This Week's Citation Classic

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Cohen M H & Turnbull D. Molecular transport in liquids and glasses.
J. Chem. Phys. **31**:1164-9, 1959.
[Univ. Chicago, Chicago, IL and General Electric Res. Lab., Schenectady, NY]

Molecular motion in dense liquids and glasses is treated via the freevolume model using the notion that statistical redistribution occasionally opens up voids large enough for diffusive displacement. Good agreement with fluidity and diffusion data is obtained for a wide range of materials. [The *SCI*® indicates that this paper has been cited over 540 times since 1961.]

Morrel H. Cohen
James Franck Institute and
Department of Physics
University of Chicago
Chicago, IL 60637

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"David Turnbull and I shared an office for six months at the Cavendish Laboratory in 195758. We tried working together, but did not find a subject of sufficient mutual interest. Finally, before returning to the General Electric Research Laboratory, Dave proposed working on the glass transition and had already prepared a paper which he suggested I coauthor. There ensued a fruitful collaboration which ended in 1970.

"Six months later, returning from Cambridge to Chicago, I stopped at Schenectady and stayed one night at the Turnbulls. That evening David patiently introduced me to the freevolume model of liquids and glasses, to Doolittle's work on fluidity,[1] and to the work of Williams, Landel, and Ferry on relaxation in glasses.[2] We were particularly struck by the remarkable simplicity of Doolittle's equation for the fluidity ϕ,

$$\phi = \phi_o \exp[v^*/v_f] \quad (1)$$

where ϕ_o is a constant, v^* is approximately equal to a molecular volume, and v_f is the average free volume per molecule. Dave had a clear physical conception of the mechanism of molecular transport but did not see how to derive the Doolittle equation from it. The next morning I had a 'derivation' of equation (1) to present to Dave at breakfast.

"It appeared essentially unchanged in the paper submitted for publication over seven months later. It was based on the StokesEinstein relation, on the notion that free volume was freely redistributed so that Boltzman statistics applied, and on the notion that a diffusive step occurred only when a void of molecular size opened during redistribution.

"I was unaware of the widespread attention the paper received, often in fields far from my interests. Only recently did I learn that it was my mostcited paper, and only within the last two years did I learn why. I did not attach any particular importance to the work at the time it was done because of the very great oversimplifications that I thought it contained. However, I was recently told by Austin Angel I that he started his work on glasses after reading our paper because its very simplicity stimulated him to believe that progress might be possible after all.

"I have tried many times to go more deeply into the freevolume model than Turnbull and I had managed. Finally, three years ago I saw the missing piece, stimulated by a question from Richard Zallen. With Gary Crest, the original freevolume model was deepened, made more precise, and shown capable of accounting quantitatively for the molecular transport, the structural relaxation, and the lowtemperature tunneling states of glasses.[3] Though deep questions remain and the theory is only very roughly worked out, it is clear that its central ideas transcend the limitations of the freevolume model."

1. **Doolittle A K.** Studies in Newtonian flow. II. The dependence of the viscosity of liquids on freespace. *J. Appl. Phys.* **22**:147-15, 1951.
2. **Williams M L, Landel R F & Ferry J D.** The temperature dependence of relaxation mechanisms in amor phous polymers and other glassforming liquids. *J. Amer. Chem. Soc.* **77**:370-17. 1955.
3. **Cohen M H & Grest G S.** Liquidglass transition, a freevolume approach. *Phys. Rev. B* **20**:1077-98, 1979.