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Matter through the eye of the association theory camera

Robert Ginell

Association Theory is a conceptual scheme for picturing the activity of molecules that employs a kind of stop-motion mental photography. Its basic simplicity proves to be misleading in that Association Theory has already proven its capability in making precise and sophisticated quantitative predictions about a variety of phase transformations. This success lends substantial credence to the elegant insight it gives into molecular activity.

The equilibrium state is a convenient and useful concept because it eliminates time as an explicit variable. Hence, it has the capability of simplifying descriptions of a variety of natural phenomena. In the equilibrium state a substance has the same macro-properties (p, v, T, etc.) now as it had when it went into this state, and it continues to have these same properties as long as it is in this state. *The convenience of the equilibrium state is so great that we often invent hypothetical ones*, ones that are poised between what is possible and what is impossible, and which only approximate real conditions.

Here we shall introduce Association Theory as an equilibrium concept and with it develop a theory of the molecular structure of matter and the nature of the transitions between states of matter. We will talk about the gaseous, liquid, and solid states, include transitions among them, and even show how association theory deals with the critical state, super cooling, and nucleation. The reader is here not unduly burdened with underlying mathematical details; but is instead referred to original publications where such details are developed.

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Kinetic-molecular theory through conceptual stop-motion photography

The usual modern concept of the nature of matter starts with a time-dependent picture, the Kinetic-Molecular Theory. This familiar theory states that matter in the gaseous state consists of molecules that are in constant motion. They move in straight lines, collide with one another and the walls of the containing vessel. According to this theory, the heat contained in the substance is a function of the total energy of this system; the temperature, a function of the kinetic energy of the particles; and the pressure, a function of the momentum of the particles. The attempts to describe matter by using this picture are the province of Statistical Mechanics, which uses time as an explicit variable and considers equilibrium as a special case of a time-dependent phenomenon. While these attempts are undoubtedly true and useful, in many situations they yield cumbersome mathematics and necessitate assumptions that lead to little growth in understanding.

An alternative, and in many ways a simpler approach, follows from association theory. To justify this approach let us start with a thought experiment. Imagine that we had a motion picture camera of such speed and resolution that it could resolve and take pictures of molecular motion. With this camera let us then take a motion picture of a gas at equilibrium. The projected film would show us in slow motion, according to the Kinetic-Molecular Theory, particles (molecules) moving in straight lines, colliding with each other, colliding with the walls and rebounding. We would see a kaleidoscopic pattern of binary collisions, maybe some ternary collisions, perhaps quaternary collisions, etc. The collisions would not be instantaneous but would last a short interval of time, and the molecules would exhibit a volume. All this would be so if the Kinetic-Molecular Theory is a correct picture. In this work I do not dispute that it is and assume that this is what we would see. This is the picture that classical statistical mechanics describes in terms of momenta and position coordinates.

However, this is not the only way in which this film can be used (*1*). Rather than project it at normal speeds, let us stop the projector and examine a frame. On the first frame we, of course, see no motion; we see a number of single, isolated particles. We also see a number of double