



Towards a Phenomenological Definition of the Term ‘Gel’

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ABSTRACT

The term ‘gel’ is used so indiscriminately that it has become ambiguous. Existing definitions are reviewed, examples of unfortunate uses of the term are discussed, and important phenomenological characteristics of gels are identified. We propose that the term ‘gel’ should be limited to systems which fulfil the following phenomenological characteristics: (a) they consist of two or more components one of which is a liquid, present in substantial quantity and (b) they are soft, solid, or solid-like materials. We further propose a definition of the solid-like characteristics of gels in terms of the dynamic mechanical properties, viz. a storage modulus, $G'(\omega)$, which exhibits a pronounced plateau extending to times at least of the order of seconds and a loss modulus, $G''(\omega)$, which is considerably smaller than the storage modulus in the plateau region.

INTRODUCTION

Jellies made from cooked-down meat juice or from fruit juice cooked with sugar are soft, solid or solid-like materials which have been used in

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households for centuries. Already in the 19th century, chemists knew of several other systems, both organic and inorganic, which were capable of forming jellies. Thomas Graham reported on the unusual diffusion properties of jellies¹ and studied the replacement of water with other liquids in jellies of silicic acid.² He introduced the terms *hydrosol* and *hydrogel* for the liquid and gelatinous hydrates of silicic acid, respectively, and *alcosol* and *alco-gel* for the corresponding alcoholic bodies.²

Different types of gels have widely different structures and are studied by scientists with different backgrounds, i.e. physicists, chemists, chemical engineers, biologists, medical researchers, etc. It is therefore not surprising that it has been impossible to reach a consensus as to what constitutes a gel. This hampers communication between workers in different areas and frustrates students who would like to understand the meaning of the term 'gel'.

Examples of typical gels

Examples of typical gels formed by cooling of solutions of biological systems are gelatin, pectin, agarose, carrageenan, and agar gels.³⁻⁵ Fibrin clots are also typical biological gels which, however, are formed by polymerization of fibrinogen monomer through a series of enzymatic reactions.⁶ A number of synthetically prepared organic systems exhibit similar properties. Dilute solutions of polyvinylchloride in di(2-ethylhexyl) phthalate form gels on cooling.⁷ Typical examples of covalently crosslinked networks are a styrene-divinylbenzene copolymer swollen in an organic solvent⁸ and a 2-hydroxyethyl methacrylate ethyleneglycol dimethacrylate copolymer swollen in water (the material used for soft contact lenses).^{9,10} Silica gel in the swollen state is a typical example of an inorganic gel.^{2,11} All of these gels are soft, solid, or solid-like materials, which contain substantial quantities of a liquid.

Examples of the indiscriminate use of the term 'gel'

Usage of the term 'gel' has gradually been expanded to include a number of 'dry' systems, i.e. systems that contain no liquid. Dried silica gel,¹¹ unswollen crosslinked rubber,¹¹ and aerogels¹² are examples. Rigid materials have also been characterized as gels. Dried silica gel, which is a very rigid and brittle material, can be mentioned also in this context. Polyisocyanurate networks with moduli of the order of 10^8 Pa prepared in the presence of small quantities of solvent are yet another example.¹³

The picture has been further clouded by the introduction of a number

of related terms, e.g., 'weak gel',³ 'quasi-gel',¹⁴ 'temporary' gel,¹⁴ 'pseudo gel',¹⁵ 'heterogel',¹¹ 'isogel',¹¹ 'microgel',^{16,17} and 'nanogel'.¹⁸

Purpose of this paper

The purpose of the present paper is to suggest limitations which will allow the specification of phenomenological characteristics common to all gels, independent of composition and molecular structure.

EXISTING DEFINITIONS

The widely used physical chemistry textbook of P. W. Atkins gives the following definition:¹⁹

A **gel** is a semi-rigid mass of a lyophilic sol in which all the dispersion medium has been absorbed by the sol particles.

The *Encyclopedia of Polymer Science and Engineering* gives this definition:²⁰

A gel is a crosslinked polymer network swollen in a liquid medium. Its properties depend strongly on the interaction of these two components.

These two definitions have little in common except their emphasis on two or more components. Clarification on what constitutes a gel is clearly needed.

The following purely phenomenological definitions of the classical types of gel can be found in Webster's *New Twentieth Century Dictionary*:²¹

Gel, a jellylike substance formed by a colloidal solution in its solid phase: opposed to *sol*.

Jelly, a soft, resilient, partially transparent, semisolid, gelatinous food resulting from the cooling of fruit juice boiled with sugar, or of meat juice cooked down.

The latter definitions are very good for the classical types of gel, stating that a gel is a solid or semisolid material which consists of at least two

components, one of which is a liquid, and that it is soft and resilient. The latter property means that the mechanical damping in the material is small, i.e. $\tan \delta = G''(\omega)/G'(\omega) \ll 1$ in the relevant frequency range,^{22,23} $G'(\omega)$ being the storage shear modulus and $G''(\omega)$ the loss shear modulus.

Definitions based on structural characteristics

During most of this century, the main effort in the study of gels has been directed toward explaining gel properties and the gelation process in terms of structure and changes in structure. That this is a complicated matter was already recognized by D. Jordan Lloyd, who in the paper ‘The Problem of Gel Structure’ made the following introductory statement:²⁴

The colloidal condition, the “gel,” is one which it is easier to recognize than to define, and even recognition is confused by the fact that the limits between gel and sol, on the one hand, and gel and what may be termed curd, on the other, are not precise, but consist of a gradual change. For this reason some workers classify as “gels” systems which others exclude. Only one rule seems to hold for all gels, and that is that they must be built up from two components, one of which is a liquid at the temperature under consideration, and the other of which, the gelling substance proper, often spoken of as the gelator, is a solid. The gel itself has the mechanical properties of a solid, i.e., it can maintain its form under the stress of its own weight, and under any mechanical stress it shows the phenomenon of strain.

Later in the same paper Jordan Lloyd wrote: ‘There is no need to assume that all gels have the same molecular architecture. There is little doubt, however, that they all possess a solid phase, . . .’

The works of Flory and of Stockmayer on the theory of gelation in non-linear polymerizations and crosslinking of linear polymer chains^{25–28} were important milestones. Attempts were therefore made to include structural characteristics in the definitions of gels, such as infinite network, three-dimensional structure, coherence, connectedness, etc.

Bungenberg de Jong gave the following definition:²⁹

Gel, a colloidal system of solid character, in which the colloidal particles somehow constitute a coherent structure, the latter being interpenetrated by a (usually liquid) system consisting in kinetic units smaller than colloidal particles. If this liquid system is almost entirely or wholly removed the gel will be called a *Xerogel*.

and P. H. Hermans gave this definition of gels:¹¹

- a. They are coherent colloid disperse systems of at least two components.
- b. They exhibit mechanical properties characteristic of the solid state.
- c. Both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system.

Both definitions clearly exclude one-component systems such as fully crosslinked linear polymers produced, for example, by radiation cross-linking. These definitions therefore appear to be in conflict with the Flory–Stockmayer gelation theory.^{26,27} However, Hermans qualifies his definition by mentioning in his introduction that substances which are capable of swelling in the presence of a second component are often included in the family of gels.¹¹

Flory later proposed a classification of gels based on structural criteria:³⁰

- (1) Well-ordered lamellar structures, including gel mesophases.
- (2) Covalent polymeric networks; completely disordered.
- (3) Polymer networks formed through physical aggregation; predominantly disordered, but with regions of local order.
- (4) Particulate, disordered structures.

Unlike Hermans's definition, Flory's structural classification contains no statement about the minimum number of components in the system. This means that undiluted crosslinked rubbers, which consist of one giant molecule, are included as genuine gels.

Although Flory's structural classification apparently contains no requirement of solid-like behaviour, it should be noted that Flory carefully states in the general section of his paper that 'The one feature identified almost universally as an essential characteristic of a gel is its solid-like behaviour. When deformed, its reponse is that of an elastic body.' He further states that '... the modulus of elasticity is low.'³⁰

The definition of gels based on structural criteria is clearly a formidable task. The identification of phenomenological characteristics common to all gels therefore seems to be a necessary first step.

Phenomenological definitions

With the statement that a gel 'is a substantially diluted system which exhibits no steady-state flow', Ferry³¹ excluded viscoelastic liquids irrespective of the magnitude of the longest relaxation time. Only true

solids are accepted by this definition. The rigidity of a viscoelastic solid may be expressed in terms of the frequency-dependent storage modulus. Djabourov proposed to use the limiting value of the storage modulus $G'(\omega)$ as a measure of gel rigidity:³²

$$E = \lim_{\omega \rightarrow 0} G'(\omega) \quad (1)$$

where ω is the angular frequency and E is termed 'the relaxed shear modulus'. However, it is well known that $\omega \rightarrow 0$ is an unattainable limit. A transition from the plateau region to the liquid state may occur at a frequency lower than the lowest experimental frequency which typically is of the order of 10^{-2} rad/s.

It is becoming increasingly clear that to require gels to be true solids may be overly restrictive. Many systems, which behave as typical gels in all respects except for the lack of an equilibrium modulus, are known. Burchard and Ross-Murphy¹⁴ admitted some of these systems as gels with the following general statement '... that they all possess at least one property which can stand as the operational definition of a gel; they possess a plateau in the real part of the complex modulus extending over an appreciable window of frequencies—i.e. they are, or can be coaxed under appropriate conditions to be, viscoelastic solids.' We believe that Burchard and Ross-Murphy have identified the key mechanical property of gels. However, the statement needs to be qualified as discussed below.

PROPOSAL FOR A MORE PRECISE PHENOMENOLOGICAL DEFINITION

Solid-like behaviour

A **solid** has by definition a definite shape. This means that a deformed solid body returns to its original shape after removal of the deforming force.³³ True solids exhibit an equilibrium modulus. **Solid-like** behaviour means that the material behaves as a solid in some, but not all, respects.

It is well known that $G''(\omega) \gg G'(\omega)$ is observed when dilute and even some moderately concentrated solutions of linear polymers are measured in the commonly studied frequency range of 10^{-2} – 10^2 rad/s. Such systems are liquids with terminal relaxation times of less than a few milliseconds. However, solutions of extremely high molar mass polymers can exhibit very long terminal relaxation times even at fairly low concentrations. An example is shown in Fig. 1 for a 5 million

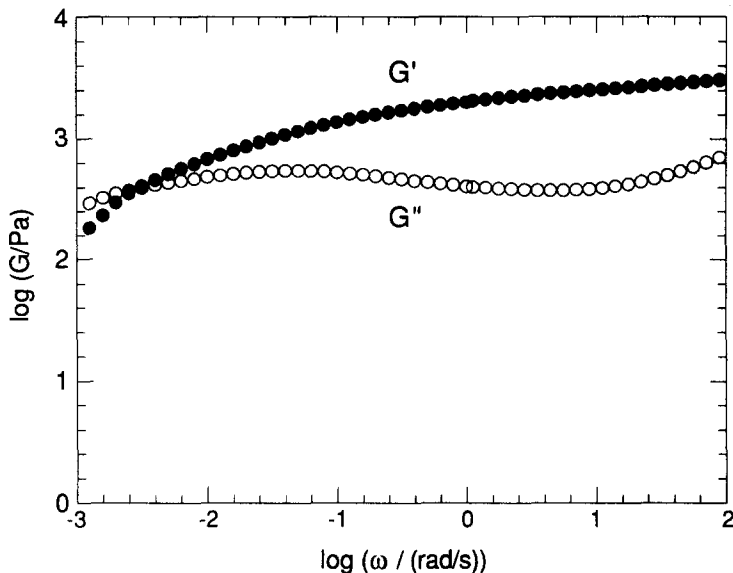


Fig. 1. Log–log plot of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, versus angular frequency for a 13.9% (w/w) solution of polystyrene in di(2-ethylhexyl) phthalate. The molecular weight of polystyrene is 4.7×10^6 . Measurements were made at 25°C on a Rheometrics RMS 800 instrument, using parallel plates. We propose to accept such solutions as gels since $G'(\omega)$ exhibits a plateau extending to frequencies lower than 1 rad/s, i.e. times longer than 1 s, and $G'(\omega)$ is much larger than $G''(\omega)$.

molecular weight polystyrene in di(2-ethylhexyl) phthalate. The experimental details have been given in a previous study.³⁴ It can be seen that this solution exhibits a well-pronounced plateau in $G'(\omega)$ with $G'(\omega) > G''(\omega)$ for several decades of frequency. The solution enters the terminal zone at angular frequencies less than about 10^{-3} rad/s, which corresponds to a terminal relaxation time of the order of 10^3 s. This system therefore behaves as a solid on a time scale of seconds. Although the plateau in $G'(\omega)$ is sloped, the mechanical properties shown in Fig. 1 are similar to those of typical gels such as gelatine gels.³⁵ Thus, we will argue that swollen uncrosslinked polymers, unlike undiluted polymer melts, should be admitted as genuine gels when the transition to liquid behaviour occurs at sufficiently low frequencies, i.e. when the longest relaxation time is sufficiently long.

We propose that the solid character should be directly observable to humans, i.e. the material must appear elastic and resilient to the human touch. Due to the limitations of human perception, the longest relaxation time should therefore be at least of the order of seconds. A consequence of this is that a gel on a time scale of seconds should exhibit no flow under its own weight.

Although semidilute solutions of rigid rods may be gels,^{32,36} infinitely dilute solutions are not. Nonetheless, very dilute solutions of tobacco mosaic virus (TMV) and TMV aggregates were found by Ferry and coworkers³⁷ to exhibit a pronounced plateau in $G'(\omega)$ as shown in Fig. 2. This means that the Burchard–Ross–Murphy criterion¹⁴ is fulfilled for a system which clearly is not a gel. A proposal for the characteristics of

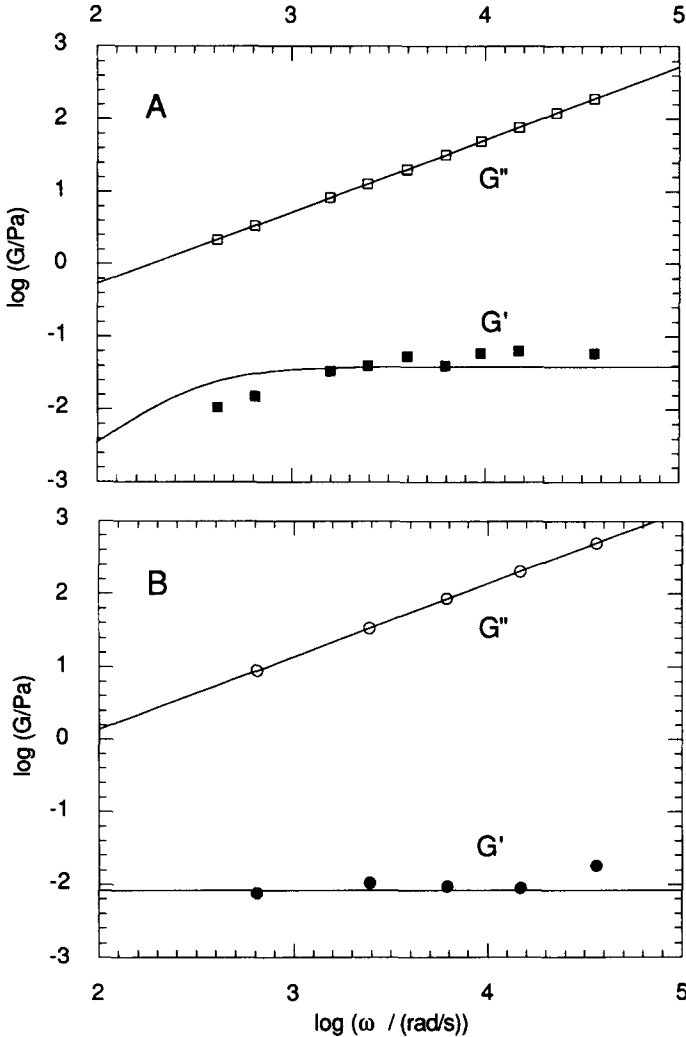


Fig. 2. Log–log plots of $G'(\omega)$ and $G''(\omega)$ versus angular frequency for very dilute solutions of tobacco mosaic virus. A, individual TMV rods; B, TMV aggregates. The points are calculated for a concentration of 1 mg/ml from infinite dilution results given by Ferry and coworkers,³⁷ using $G' = [G']c$ and $G'' = [G'']c + \omega\eta_s$, where c is the concentration of TMV and η_s is the solvent viscosity. The solid curves are theoretical for dilute solutions of long rigid rods.³⁷ Although $G'(\omega)$ exhibits a plateau in both cases, these solutions are not gels since $G'(\omega) < G''(\omega)$ in the plateau region.

a gel must exclude the TMV solutions and similar very dilute systems. Figure 2 shows that the loss modulus $G''(\omega)$ is greater than the storage modulus $G'(\omega)$ for all frequencies, which means that the solution is far from being resilient.^{22,23} The dissipated energy will in fact always be larger than the stored energy, preventing the deformed solution from returning to its original shape. This example illustrates that it is not sufficient that $G'(\omega)$ exhibits a plateau. In addition to the requirement of a longest relaxation time being 'at least of the order of seconds', it is a requirement that $G'(\omega)$ is considerably larger and preferably more than 10 times larger than $G''(\omega)$ in the plateau region to ensure that the gel is solid-like and resilient.

Presence of a liquid

The great majority of systems which have been characterized as gels are soft materials which contain a substantial quantity of liquid. It is therefore unfortunate that it has become common practice also to admit Xerogels, i.e. dried gels,^{11,29} and certain undiluted materials into the gel family.¹¹

Crosslinking of polymer melts, which are liquids at sufficiently low frequencies, forms new species with extremely long relaxation times.³⁸ Up to and well beyond the so-called gel point, the system is therefore a multicomponent system of which the main component is a liquid. However, no liquid is present in a highly crosslinked polymer which consists of one giant macromolecule, i.e. the chemical reaction creates a material which at high degrees of crosslinking no longer is a gel according to the usual characteristics.

Our conclusion is that Xerogels and undiluted systems should not be admitted as gels.†

Phenomenological characteristics of gels

As a result of the preceding arguments, the following phenomenological characteristics can be specified:

- (a) A gel consists of two or more components, one of which is a liquid, present in substantial quantity.
- (b) A gel is a soft, solid or solid-like material.

For gels which are only solid-like, we propose that the characteristics

†Editor's footnote: This statement does *not* necessarily reflect the future policy of this journal. In any case we are also concerned with polymer networks, which need not be associated with solvent.

should be defined in terms of the dynamic mechanical properties, e.g. a storage modulus, $G'(\omega)$, which exhibits a pronounced plateau extending to times at least of the order of seconds, and a loss modulus, $G''(\omega)$, which is considerably smaller than the storage modulus in the plateau region.

It should be noted that materials that are heterogeneous to the naked eye or at low magnification in a microscope cannot be accepted as gels. An ordinary sponge may serve as an example of this (Djabourov, M., pers. commun., 1992).

CONCLUSIONS

Indiscriminate use of the term 'gel' is so common that it has become ambiguous. Limitations of its use are therefore required. Focusing on the phenomenological characteristics, we propose the following phenomenological definition:

- (1) A gel is a soft, solid or solid-like material of two or more components one of which is a liquid, present in substantial quantity.
- (2) Solid-like gels are characterized by the absence of an equilibrium modulus, by a storage modulus, $G'(\omega)$, which exhibits a pronounced plateau extending to times at least of the order of seconds, and by a loss modulus, $G''(\omega)$, which is considerably smaller than the storage modulus in the plateau region.

It should be noted that above definition essentially is the same as Ferry's definition³¹ except for the inclusion of certain viscoelastic liquids as proposed by Burchard and Ross-Murphy.¹⁴ In consideration of the limitations of human perception, we have specified that the plateau in the storage modulus must include times 'at least of the order of seconds'. In order to ensure resiliency,^{22,23} we have further specified that the loss modulus must be considerably smaller than the storage modulus in the plateau region. Materials with moduli of the order of 10^8 Pa are in our opinion far too rigid to be included in the family of gels. However, the term 'soft' has different meanings in different areas of science and we have been unable to find a natural upper limit for it.

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