VI.C). This leads, for $(T,S; p,V)$ as relevant thermodynamic variables, to the von Laue thermodynamics including temperature fluctuation $\delta T$ also for the above minimal subsystems in the one-nanometer range (Refs. 32,41 §112, and Chap. 14).

A thermodynamics based on the dynamic compliances $(\alpha''(\omega) \sim \omega^2(\omega))$—without any restriction of fluctuation of thermodynamic variables, similar to the von Laue thermodynamics—may possibly be associated with a statistical basis different from the more "static" Gibbs distribution. In particular, the separation into mechanics $(E(p,q))$ and thermodynamics $(k_BT)$ of the Gibbs distribution may be lost. Possibly, there exists a molecular, microscopic von Laue distribution with different consequences near the defects, related to the Levy distribution as representative of minimal subsystems and reflecting the pluralisms (different $\alpha$ for different activities) more explicitly.

From the von Laue fluctuation formulas we get directly a volume that can be interpreted as volume of the minimal subsystem when applied to the main transition $mt$. We start from one defect as the smallest representative thermodynamic unit (Section VI.C). In the general von Laue fluctuation formula for temperature, $\Delta T^2 = k_BT^2/C_V$, the heat capacity $C_V$ is an extensive variable [J/K]. Having $N_{mt}$ molecular units in our minimal subsystem, we get

$$N_{mt} \text{ (von Laue)} = \frac{RT^2\Delta(1/c_V)_{mt}}{M_0(\delta T)_{mt}},$$

where now the small $c_V$ letter is the specific heat capacity [J/kg·K]: $\Delta(1/c_V)_{mt}$ is the step of $1/c_V$ across the $mt$, $R$ is the molar gas constant, and $M_0$ is the molecular mass of what is considered as molecular unit. The characteristic length is obtained from the average volume needed by the $N_{mt}$ molecular units; $N_{mt}$ was called "the cooperativity" for the defect of the $mt$.

We discuss now the extensivity (being the expression of the Levy sum). Put $v$ the number of minimal subsystems in the sample; i.e. Eq. (64) is for $v = 1$. To get the extensivity of $C_V$, we multiply the heat capacity of one minimal subsystem with $v$ and get then for the temperature fluctuation of the sample $\Delta T^2 \sim 1/v$, $\Delta T \sim 1/\sqrt{v}$, as expected. But how to get $(\delta T)^2_{mt}$, the temperature fluctuation of the minimal subsystem, from a bulk measurement? The Representativeness Theorem makes the
relevant responsibility \((\alpha' (\omega) \sim \omega \Delta^2 (\omega))\) indepent from the system size, i.e. the width \(\Delta \log \omega\) of the \(m t\) dispersion zone (DZ) of Fig. 3 does not become smaller for large subsystems or samples. We get, across the DZ, a temperature difference

\[ \delta T \approx (dT/d \log \omega)_{\text{along}} DT \cdot \delta \log \omega. \]  

To interprete this \(\delta T\) as \(\delta T_{mt}\), we must assume that for partial systems of the minimal subsystem, the distributions for temperature and relevant mobility fluctuations are equivalent. This is a fluctuative interpretation of Boltzmann's macroscopic temperature-time equivalence used by rheologists for a long time. [This equivalence is an approximate symmetry of susceptibility \(\alpha = \alpha(\log \omega, T)\) curves across the \(mt\) with respect to a \(\log \omega \leftrightarrow T\) exchange, called also rheological simplicity. Interpreting in this context \(\log \omega\) as a thermodynamic variable equivalent to a temperature \(T\), this symmetry can be thought to be inversely constructed from fluctuative increments for both, \(\delta \log \omega\) and \(\delta T\). This confirms our above assumption, in particular for relevant susceptibilities \(\alpha\), e.g. for temperature modulus or for entropy compliance \(\sim\) dynamic heat capacity, \(C(\omega, T)\). In the FDT as thermodynamic equation for an experiment, this equivalence is mediated by the Planck radiation formula in Nyquist's transmission lines, cf. Fig. 3.6b of Ref.2; a detailed preliminary discussion of this issue is also in\(^4\), pp.263-268. A critique of this argumentation is in\(^9\).

Eq. (64) is from the fluctuation of an intensive variable, the corresponding susceptibility is a modulus. From a Gibbs fluctuation of energy, \(\langle \Delta E^2 \rangle_V = k_B T^2 C_V\) (with the restriction \(\delta T = 0\)), we get from an analogous treatment\(^4,46\)

\[ N_{mt} \text{ (Gibbs)} = \frac{RT^2}{M_0 \langle \Delta C_V \rangle_{mt} \delta T_{G,mt}^2}. \]  

This is from the fluctuation of an extensive variable, the susceptibility is a compliance; \(\delta T_{G,mt}\) is the transformation interval after correction for partial freezing around the thermal glass temperature \(T_G\). The ratio is unexpectedly large, of order

\[ \frac{N_{mt} \text{ (Gibbs)}}{N_{mt} \text{ (Laue)}} \approx \left( \frac{c}{\Delta c} \right)^2, \]  

where \(\Delta c\) is the step height across the \(mt\) of the heat capacity used for the estimation\(^47\), and \(\delta T^2 \approx \delta T_{G,mt}^2\) which assumption is not a point of issue. For e.g. \(\Delta c/c = 10\) per cent we get the ratio of 100 (!)

The two experimental cooperativities as obtained from dynamic calorimetry between mHz...kHz frequencies (3\(\omega\) method) are compared in Fig. 6\(^{48,49,50}\). We see three things.

(i). The Gibbs cooperativities are much larger than the von Laue cooperativities. The related Gibbs lengths correspond about to the diameter of the cage from next molecular neighbors plus parts of the second shell, as expected for Landau subsystems from the energetically motivated independence due to the Boltzmann factor.

(ii). There is no indication for any singularity (cusp or so) at the crossover temperature\(^{28,29}\) (for the substances where \(T_c\) is included) that could be expected from a critical temperature from closing the cage of the pristine = idealizing model for mode coupling theory MCT\(^{20,27}\).

(iii). The von Laue cooperativities from calorimetry increase continuously with falling temperature. The increase corresponds to a continuous decrease of bulk free volume. Some of the cooperativities are, for high temperature above the crossover, \(T > T_c\), smaller than one molecular cage from the next neighbors and suit, therefore, to the extraordinary entropy fluctuation accompanying the diffusion step through the cage door induced by the preponderant component in the midst of the defect center. Sometimes, the cooperativities are of order \(N_{mt} \approx 1\): one molecular diameter near \(T_c\). Some bend in the crossover region is also observed. For low temperature, the increasing cooperativities seem to indicate the increase of the defect periphery to collect enough free volume for the center to maintain the cage door open also for short free volume, as required by the Representativeness Theorem.
FIG. 6: Comparison of von Laue and Gibbs cooperativities (Eqs. (64) and (66)) of the main transition $m_{t}$ as a function of reduced temperature $x = (T - T_{c})/(T_{0} - T_{c})$. The full experimental data are in Ref. 48, see also Refs. 49,50 and the references cited therein. The colors are: blue for poly (n alkyl) methacrylates, green for other polymers, and red for small-molecule substances. For polymers, the particles are the monomeric (repeat) units. The numbers are: 2, 3, 7, 8, 10 for poly (n alkyl) methacrylates: 2 - n propyl, 3 - n butyl, 7 - n pentyl, 8 - n hexyl, 10 - n decyl; 4 - random copolymer poly (n butyl methacrylate-stat-styrene) with 2 percent styrene; 13 - polystyrene, 16 polycarbonate, 19 diglycid ether of bisphenol, 20-poly [phenyl glycidil ether - co - formaldehyde]; 21 - benzoin isobutyl ether, 24 ortho cresyl glycidyl ether, and 25 - a fulven derivative (TP-CPBO). The bars mean an error estimation of the single absolute values.

The experimental characteristic lengths from the von Laue approach are, therefore, considered as size of the Glarum Levy defects.

### B. Experimentum Crucis

Is there an Experimentum Crucis that can decide between using von Laue or Gibbs thermodynamics and, if von Laue is the winner, would indirectly prove the Levy defects in the main-transition ($m_{t}$) dispersion zone of the dynamic glass transition (Fig. 3; see also Ref. p.187, 50)? Since the local density effects expected from the cage doors for diffusion are small due to the steep repulsion potentials of the particles, it seems at present difficult to detect the defects directly in the structure factors used e.g. for the evaluation of dynamic neutron or photon scattering. Additionally, the inter/intra molecular potentials used for adjustments are also uncertain.

Therefore, an indirect experimental proof via characteristic lengths is suggested. Dynamic scattering of relevant contributions from $m_{t}$ process allows to construct a raster of wave vectors $Q$, mobilities $\log \omega_{0}$, and isotherms $T = \text{const}$. Transferring the maximum frequency $\omega_{0}^{DC}$ for the heat capacity peak of $C_{p}(\omega, T)$ at different temperatures from dynamic calorimetry (DC) into the $\log \omega_{0}$-$T$ lines of this raster, the resulting length $\xi = 2\pi/Q$ from scattering can be compared with the characteristic lengths from the calorimetric cooperativities, Eqs. (66) or (64). Since their ratio: Gibbs/von Laue is large, in particular for high temperatures (Fig. 6), even a rough comparison can give a decision. If we obtain von Laue lengths, then this result is considered as a certain experimental proof of the defects (see below).
What about the physical relevance of calorimetry for neutron scattering in the frame of pluralism (different exponents \( \alpha \))? Roughly, by thermodynamics, scattering corresponds to some density fluctuation, i.e. to a volume, and calorimetry to an entropy fluctuation. The von Laue fluctuations are related by thermal expansion: \( \Delta S / \Delta V = k_B T \partial (\partial V / \partial T) \). This defines a certain relationship between them. The general basis for comparison, however, is the \( \omega \)-identity of the FDT \( \phi \), p.279). Take thus dynamic heat capacity and the diffusion part of dynamic scattering as the two responses that are to be compared. Then the comparison of maximal frequency \( \omega_0 \) of the two compliances Eq. 3 seems reasonable, since the frequencies of different activities (even for different Levy exponents \( \alpha = \alpha_{\text{KWW}} \)) are identified by the \( \omega \)-identity. The Kohlrausch function from the relevant intermediate scattering function, \( S(t) \sim \exp\{-t/\tau_{\text{KWW}}(Q)\} \) must be transferred to a dynamic compliance, \( \alpha''(\omega) \). The maximum frequency \( \omega_0 \) can then be calculated from Ref. 3, p.306:

\[
\ln(\omega_0 \tau_{\text{KWW}}) = 0.60607 (\alpha - 1),
\]

where \( \ln \) means the natural logarithm, \( \omega_0 \) is the angular frequency in rad/s, with \( \omega = 2\pi f \), \( f \) the frequency in hertz. We get \( \omega_0(Q) \). The reduction to frequencies avoids further comparison of times from different activities.

Consider a fictitious example following partly Ref. 40 (Fig. 7). From dynamic neutron scattering (DNS) one can separate a relevant intermediate scattering function \( S_{\text{rel}}(Q,t) \) that is informative about diffusive (Eq. 3) and related relaxation processes. This is one of our response. Calculation of \( \omega_0^\text{DNS}(Q,T) \) from a Kohlrausch fit with \( \tau_{\text{KWW}}(Q) \) as a function of wave vector \( Q \) allows to construct a raster of isotherms in an \( \log \omega_0^\text{DNS} \) vs \( \log Q \) plot. This raster allows then to locate the maximum (\( \log \omega_0(T) \)) pairs from dynamic calorimetry (as the other response) in the diagram Fig. 7 (\( \triangle \)) by using \( \omega_0^\text{DC} = \omega_0^\text{DNS} \) from the \( \omega \)-identity of the FDT, possibly after some extrapolation of the DNS raster to lower temperatures. Then the abscissa of the \( \triangle \) points gives the \( Q \) vector that is to be associated with dynamic calorimetry, from which the length \( \xi = 2\pi / Q \) can be compared with the characteristic lengths from 64 and 66, \( (\xi_{\text{DC}})^3 = N_m \times \) average volume occupied by one particle.

![FIG. 7: Fictitious diagram for the Experimentum Crucis. The maximum frequency values \( \omega_0^\text{DC}(T) \) of dynamic heat capacity \( C_\varepsilon''(\omega,T) \) for different given temperatures, (\( \triangle \)), [located by the raster of isotherms, and using \( \omega_0^\text{DC} = \omega_0^\text{DNS} \) from the FDT] in a log frequency (\( \log \omega_0^\text{DNS} \)) – log wave vector (\( \log Q^\text{DNS} \)) diagram for that part of dynamic neutron scattering which is informative about diffusive and corresponding relaxation processes. DC the dynamic calorimetry, DNS the dynamic neutron scattering. The \( \log Q \) abscissa values of the DC triangles \( \Delta \) give qualitative measures of the lengths \( \xi = 2\pi / Q \) that can be associated with DC and can be compared with the calorimetric characteristic lengths from 64 and 66. Fig. 6. Details see text.](image)

In Ref. 40, DNS for polyvinylacetate PVAC is compared with the peak of \( \varepsilon''(\omega) \), the dielectric loss. The authors get a length of about 1 nanometer (from \( Q = 0.65 \text{ Å}^{-1} \)). In our experience with DC and pluralism, the trace of \( \varepsilon'' \) in the relaxation chart is usually located not too far from the \( C_\varepsilon'' \) trace. The extrapolation of von Laue cooperativities to \( x = 1 \) (crossover) gives the order of one or a few particles, i.e. the same length order. The Gibbs length would give cooperativities \( N_m \) of order 100 - 1000, corresponding to lengths of about 2 - 5 nanometer, i.e. (much) larger. This preliminary comparison actually indicates von Laue thermodynamics.
In a way, the defect model is directly supported by DNS for polyisoprene in a large \( Q \) interval (0.1 \( \text{Å}^{-1} \) to 5.0 \( \text{Å}^{-1} \)) and time interval (\( \tau_{\text{KWW}} = 0.03 \text{ ns...200 ns} \)). The raster of Fig. 7 corresponds to a large "homogeneous" region (Levy diffusion) for small \( Q \) values (large lengths \( \xi = 2\pi/Q \)), which is continued by a "heterogeneous" region for large \( Q \) values (smaller lengths). The \( \tau_{\text{KWW}} \) times there are above the raster extrapolation. The crossover between the two regions is at \( Q \approx 1.3 \text{ Å}^{-1} \), corresponding to \( \xi \approx 5 \text{ Å} \), close to the maximum of the static structure factor, \( S(Q) \). This observation can be interpreted by our defect model, Fig. 2c. The homogeneous region corresponds to the fractal center of the defect. The large lengths can be explained by the analytical continuation as used for the Levy diffusion to the Fischer modes (Section VI.F). The heterogeneous region corresponds to the diffusion step through the cage door. A responsibility part of this region corresponds to the preponderant component of the Levy sum, being, so to speak, an "inhomogeneous" contribution from the homogeneous Levy distribution. The other part is from the heterogeneous molecular contributions in the construction of the cage door up to large \( Q \) (i.e. down to small lengths). The observation of the homogeneous part supports one of our basis assumption for the Levy statistics, that the large numbers needed for limit distributions come from the many dynamic attempts in the partial systems, and is not directly the number of particles participating at the cage door.

Distinguish two results from the Experimentum Crucis. (A). Decision between von Laue or Gibbs thermodynamics for minimal subsystems in liquids, and (B). The values of the bulk characteristic lengths per se, in nanometers, indicating the spatial extent of the entropy or temperature responsibility in the defects.

It should be tried to widen the reliable experimental ranges of dynamic neutron scattering along the \( mt \) dispersion zone to lower frequencies than today really available (about several \( 10^7 \text{Hz} \)) and of dynamic calorimetry to higher frequencies (than the today \( 10^4\text{Hz} \)), so that both methods can overlap for the same substances e.g. in the crossover region of the \( mt \) (usually in the \( 10^4\text{Hz} \) range, cf. Ref 2, p.222-223). This would decide which alternative for the characteristic length would be consistent with scattering. The typical glass transition crossover frequency can be reached by dynamic neutron scattering in the next years, if e.g. the impressive series of experiments by Dieter Richter’s group (e.g. \( 38,39,52 \)) is continued to low frequencies. Reliable dynamic calorimetry in the megahertz range, however, remains to be done. Dynamic photon scattering can probably be applied in the \( \alpha \)-process dispersion zone at low frequencies, a few frequency decades above freezing-in around the glass temperature \( T_g \). Experimental data from dynamic calorimetry is available here.\( 47,48 \)

The decision for von Laue would become a conclusive experimental argument for Levy defects, if our treatment from defects to von Laue thermodynamics has a robust reversal. This includes three main steps: (1) Freely fluctuating subsystems should give a sound thermodynamic basis for the components of a Levy sum with Levy exponent \( \alpha \leq 1 \) (Representativeness Theorem). (2). In particular, such equivalent subsystems should give a thermodynamic basis for the way from Kohlrausch correlation functions to the Levy sum (Theorem 1). (3). We need a sound explanation to have a Levy instability in the liquid giving \( \alpha < 1 \) (free volume picture Fig. 1 and Theorem 2). I think we can explicitly find the robust reversal in these steps.

There are general consequences for thermodynamics, if the temperature fluctuation at so small, one-nanometer lengths could be confirmed by the Experimentum Crucis. Since we do not have a molecular spatio-temperature field in this length range, i.e. no \( T(r,t) \) there, we cannot illustrate temperature fluctuations by additional hydrodynamic arguments using forces and fluxes. Instead, \( \delta T \) must be included in the many possibilities of the molecular origin for the random components of a Levy sum which is agitated by the high attempt rates of dynamics. Instead of hydrodynamics, the Levy defect forms some Levy diffusion. Temperature fluctuation is there a necessary part of the dynamic molecular play in liquids.

Teaching thermodynamics, we could leave the thermodynamic limit for the definition of temperature. If \( \delta T \neq 0 \) would be confirmed, then the Gibbs distribution comes from a "static" restriction: we start from a more general thermodynamics for subsystems with \( \delta T \neq 0 \) and come to the limit \( N \to \infty \) with \( \delta T = 0 \), e.g. by means of a heat reservoir. The use of this restriction as a basis of the general definition of temperature (as sometimes advocated) would not longer be reasonable. Temperature \( T \) is essentially different from an energy \( \Delta E \), irrespective of the frequent occurrence of an equation of type \( \hat{T} = \Delta E/k_B \). In liquids, such an equation comes from Planck’s black body radiation of the quantums \( \Delta E = \hbar \omega \) in Nyquist’s transmission lines for a thermodynamic measurement, \( \hbar \omega = k_B T \). In the FDT, this equation connects temperature fluctuations and frequency fluctuations for a specific response, as used above.

In summary, an Experimentum Crucis which confirms the lengths calculated from von Laue thermodynamics would overcome
the nonfluctuation of temperature — i.e. brings a new (the old) definition of temperature in liquids beyond (and before) the Gibbs definition with the latter’s heat reservoir without fluctuation. The consequence for liquids could be that mechanics and thermodynamics cannot be separated into denominator over nominator, \(E(p,q)/k_B T\), as for Gibbs. The "statistical mechanics" could be influenced by a thermodynamics with Levy defects in the liquid. Then the observables, in particular the dynamic susceptibilities, cannot exactly be calculated from mechanical computer simulation plus Gibbs thermodynamics alone.

VIII. CONCLUSIONS

Most of the qualitative attributes for the arrangement and properties of the dispersion zones \((a, \alpha, \beta, \phi)\) in the relaxation chart of the dynamic glass transition (as a synonym of classical liquid dynamics) can be explained by a weak underlying fluctuating free-volume pattern with strong dynamic Levy defects. Eight Examples are:

1. The Levy defect explains the concentration of the main transition \((mt)\) dynamics into a relatively narrow dispersion zone with a half-width of about \((1/\alpha)\) decades, with \(\alpha \leq 1\) the Levy exponent. The spectral densities for extensive variables are Levy distributions, their correlation functions are stretched exponentials.

2. The spatial position of the Johari Goldstein \(\beta\) process in the pattern is the center of the Glarum Levy defect of the \(\alpha\) process; the continuous part of the \(\beta\) process comes from the cooperative periphery.

3. The location of the crossover region in the relaxation chart is defined by virtual crossing of a quasi mechanical molecular barrier mechanisms (Arrhenius process underlying the \(\beta\) process) with the main \(mt\) process being not an Arrhenius process.

4. The emerging von Laue thermodynamics allows an experimental determination of the characteristic length for the main transition by bulk dynamic calorimetry. This length is the size of minimal representative subsystems and characterizes the size of the Glarum Levy defects (including its preponderant component, its fractal center and its cooperative periphery) and their mutual average distance in the pattern.

5. The preponderant component of the \(mt\) Levy sum for the defect may induce an extraordinary molecular event of dynamics: The diffusion step through the cage door opened in the cage of equivalent next molecular neighbors.

6. The non-Arrhenius behavior of the main transition \(mt\) \((= a + \alpha \) process) is connected with the increase of cooperativity \(N_{mt}\) at low temperatures.

7. The position of the dispersion zone for the Fischer modes \(\phi\) relative to the main transition in the relaxation chart is determined by the diffusion-relevant Levy exponent \(\alpha\) from the \(mt\) Glarum Levy defects without the need to refer to any thermodynamic collective structure formation beyond the Levy distribution (no "clusters"). The Fischer speckles are the Levy defects of a Levy sum from a large number of minimal subsystems.

8. At low temperatures (or mobilities), the main transition is probably exhausted. The operational freedom in the periphery for large cooperativities \(N_{mt}\) becomes so small that spatially distributed, random traces of foreign processes can take the control over from the main process. This restricts the Levy exponent from below, \(\alpha(mt) \gtrsim 0.4\).

The way from the widely observed stretched exponential (Kohlrausch function) to a Levy distribution for the spatial fluctuation pattern with preponderant components as midst of the defects is explained by a succession of theorems which are partly known before. Their original mathematical proofs are partly modified and completed by physical arguments and comments. Two things are additionally needed for this way: Mathematically, (1) a sum of Levy sum components and (2) an
explanation of small Levy exponents $\alpha < 1$. This corresponds physically (ad 1) to a sum of spatially separable statistically independent subsystems or partial systems and (ad 2) to a Levy instability from a local breakthrough of mobility. The latter is characterized by more free volume in the center as well as a spectrum of relaxation in the cooperative periphery of the defect. This "inside explanation" is confirmed by an "outside" one from the Representativeness Theorem for thermodynamics of liquids, operating with a sum of representative minimal subsystems. An Experimentum Crucis for the whole argumentation is suggested: the comparison of characteristic lengths from thermodynamics (dynamic calorimetry) with lengths from dynamic neutron (or photon) scattering.

The Levy distribution gets a “shaping power of statistics” if it is imbedded in certain additional circumstances. For the dynamics in classical liquids, e.g., the following is sufficient: (a). Many equivalent independent spatially separable partial systems for its establishment as a limit distribution, (b). An instability whose stabilization by the limit distribution is different from Gauss (exponent $\alpha < 2$, in particular $\alpha < 1$ for the existence of a preponderant component in the Levy sum), and (c). A general time (mobility)-length scaling of relevant fluctuation modes to get a fluctuating space pattern with defects. The latter are thus considered as the results of the shaping power.

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