History of RSB Interview:

Peter G. Wolynes

October 2, 2023, 19:00 to 21:00 (CET). Final revision: January 21, 2024

Interviewer:

Patrick Charbonneau, Duke University, <u>patrick.charbonneau@duke.edu</u> Francesco Zamponi, Sapienza Università di Roma **Location:** Over Zoom, from Prof. Wolynes' office at Rice University in Houston, TX, USA. **How to cite**:

P. Charbonneau, *History of RSB Interview: Peter G. Wolynes*, transcript of an oral history conducted 2023 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2024, 37 p. https://doi.org/10.34847/nkl.3df5b08z

- **PC:** Good morning, Prof. Wolynes. Thank you very much for joining us. As we've mentioned ahead of this interview, the theme of this series is the history of replica symmetry breaking in physics, which we bound roughly from 1975 to 1995, but obviously we're going to be bleeding on both ends of this timeline in this particular interview. To get us started, I have a couple of background questions I'd like to go through with you. In your scientific memoir, which you published in 2013¹, you mentioned reading extensively about physics and mathematics throughout your adolescence. What drew you to chemistry?
- **PGW:** [0:00:49] I started probably in chemistry because when I was a little boy my father was a chemical engineer. So, it was sort of natural to think about chemistry things. In our library in our basement, we had lots of books that were the books my father had used in college in chemical engineering. That's probably where I read them. There were other sorts of popular science-ish things, say from Isaac Asimov, which were very chemically oriented, because he was a biochemist². I'm sure that's part of it.

In fact, I do remember one weird thing. Very early on, I guess everyone thought I would be a chemist. My aunt one time when I was saying I was also interested in other things advised me: "Oh no! You gotta really concentrate and only go in one area." I didn't follow her advice very well.

¹ P. G. Wolynes, "A Scientific Memoir," *J. Phys. Chem. B* **117**, 12672–12675 (2013). <u>https://doi.org/10.1021/jp407073n</u>

² Isaac Asimov was professor of biochemistry at Boston University. <u>https://en.wikipedia.org/wiki/Isaac_Asimov</u>

Obviously, in school, in the lower grades and such, there's not that much opportunity—in the school itself—to do chemistry, so it was probably more that I was recognized for doing mathematical things when I was a boy. When I went to college, for example, initially the mathematicians were trying to get me to become a mathematician, not to be a chemist, but I sort of didn't quite go that way either.

PC: In that same memoir, you described how in graduate school you initially wanted to work on critical phenomena but felt that others were already well underway with the topic. So, instead you looked into formalizing hydrodynamics through a mode-coupling theory description³. How did you get to that particular problem from your readings and the rest?

PGW: [0:02:51] That's an interesting question. I'm not quite sure. If you know as you do, I'm sure—the real history, for critical phenomena the basic ideas had already really been figured out by the time I was in grad school, but I wasn't really aware of that. There was still the sense of: "Well, it's not clear what's really going on." The Kadanoff-Widom papers were considered very speculative⁴. Wilson just became well known, I would say, in my second year⁵. I remember going to Wilson's talks, which he gave at Harvard. It seemed to me that the renormalization group was primarily a method of numerical integration, judging from the way he presented it. I thought it was clever and interesting, but it didn't seem to be the powerful general way of looking at things that it turned out to be. But it was clear that in some sense the static problem was solved, and I had always been interested in dynamics, because I was fascinated with that through chemistry. So, I got interested in dynamic critical phenomena, which were still a little more on the on the edge of understood. Of course, dynamic critical phenomena also got connected up with the problem of long-time tails in hydrodynamics⁶. That's how I got onto mode coupling originally. My first paper, as I said in the memoir, is my only (almost) rigorous paper in the sense that it proves some bounds within a certain model of mode-

³ Peter Guy Wolynes, *Hydrodynamic boundary conditions and mode-mode coupling theory*, PhD Thesis, Harvard University (1976). <u>https://id.lib.harvard.edu/alma/990040168510203941/catalog</u> (Accessed November 2, 2023.)

⁴ Also known as the Widom-Kadanoff scaling laws. See, *e.g.*, B. Widom, "Equation of state in the neighborhood of the critical point," *J. Chem. Phys.* **43**, 3898-3905 (1965).

https://doi.org/10.1103/PhysicsPhysiqueFizika.2.263

⁵ See, *e.g.*, K. G. Wilson, "Renormalization group and critical phenomena. I. Renormalization group and the Kadanoff scaling picture," *Phys. Rev. B* **4**, 3174 (1971). <u>https://doi.org/10.1103/PhysRevB.4.3174</u>

⁶ B. J. Alder and T. E. Wainwright, "Decay of the Velocity Autocorrelation Function," *Phys. Rev. A* **1**, 18 (1970). <u>https://doi.org/10.1103/PhysRevA.1.18</u>

coupling theory⁷. When I looked at hydrodynamics, which was already being studied at MIT not at Harvard, I said: "The one thing that was missing was the understanding of the boundary conditions." So, that's why I thought would be an interesting problem to turn to, [namely] whether boundary conditions could be understood or not⁸.

- **PC:** Being in Cambridge at a time, were you at all in touch with people like Irwin Oppenheim⁹, who were also working on mode-coupling ideas?
- **PGW:** [0:05:24] Oh, yeah, I was. Although not in the sense of working with them specifically. Although maybe this was a bad thing—as I also mentioned it in the memoir—there was then a sense that you really were supposed to find your own project and work on it not carry out someone else's research program. It wasn't the way nowadays we do research in theoretical groups, where students expect their advisor to give them problems. I was never given any problems. There was a stage, however, when I said I really needed to go talk to people other than my official advisor, who was Roy Gordon¹⁰, and I'm sure I saw Oppenheim at that time, probably. A person I really did seriously talk to was John Ross¹¹, who was at MIT, and also I met John Deutch¹², who was also then about to go on sabbatical to Harvard. So, those people I talked to a little bit; John Deutch much more so than Oppenheim.
- **PC:** What about Sydney Yip and Gene Mazenko¹³, who were also around?
- **PGW:** [0:06:41] I do remember meeting with Sidney Yip at some point in time, but I'm not sure whether I did that when I was a student. As you know, after I was a student at Harvard, I postdoc'ed at MIT for about six months and then I came back to Harvard as assistant professor. I think I met Yip sometime during that period when I was an assistant professor. Mazenko, I never met. I thought he was at Chicago around this time.

⁷ P. G. Wolynes, "Bounds for convective contributions to transport coefficients," *Phys. Rev. A* **11**, 1700 (1975). <u>https://doi.org/10.1103/PhysRevA.11.1700</u>

⁸ P. G. Wolynes, "Hydrodynamic boundary conditions and mode-mode coupling theory," *Phys. Rev. A* **13**, 1235 (1976). <u>https://doi.org/10.1103/PhysRevA.13.1235</u>; P. G. Wolynes and J. M. Deutch, "Slip boundary conditions and the hydrodynamic effect on diffusion controlled reactions," *J. Chem. Phys.* **65**, 450-454 (1976). <u>https://doi.org/10.1063/1.432788</u>

⁹ Irwin Oppenheim: <u>https://de.wikipedia.org/wiki/Irwin_Oppenheim</u>

¹⁰ Roy G. Gordon (1940-). See, *e.g.*, "Roy Gerald Gordon," *Mathematics Genealogy Project* (n.d.) <u>https://www.genealogy.math.ndsu.nodak.edu/id.php?id=1350</u> (Accessed November 2, 2023.)

¹¹ John Ross: https://en.wikipedia.org/wiki/John Ross (chemist)

¹² John M. Deutch: <u>https://en.wikipedia.org/wiki/John M. Deutch</u>

 ¹³ See, *e.g.*, P. Charbonneau, *History of RSB Interview: Sidney Yip*, transcript of an oral history conducted
 2022 by Patrick Charbonneau, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2023, 13
 p. <u>https://doi.org/10.34847/nkl.7740w7ht</u>

- **PC:** Let me phrase this line of questioning differently. Can you describe the Cambridge community working on the statistical mechanics of liquids at that time? How was it structured? Were there meetings?
- **PGW:** [0:007:31] I think the statistical mechanics of liquids was being studied at MIT by Oppenheim and Deutch. John Ross had done this sort of work at one time in the past. He was a postdoc of Kirkwood in the '50s. There was a weekly seminar at MIT. At Harvard, no one was interested in liquids in the chemistry department at that time, and no one was particularly interested in liquids in the physics department. I should be a little careful in saying that in the sense that I think David Nelson¹⁴ probably came when I was an assistant professor around that time. We certainly knew each other.
- **PC:** What about Paul Martin¹⁵?
- **PGW:** [0:08:20] I took classes from Paul Martin, but he actually did very little on classical liquids. He had written the Kadanoff-Martin paper on hydrodynamics¹⁶, which was very important for me. He was on my PhD thesis defense. I would say in general, however, ordinary liquids were not considered interesting.
- **PC:** Were there conferences, larger group meetings, or seminar series that were bringing people together? Or this was really just individual people working on in isolation?
- **PGW:** [0:09:00] It was individual people. The only thing that was probably quite relevant, and even relevant for my story about the glasses, was that Ben Widom¹⁷ did come and give lectures at Harvard probably in my last year or maybe the year before—I can't quite remember. These were on critical phenomena, which I attended. These had a big stylistic impact on me.

¹⁷ Widom was Visiting Professor of Chemistry at Harvard University in 1975. See, *e.g.*, B. Widom, "Curriculum Vitae of Benjamin Widom," *J. Phys. Chem. B* **122**, 3211 (2018). <u>https://doi.org/10.1021/acs.jpcb.8b00124</u>; Benjamin Widom: <u>https://en.wikipedia.org/wiki/Benjamin_Widom</u>

¹⁴ David R. Nelson: <u>https://en.wikipedia.org/wiki/David_Robert_Nelson</u>

¹⁵ See, *e.g.*, P. C. Martin and S. Yip, "Frequency-Dependent Friction Constant Analysis of Diffusion in Simple Liquids," *Phys. Rev.* **170**, 151 (1968). <u>https://doi.org/10.1103/PhysRev.170.151</u>; P. C. Martin, P. Parodi and P. S. Pershan, "Unified hydrodynamic theory for crystals, liquid crystals, and normal fluids," *Phys. Rev. A* **6**, 2401 (1972). <u>https://doi.org/10.1103/PhysRevA.6.2401</u>

¹⁶ L. P. Kadanoff and P. C. Martin, "Hydrodynamic equations and correlation functions," *Ann. Phys.* **24**, 419-469 (1963). <u>https://doi.org/10.1016/0003-4916(63)90078-2</u>

Edward Brézin¹⁸ also gave a class on calculating huge numbers of diagrams in the renormalization group, which I went to. Liquids not near a critical point were not really considered interesting. Overall, Harvard, I would say, had a somewhat negative view on statistical mechanics as a whole. One of the nicest people in the physical chemistry group was a guy named Bill Klemperer¹⁹—who is actually a very nice person—but I remember he was famous for saying that if you were doing an experiment that required statistical mechanics to interpret it, you were doing the wrong experiment. That was the attitude.

- **PC:** As you mentioned earlier, after your PhD and a quick postdoc at MIT, you came back to Harvard as junior faculty. During that time, you worked on what looks from the outside, more classical physical chemistry problems, such as solvation, electron hopping, and biopolymer dynamics²⁰. In general, what drew your choice of research problems at that point?
- **PWG:** [0:10:38] I defined my work as many-body chemistry. Especially at Harvard, the attitude was that—and is still true through most chemistry departments—the molecule is the main thing. Your goal was to get down to studying an individual molecule and what molecules do. In that view, that statistical mechanics would seem a failure. But this view left out most phenomena that would have many-body aspects, which I'd been interested in even as an undergrad. So, I looked around. I was always interested in chemical rate phenomena, and again that was more or less ignored in the liquid phase. So, I said: "Oh, here is an opportunity to say something interesting and new." Of course everyone nowadays knows the Kramers theory²¹, but the Kramers theory was basically completely unknown in the chemical community at that time. The general idea of what goes on in reactions in liquids was very unclear.

²¹ Kramers theory of reaction rate:

¹⁸ Brézin visited Harvard in 1974. See, *e.g.*, E. Brézin, "Amplitudes of the logarithmic singularities for the four-dimensional critical behavior," *J. Physique Lett.* **36**, 51-53 (1975).

https://doi.org/10.1051/jphyslet:0197500360305100; P. Charbonneau, *History of RSB Interview: Édouard Brézin*, transcript of an oral history conducted 2020 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2021, 20 p. https://doi.org/10.34847/nkl.9573z1yg

¹⁹ William Klemperer: <u>https://en.wikipedia.org/wiki/William_Klemperer</u>

²⁰ See, e.g., P. G. Wolynes, "Molecular theory of solvated ion dynamics," J. Chem. Phys. 68, 473-483 (1978). <u>https://doi.org/10.1063/1.435777</u>; K. Schulten and P. G. Wolynes, "Semiclassical description of electron spin motion in radicals including the effect of electron hopping," J. Chem. Phys. 68, 3292-3297 (1978). <u>https://doi.org/10.1063/1.436135</u>; J. A. McCammon, B. R. Gelin, M. Karplus and P. G. Wolynes, "The hinge-bending mode in lysozyme," Nature 262, 325-326 (5566). <u>https://doi.org/10.1038/262325a0</u>

https://en.wikipedia.org/wiki/Transition_state_theory#Kramers_theory_of_reaction_rates

In fact, the glass problem—which I guess is where RSB comes in—came to my attention when I was assistant professor. It seemed to me that it was going to be a very easy problem, that the main thing that was not understood was how you could get a barrier in a translationally invariant system. It seemed to me, first of all, that it was obvious that glasses involved something that had activated dynamics. In that sense, the glass problem had to be the same as the reactions that I was studying. These must be some kind of collective activation barrier that involved a barrier being created by the coupling of other degrees of freedom to an existing barrier. So, I was pretty sure that we could do that problem.

With this optimistic view, I concocted a sort of *envoi* problem that I gave to Jim Skinner, who was my first research student²². With the goal of looking at glasses, I had the idea that such coupling would be going on in solid polymers. We came up with this way of describing the dynamics of crystalline polymers using solitons, which led to two papers²³. Then, Jim went off and did sort of one-dimensional kinetic Ising models, with again the same idea of overcoming a barrier that's coupled to something next to it and so²⁴. I guess we would now call it a facilitation model. (I think Jim's paper predates the Fredrickson-Anderson model²⁵.) That was that was the only published work that came out of that.

I remember knowing two things about glasses at Harvard, though. One was I remember Turnbull²⁶ gave a seminar, which I went to. That seminar impressed me that there was really an interesting general phenomenon here. I got interested enough from this that I invited Austen Angell²⁷ to give a Harvard/MIT physical chemistry colloquium. He came, and he actually had a demo of making a glass that was very good. That was really an excellent seminar. It went over like an absolute lead balloon. Nobody else thought it was interesting at all. He felt the audience's indifference. He wanted to not accept his honorarium or travel expenses, because he

https://doi.org/10.1063/1.445976

²² James Lauriston Skinner, *Kinetic models of activated events*, PhD Thesis, Harvard University (1979). https://id.lib.harvard.edu/alma/990039219600203941/catalog See also, J. L. Skinner, "Autobiography of James L. Skinner," *J. Phys. Chem. B* **118**, 7671–7672 (2014). https://doi.org/10.1021/jp504477e

 ²³ J. L. Skinner and P. G. Wolynes, "Transition state and Brownian motion theories of solitons," *J. Chem. Phys.* **73**, 4015-4021 (1980). <u>https://doi.org/10.1063/1.440629</u>; "Solitons, defect diffusion, and dielectric relaxation of polymers," *J. Chem. Phys.* **73**, 4022-4025 (1980). <u>https://doi.org/10.1063/1.440630</u>
 ²⁴ J. L. Skinner, "Kinetic Ising model for polymer dynamics: Applications to dielectric relaxation and dynamic depolarized light scattering," J. Chem. Phys. **79**, 1955-1964 (1983).

²⁵ G. H. Fredrickson and H. C. Andersen, "Facilitated kinetic Ising models and the glass transition," *J. Chem. Phys.* **83**, 5822-5831 (1985). <u>https://doi.org/10.1063/1.449662</u>

²⁶ David Turnbull: <u>https://en.wikipedia.org/wiki/David Turnbull (materials scientist)</u>

²⁷ Austen Angell: <u>https://en.wikipedia.org/wiki/Austen_Angell</u>

felt his talk was so poorly received, but I somehow got him to accept the money. It was just kind of silly.

- PC: So, was it through Turnbull's exposé that you became aware of the glass problem?
- PGW: [0:15:10] I probably say that's what made me realize there was something big there, that there was a sort of a hard-to-understand problem. Of course, Turnbull had done practical things with this, and even made key contributions to the understanding of the phenomenon very early on²⁸. But at this point he was more interested in practical things with making metallic glasses and stuff like that²⁹.
- **PC:** You then moved to Illinois, where you pursued different yet similar problems on solvation and quantum mechanical effects in chemistry³⁰. Can you describe the chemical physics community at Illinois? Was it in any way different from what you had in Cambridge?
- **PGW:** [0:16:04] Obviously, one of the differences was now I was one of the senior people. When I first came, obviously, David Chandler³¹ was the person who invited me to come, and I interacted with him. We collaborated on some quantum things³². I'd been interested in quantum effects on rates. Our collaborative work turned out to be quite well-known.

These was a strong theory group in physics. I just went over and interacted through seminars and things of that sort primarily. [Also,] I interacted very deeply with Hans Frauenfelder³³, who was an experimentalist. He was

³¹ David Chandler: <u>https://en.wikipedia.org/wiki/David Chandler (chemist)</u>

https://doi.org/10.1063/1.441588; K. S. Schweizer, R. M. Stratt, D. Chandler and P. G. Wolynes,

"Convenient and accurate discretized path integral methods for equilibrium quantum mechanical calculations," J. Chem. Phys. **75**, 1347-1364 (1981). <u>https://doi.org/10.1063/1.442141</u>; D. Chandler, K. S. Schweizer and P. G. Wolynes, "Electronic states of a topologically disordered system: Exact solution of the mean spherical model for liquids," *Phys. Rev. Lett.* **49**, 1100 (1982). https://doi.org/10.1103/PhysRevLett.49.1100

 ²⁸ See, *e.g.*, D. Turnbull and M. H. Cohen, "Free-volume model of the amorphous phase: glass transition,"
 J. Chem. Phys. 34, 120-125 (1961). <u>https://doi.org/10.1063/1.1731549</u>

²⁹ See, *e.g.*, P. Chaudhari, B. C. Giessen and D. Turnbull, "Metallic Glasses," *Scientific American* **242**(4) 98-117 (1980). <u>https://www.jstor.org/stable/24966305</u>

 ³⁰ See, *e.g.*, D. F. Calef and P. G. Wolynes, "Classical solvent dynamics and electron transfer. 1. Continuum theory," *J. Phys. Chem.* 87, 3387-3400 (1983). <u>https://doi.org/10.1021/j100241a008</u>; P. G. Wolynes, "Quantum theory of activated events in condensed phases," *Phys. Rev. Lett.* 47, 968 (1981). https://doi.org/10.1103/PhysRevLett.47.968

³² D. Chandler and Peter G. Wolynes, "Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids," *J. Chem. Phys.* **74**, 4078-4095 (1981).

³³ Hans Frauenfelder: <u>https://en.wikipedia.org/wiki/Hans_Frauenfelder</u>

interested in dynamics in biological molecules and also in glasses³⁴, so he was a key person that encouraged me and encouraged other people to interact with me at Illinois. So, over the years my interaction with the physics theorists grew. Although I don't think I ended up having any collaborative papers with theorists in the physics department, I felt part of their team of people.

- **PC:** With your first Illinois PhD student, James Peter Stoessel³⁵, you came back to more liquid state interests, looking specifically at glasses. What made you think that this was now the right time to tackle this?
- **PGW:** [0:18:06] Well, I never stopped. I thought about glasses all of this time. I had a specific idea. I'd long been interested in the problems of chaos and the origins of chaos. It seemed to me that the problem of glass was the question of why you have something that's a crystal but it's not a periodic crystal but a chaotic aperiodic crystal. It struck me that we could use some ideas about transitions from periodicity to chaos.

I started with the idea that maybe you could do hard sphere crystallization by transfer matrix method. For the transfer matrix, you'd study hard spheres in a tube. The idea is you would march along the tube and using a density functional, the minimization problem would be time development as you moved along the tube. It seemed like there would be a transition first to having periodic tube states to at some point having period doubling and then chaos and blah blah. That's where I really wanted to go. That idea never really fully blossomed, but I said: "Well, look, we already know there are aperiodic chaotic minima, because of this work of Bernal³⁶." So, I said: "Why don't we start with those and try to do the theory of aperiodic structures, and just check whether they're stable or not³⁷." That's what came out of doing this.

PC: That was a pretty unique approach at a time, as far as I can tell. No one had really started from the stability of the amorphous solid. Where did he get exposed to these ideas of Bernal and Finney about disordered solids?

³⁴ See, *e.g.*, A. Ansari, J. Berendzen, S. F. Bowne, H. Frauenfelder, I. E. Iben, T. B. Sauke, E. Shyamsunder and R. D. Young, "Protein states and proteinquakes," *Proc. Nat. Acad. Sci., U.S.A.* **82**, 5000-5004 (1985). <u>https://doi.org/10.1073/pnas.82.15.5000</u>

³⁵ James Peter Stoessel, *Self-consistent phonon theory of aperiodic solids and density functional theories of freezing and vitrification*, PhD Thesis, University of Illinois at Urbana-Champaign (1985). <u>https://i-share-uiu.primo.exlibrisgroup.com/permalink/01CARLI_UIU/gpjosq/alma9988801312205899</u>

³⁶ See, *e.g.*, J. L. Finney, "Bernal's road to random packing and the structure of liquids," Philo. Mag. **93**, 3940-3969 (2013). <u>https://doi.org/10.1080/14786435.2013.770179</u>

³⁷ J. P. Stoessel and P. G. Wolynes, "Linear excitations and the stability of the hard sphere glass," *J. Chem. Phys.* **80**, 4502-4512 (1984). <u>https://doi.org/10.1063/1.447235</u>

- **PGW:** [0:20:04] Probably very early when [I] read about metallic glasses, I would guess. I must have read about Bernal. It seems like I always knew about Bernal.
- PC: So, you didn't meet Finney at any point?
- **PGW:** [0:20:20] It's conceivable I might have met Finney at some point. I remember he worked on water, and I think I saw him at a Water Gordon conference or something³⁸, but I never interacted with him on glasses.
- **PC:** Had you paid any attention to the works of Götze and co-workers as well as Leutheusser³⁹, at that time?
- **PGW:** [0:20:40] Yeah, because of mode coupling theory, I guess.
- PC: When did you become acquainted or aware of this?
- **PGW:** [0:20:47] I probably knew about it when their papers came out, I would guess. At this point, I had never met Götze⁴⁰. Some years later, after I had done the work of mapping the mode coupling theory on the density functional and so on, I was at a conference in Copenhagen⁴¹ where I met Götze. It was a kind of an odd interaction. I was basically on Götze's side. He gave a talk on the mode coupling theory of the glass transition. I thought he was basically right, but he was incredibly obnoxious. All the people who came from the spin glass community, they just attacked him viciously and he gave back as much as he got. I was kind of on his side, but he wasn't somebody who wanted any allies, I thought. That's the only time I ran into him.
- **PC:** Getting back to 1985, about your work with your first student at Illinois, you used two approaches: you looked at the linear stability and then a density-functional theory (DFT) approach⁴². Where did you become acquainted with DFT?

³⁸ See, *e.g., Gordon Research Conference: Water and Aqueous Solutions*, H. Eugene Stanley, Marie-Claire Bellissent-Funel and Jose Teixeira, Holderness, NH, USA, August 2-7, 1998. <u>https://www.grc.org/water-and-aqueous-solutions-conference/1998/</u> (Accessed January 20, 2024.)

³⁹ U. Bengtzelius, W. Götze and A. Sjolander, "Dynamics of supercooled liquids and the glass transition," *J. Phys. C* **17**, 5915 (1984). <u>https://doi.org/10.1088/0022-3719/17/33/005</u>; E. Leutheusser, "Dynamical model of the liquid-glass transition," *Phys. Rev. A* **29**, 2765 (1984). https://doi.org/10.1103/PhysRevA.29.2765

⁴⁰ Wolfgang Götze: <u>https://en.wikipedia.org/wiki/Wolfgang_G%C3%B6tze</u>

⁴¹ CONFERENCE DETAILS?

⁴² Y. Singh, J. P. Stoessel and P. G. Wolynes, "Hard-sphere glass and the density-functional theory of aperiodic crystals," *Phys. Rev. Lett.* **54**, 1059 (1985). <u>https://doi.org/10.1103/PhysRevLett.54.1059</u>

- **PGW:** [0:22:15] I think whenever you looked at the theory of liquids around this time, density functional theory was sort of a natural thing to do. So, I knew this because of all the sort of diagrammatic theory of liquids that was around. Probably the papers of Oxtoby and Rice on periodic crystal formation were on my mind⁴³. So, I thought there must be some sort of transition from periodicity to chaos. But it was very awkward to try to build structures out of density waves. At some point, I think I said: "Oh, but we already know there are structures, let's just use Gaussians!" We had originally thought of the Gaussians, and about the same time, a little bit afterwards, a guy named Tarazona did Gaussians for the ordinary periodic crystal⁴⁴. He sort of scooped us in a way, but I didn't even think to apply the idea to periodic structures. I thought it was clear it would work for the periodic crystal, so why bother.
- **PC:** Was all this mostly through papers or were you in touch with these people?
- **PGW:** [0:23:39] Yeah, just papers.
- **PC:** Were there no gatherings or conferences that you attended?
- **PGW:** [0:23:45] I'm sure I went to the Liquids Gordon conferences in those times, and I'm sure I talked about the density functional theory of the aperiodic crystal at one of them. I think I did at a Liquid Gordon conference⁴⁵. I'm not 100% sure at that time.
- **PC:** In that 1985 PRL, you cited Mézard and co-workers who worked on spin glasses⁴⁶. How familiar were you with spin glasses and ideas of replica symmetry breaking at that point?

⁴³ See, *e.g.*, A. D. J. Haymet and D. W. Oxtoby, "A molecular theory for the solid–liquid interface," *J. Chem. Phys.* **74**, 2559-2565 (1981). <u>https://doi.org/10.1063/1.441326</u>; B. Bagchi, Biman, C. Cerjan and S. A. Rice, "Contribution to the theory of freezing," *J. Chem. Phys.* **79**, 5595-5604 (1983). https://doi.org/10.1063/1.445680

⁴⁴ P. Tarazona, "A density functional theory of melting," *Mol. Phys.* 52, 81-96 (1984). <u>https://doi.org/10.1080/00268978400101071</u>

⁴⁵ PC: Prof. Wolynes did not present in 1985 GRC, but he did so at the 1987 one in a session entitled "Chemical Dynamics in Liquids". *Physics and Chemistry of Liquids Gordon Research Conference*, David Chandler, Holderness School, August 10-14, 1987. See A. M. Cruickshank, *Science* 227, 1067-1106 (1985). <u>https://www.jstor.org/stable/1694821</u>; "Gordon research conferences." *Science* 235, 1233-1261 (1987). <u>https://www.jstor.org/stable/1698262</u>

⁴⁶ M. Mézard, G. Parisi, N. Sourlas, G. Toulouse and M. Virasoro, "Replica symmetry breaking and the nature of the spin glass phase," *J. Physique* **45**, 843-854 (1984). https://doi.org/10.1051/jphys:01984004505084300

- PGW: [0:24:25] I hardly knew anything, really. I knew the Edwards and Anderson papers⁴⁷, which I think don't get appreciated as much as they really ought to be. I really am a fan of those papers, because I think they really did identify a natural mean-field-ish approach. But their papers actually put forward two really different mean-field approaches, one of which was the one that took off in the big way, which was just the replica trick for averaging over the J_{ij} . But then they also had something where they said: "We could look at this in a dynamical way. We could take a spin and it would be moving and it has a random force put on it by the other spins due to the J_{ii}, which gives some kind of additional damping to their motion." I realized that was more or less the same theory as dielectric friction, which I had already worked on⁴⁸. So, I said: "Oh, that's really a good way to think about this problem, that it's a crisis of friction in the spin glass." Those things I knew quite well. I knew, therefore, the replica general technique from those early papers. Then, the elaborated technologies of showing that there were multiple stages of replica symmetry breaking and so on, I knew they existed. I looked at those papers. I'm sure I had to, [as] I cited them, but I would say they were pretty obscure to me as to what was going on.
- **PC:** What was the immediate response to these first couple of papers on glasses? Do you have any recollection?
- **PGW:** [0:26:33] I don't remember any particular response from people. Maybe they were of interest, certainly in a broad way. I may have met Ted Kirkpatrick earlier because of his connection with the University of Maryland and he was a student of Dorfman⁴⁹, and Dorfman knew me from my thesis on mode coupling. So, I must have met him earlier, but I definitely talked to him at an Aspen meeting, which was probably in '85⁵⁰.

primo.hosted.exlibrisgroup.com/permalink/f/ji7ros/01RU_ALMA2122306170004157; J. R. Dorfman, T. R. Kirkpatrick, J. V. Sengers, "Ezechiel Godert David Cohen," *Physics Today* **71**(6), 65 (2018). https://doi.org/10.1063/PT.3.3954

 ⁴⁷ S. F. Edwards and P. W. Anderson, "Theory of spin glasses," *J. Phys. F* 5, 965 (1975).
 <u>https://doi.org/10.1088/0305-4608/5/5/017</u>; "Theory of spin glasses. II." *J. Phys. F* 6, 1927 (1976).
 <u>https://doi.org/10.1088/0305-4608/6/10/022</u>

⁴⁸ See, *e.g.*, J. B. Hubbard and P. G. Wolynes, "Dielectric friction and molecular reorientation," *J. Chem. Phys.* **69**, 998-1006 (1978). <u>https://doi.org/10.1063/1.436652</u>

⁴⁹ PC: Prof. Kirkpatrick was a graduate student at Rockefeller University with Prof. Eddie Cohen, who was a long-time collaborator of Jay Dorfman at the University of Maryland. See, *e.g.*, Theodore Ross Kirkpatrick, *On the Theory of Light Scattering from Fluids in Nonequilibrium Steady States*, PhD Thesis, Rockefeller University (1981). <u>https://rockefeller-</u>

⁵⁰ *Glassy Dynamics*, Aspen Center for Physics, Aspen, CO, USA, Daniel Fisher, Daniel Stein and Richard Palmer (1985). See, *e.g.*, R. N. Bhatt, "Condensed Matter Physics at the Aspen Center for Physics during the First Fifty Years," *Aspen Center for Physics* (2011).

https://www.aspenphys.org/science/sciencehistory/cm.html (Accessed November 6, 2023.)

So, it must have been soon [after] this. I said that it seemed to me that the mode coupling theory and the density functional theory must be related because they have the same mathematical objects in them: direct correlation functions and blah blah blah.

That's where I realized you could do mode coupling theory of the structural glass transition more or less along the lines of the Edward-Anderson argument. The Edwards-Anderson argument gave a friction crisis, and that's how I derived a so-called naive mode-coupling theory. So, he and I, we more or less worked out everything of that paper at this meeting in Aspen, except perhaps the closed-form results for the transition densities. I had this idea from Frisch that everything should be simple in high dimensions, because the virial expansion truncates⁵¹. We first got these weird formulas that I remember getting to the stage of having a whole bunch of Bessel functions in them. Ted figured out the asymptotics, so that we got this still extremely elegant result that the density was something like $\sqrt{2\pi e}$ times something to some powers of *d*. All the powers are right, and the $\sqrt{2\pi e}$ differs from Francesco's calculation by about ten percent⁵², which is still a puzzle to me. Because $\sqrt{2\pi e}$ is a really nice answer; [4.8067...], it's a numerical result. It always bothered me.

- PC: I think you also presented that series of works at the International Conference on the Theory of Structures and Non-crystalline Solids at the Institute of Amorphous Solids at the University of Michigan, in June of '85⁵³.
- **PGW:** [0:29:24] Yes, there was a meeting there. It was mostly by this guy, Stan Ovshinsky⁵⁴, who used amorphous semiconductors for devices. That was very controversial. That's where I talked about it. Again, I would say there wasn't very much interest in that there.

⁵³ International conference on the theory of the structures of non-crystalline solids, Institute of Amorphous Solids at the University of Michigan, Bloomfields Hills, Michigan, D. Adler, J. Bicerano, 3-6 June 1985. Proceedings: J. Non-Cryst. Sol. **75**(1–3), 3-516 (1985). <u>https://www.sciencedirect.com/journal/journal-of-non-crystalline-solids/vol/75/issue/1</u>. See, in particular, P. G. Wolynes, "Microscopic theory of aperiodic crystals: Approaches for the hard sphere glass transition," J. Non-Cryst. Sol. **75**, 443-448 (1985). <u>https://doi.org/10.1016/0022-3093(85)90255-8</u>; T.R. Kirkpatrick, "Anomalous mode coupling effects in dense classical liquids," J. Non-Cryst. Sol. **75**, 437-442 (1985). <u>https://doi.org/10.1016/0022-3093(85)90254-6</u>

⁵¹ See, *e.g.*, H. L. Frisch, N. Rivier and D. Wyler, "Classical hard-sphere fluid in infinitely many dimensions," *Phys. Rev. Lett.* **54**, 2061 (1985). <u>https://doi.org/10.1103/PhysRevLett.54.2061</u>

⁵² See, *e.g.*, G. Parisi, P. Urbani and F. Zamponi, *Theory of simple glasses: Exact solution in infinite dimensions* (Oxford: Oxford University Press, 2019).

⁵⁴ Stanford Ovshinsky: <u>https://en.wikipedia.org/wiki/Stanford_R._Ovshinsky</u>

That first Kirkpatrick work happened I guess it would have been around '87, although I really should have to check exactly the dates. (I know our daughter was just six months old, so I have to check exactly when she's born⁵⁵.) I organized with Dan Stein a workshop at the ITP on *Relaxation in Complex Systems*⁵⁶. We had lots of people that were on site there for the whole time; lots of people that were there for short periods of time. I think Ted came out for maybe two or three weeks and we worked out some more stuff there.

I do remember how people responded there. There was a conference at the end, and in the conference, I know I talked about the density functional and the mode coupling density functional thing. I probably started to say something about the activated events, although I don't know for sure. We were certainly thinking about it. Somehow at the end, someone proposed that we should have a vote of the people attending the meeting, which there were about 100 people, I guess. (Maybe it was less, maybe it was 50, but a large group of people.) The vote was: "Is there a growing length scale involved in the in the glass transition?" The vote was essentially unanimous that there was not, except for two people. Those were me and Dan Stein. Later, Dan told me he really didn't believe there was a large length scale involved, but he thought I would feel upset if I was the only person who thought it. So, he was being nice to me as a friend. I would say that the idea that there was something critical, something phase transition-y going on was definitely not popular. Even though this work was presented, and probably there were other talks on spin glasses and maybe even random magnets. I think Jim Sethna⁵⁷ spent time there. But usually, there was kind of desire to believe there wasn't really a problem here.

⁵⁵ Margrethe Cull Wolynes was born in July 1986.

⁵⁶ *Relaxation in Complex Systems*, R. G. Palmer, D. L. Stein and P. G. Wolynes, January-June 1987, Institute of Theoretical Physics, Santa Barbara, CA, USA.

⁵⁷ See, *e.g.*, P. Charbonneau, *History of RSB Interview: James P. Sethna*, transcript of an oral history conducted 2022 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2022, 16 p. <u>https://doi.org/10.34847/nkl.7cbfsjjg</u>

- **PC:** In your in your first paper with Professor Kirkpatrick⁵⁸, you acknowledged conversations with your PhD student at a time, Joseph Bryngelson⁵⁹, and with Dave Thirumalai⁶⁰. Had you met Dave Thirumalai at that point?
- **PGW:** [0:32:57] I very likely had met him. I know that I talked about these things with Joe. Joe was at the workshop, and Joe worked on glassy things connected with protein folding with me. I probably tried to get him to do some calculations on regular glasses, but he didn't do anything on that to my knowledge. I knew Thirumalai because he had applied to postdoc with me years before. I didn't have any money, so he worked with Bruce Berne⁶¹. But I don't recall talking with him at all about glasses in this time period. He might have come to the meeting in Santa Barbara. I don't remember that really. I didn't directly [talk to him]. So, that acknowledgement is Ted talking to Thirumalai, I believe.
- **PC:** Professor Kirkpatrick was writing papers with Dave Thirumalai also at about the same time as you were working with him⁶². If it was not a collaboration, how was this playing out?
- **PWG:** [0:34:19] Actually, I sent you, for example, some letters that I wrote with Ted Kirkpatrick. One of the letters from Ted actually describes the sequence of collaborative events⁶³. I would say that the first paper with Ted, which talks about the high-dimensional glass, I never had the impression [Dave] was involved in any real way. Of course, that paper also is what mentions the connection to the Potts glass, as sort of an aside at the end, but that's where it's mentioned. Then, the next paper is a paper by Ted and Dave, where they analyze the *p*-spin model by mode coupling theory. Again, that paper says that it's following the suggestion of the KW paper, which is reference one, that there's a connection to spin glasses. It's a very technical paper, I would say. It had some puzzling aspects, like there

⁵⁸ T. R. Kirkpatrick and P. G. Wolynes, "Stable and metastable states in mean-field Potts and structural glasses," *Phys. Rev. B* **36**, 8552 (1987). <u>https://doi.org/10.1103/PhysRevB.36.8552</u>

⁵⁹ Joseph Donald Bryngelson, *Glassy models of protein folding*, PhD Thesis, University of Illinois at Urbana-Champaign (1988). <u>https://i-share-</u>

<u>uiu.primo.exlibrisgroup.com/permalink/01CARLI_UIU/gpjosq/alma99156595212205899</u> (Accessed November 7, 2023.)

⁶⁰ See, *e.g.*, P. Charbonneau, *History of RSB Interview: Devarajan Thirumalai*, transcript of an oral history conducted 2022 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2022, 19 p. <u>https://doi.org/10.34847/nkl.a03aux8z</u>
⁶¹ Bruce Berne: https://de.wikipedia.org/wiki/Bruce J. Berne

⁶² See, *e.g.*, T. R. Kirkpatrick and D. Thirumalai, "Dynamics of the structural glass transition and the *p*-spin— interaction spin-glass model," *Phys. Rev. Lett.* **58**, 2091 (1987).

https://doi.org/10.1103/PhysRevLett.58.2091; "*p*-spin-interaction spin-glass models: Connections with the structural glass problem," *Phys. Rev. B* **36**, 5388 (1987). <u>https://doi.org/10.1103/PhysRevB.36.5388</u> ⁶³ Letter from Kirkpatrick to Wolynes (July 21, 1987), Peter G. Wolynes personal collection.

was a dynamic transition and there was a separate thermodynamic transition, but it's written in a way that it was a little bit hard to say what's going on, I would say, for me. That's what led to the second Kirkpatrick-Wolynes paper⁶⁴, which is this paper where we basically understood the dynamical transition to be a spinodal. It was being called a first-order—like transition, or discontinuous transition. We would say the T_A was the spinodal for the transition and the T_{K} is the ultimate transition. I was convinced that the static transition had to be connected to the entropy problem, because that's what we knew from experiment. That's why we did this analysis of counting the states using this method of Thouless, Anderson and Palmer⁶⁵. You can see I was really not very comfortable with replicas. It was all done by this Thouless-Anderson-Palmer method, and we got the result that the entropy vanishes at the equilibrium transition. Then, that paper also discusses what the correlation lengths are, that one correlation length grows near $T_{A,}$ another one grows at T_K which is caused by a kind of instanton mechanism, which is discussed in that paper.

- **PC:** From a practical standpoint, most of the ideas pivoted through Prof. Kirkpatrick. So, you would hear from their work, and then they Dave Thirumalai would hear from your work.
- **PGW:** [0:37:27] Yeah, and I'm sure vice versa.
- PC: In that first paper, you understood that the mean-field theory would become exact in the limit of high space dimensionality. Given that you had some experience doing through molecular simulations, at least using Monte Carlo⁶⁶, did the idea of doing simulations in higher dimensions cross your mind at that point?
- **PGW:** [0:37:55] I would say no, because I used to have a theorem that used to be true—it's still almost true—which was that you can never learn anything about a glass transition by simulation, because the time scale problems are so severe. If you're trying to explain orders and orders of magnitude growth of time scale, the naïve way to do that would require orders and orders of magnitude more computer time. We didn't have that much time even with the supercomputers of the day. Like I say, that was a theorem. In fact, it was interesting tracing back to the sort of prehistory of this. Most

⁶⁵ D. J. Thouless, P. W. Anderson and R. G. Palmer, "Solution of 'solvable model of a spin glass'," *Philo. Mag.* **35**, 593-601 (1977). <u>https://doi.org/10.1080/14786437708235992</u>

⁶⁴ T. R. Kirkpatrick and P. G. Wolynes, "Connections between some kinetic and equilibrium theories of the glass transition," *Phys. Rev. A* **35**, 3072 (1987). <u>https://doi.org/10.1103/PhysRevA.35.3072</u>

⁶⁶ See, *e.g.*, E.C. Behrman, G. A. Jongeward and P. G. Wolynes, "A Monte Carlo approach for the real time dynamics of tunneling systems in condensed phases," *J. Chem. Phys.* **79**, 6277-6281 (1983). <u>https://doi.org/10.1063/1.445732</u>

of the people who did simulations never believed in any of this phase transitionnist stuff. For example, Stillinger⁶⁷, I'm not sure even to this day he has any belief in the entropy crisis. He did lots of simulations. I once mentioned him in the early '90s about the Parisi-style work. He said: "Oh, that ridiculous work of the foreigners." He didn't believe anything that came out of that thing. But also Hans Andersen⁶⁸. Hans Andersen, his first simulations which he published, led to his not really seeing something like a mode-coupling transition⁶⁹. Then, he invented these facilitated models where he showed that they didn't have a transition, which was motivated by his simulations⁷⁰. Then, he slowly got to—as his computer got better and better—a time where he now said⁷¹: "Oh, yes! There is a mode coupling transition, but there's no other one." I would say generally as computers got better, simulators got more and more interested. Say, finally, by the time of my festschrift, which is when I was 60, there's an article (in the festschrift) by Michael Eastwood and D. E. Shaw, where he does ortho-terphenyl, and he simulates it now for a few microseconds⁷². He says: "Oh, it looks like we're starting to see a transition." I think there was a sense that you're not going to get a transition in three dimensions.

It's possible if when I thought about higher dimensions that that would have made sense, but as you know as someone who has done simulations in higher dimensions, 3^d doesn't give you a lot of room if *d* is a very big number.

PC:

As you mentioned, you were doing TAP-type calculations, and then there were some replica ideas in your papers. How were your early couple of

⁶⁹ See, e.g., J.R. Fox and H. C. Andersen, "Molecular Dynamics Simulation of the Glass Transition," Ann. N. Y. Acad. Sci. **371**, 123-135 (1981). <u>https://doi.org/10.1111/j.1749-6632.1981.tb55656.x</u>; "Molecular dynamics simulations of a supercooled monatomic liquid and glass." J. Phys. Chem. **88**, 4019-4027 (1984). <u>https://doi.org/10.1021/j150662a032</u>; M. H. Grabow and H. C. Andersen, "Molecular Dynamics Computer Simulations of the Supercooled Lennard-Jones Liquid," Ann. N. Y. Acad. Sci. **484**, 96-100 (1986). <u>https://doi.org/10.1111/j.1749-6632.1986.tb49564.x</u>

⁶⁷ Frank Stillinger: <u>https://en.wikipedia.org/wiki/Frank_Stillinger</u>

⁶⁸ See, *e.g.*, "Andersen (Hans C.) papers," *Stanford University University Archives* SC1324 (1960s-2018). <u>https://oac.cdlib.org/findaid/ark:/13030/c8m04bwd/</u> (Accessed November 7, 2023.)

⁷⁰ See, e.g., G. H. Fredrickson and H. C. Andersen, "Kinetic Ising model of the glass transition," *Phys. Rev. Lett.* **53**, 1244 (1984). <u>https://doi.org/10.1103/PhysRevLett.53.1244</u>; "Facilitated kinetic Ising models and the glass transition," *J. Chem. Phys.* **83**, 5822-5831 (1985). <u>https://doi.org/10.1063/1.449662</u>

⁷¹ See, *e.g.*, W. Kob and H. C. Andersen, "Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture I: The van Hove correlation function," *Phys. Rev. E* **51**, 4626 (1995).

<u>https://doi.org/10.1103/PhysRevE.51.4626</u>; "Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture. II. Intermediate scattering function and dynamic susceptibility," *Phys. Rev. E* **52**, 4134 (1995). <u>https://doi.org/10.1103/PhysRevE.52.4134</u>

⁷² M. P. Eastwood, T. Chitra, J. M. Jumper, K. Palmo, A. C. Pan and D. E. Shaw, "Rotational relaxation in ortho-terphenyl: using atomistic simulations to bridge theory and experiment," *J. Phys. Chem. B* **117**, 12898-12907 (2013). <u>https://doi.org/10.1021/jp402102w</u>

papers with Professor Kirkpatrick received by the spin glass community in Europe, in particular? Were they aware of these advances?

PGW: [0:41:16] It'd be hard for me to say when. It was certainly not immediately. I wasn't in general contact with them. In fact, I'm not sure exactly when. Obviously, by the year 2000, yes, a little bit, but somewhere in the '90s, I don't remember anyone from them.

It's interesting. I knew Parisi a little bit. I didn't really know him personally, but I knew of him because he did these quantum Monte Carlo calculations on QCD⁷³. I was doing quantum Monte Carlo in the early '80s and he visited Urbana. I remember everyone saying: "Oh, he's the new Fermi⁷⁴." I always kid him about that. I said: "Well, you have a lot to live up to because you're the new Fermi." But again, I don't think there was any back and forth with that community. But somewhere or other in that time, there's some sense that there's a connection made. I don't remember exactly when.

- PC: Do you not remember going to Paris or to Rome to give seminars or talk about this.?
- **PGW:** [0:42:44] I definitely went to Paris where I spoke about my earliest glass work when I was there on my honeymoon with my wife, Kathy, in the early '80s. She wasn't too happy with my giving a seminar⁷⁵. I also did the summer of probably '93 or '94 at École normale. I mostly talked about protein folding, but it's hard for me to believe I didn't talk about the theory of glasses in one seminar. I met Derrida⁷⁶; I met Mézard⁷⁷; I met Toulouse⁷⁸. There was a fellow who invited me, Vannimenus⁷⁹. They were all very nice to me and everything, but there was no collaboration. It didn't seem like it was going to happen or anything. I was already feeling like I

⁷⁸ Gérard Toulouse: <u>https://en.wikipedia.org/wiki/G%C3%A9rard_Toulouse</u>

 ⁷³ See, *e.g.*, G. Martinelli, G. Parisi, R. Petronzio and F. Rapuano, "The proton and neutron magnetic moments in lattice QCD," *Phys. Lett. B* **116**, 434-436 (1982). <u>https://doi.org/10.1016/0370-2693(82)90162-9</u>; F. Fucito, G. Martinelli, C. Omero, G. Parisi, P. Petronzio, and F. Rapuano, "Hadron spectroscopy in lattice QCD," *Nucl. Phys. B* **210**, 407-421 (1982). <u>https://doi.org/10.1016/0550-3213(82)90129-8</u>

⁷⁴ Enrico Fermi: <u>https://en.wikipedia.org/wiki/Enrico</u> Fermi

⁷⁵ Peter Guy Wolynes married Kathleen Cull Bucher in December 1984 in Cambridge, UK.

⁷⁶ See, *e.g.*, P. Charbonneau, *History of RSB Interview: Bernard Derrida*, transcript of an oral history conducted 2020 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2021, 23 p. <u>https://doi.org/10.34847/nkl.3e183b0o</u>

⁷⁷ P. Charbonneau, *History of RSB Interview: Marc Mézard*, transcript of an oral history conducted 2022 by Patrick Charbonneau and Francesco Zamponi, History of RSB Project, CAPHÉS, École normale supérieure, Paris, 2023, 49 p. <u>https://doi.org/10.34847/nkl.abc22iqw</u>

⁷⁹ "Jean Vannimenus," *Physics Tree* (n.d.). <u>https://academictree.org/physics/peopleinfo.php?pid=777213</u> (Accessed November 7, 2023.)

was moving on to the protein stuff at this time. I kind of felt like: "Well, the glass problem is solved. Now, I need to do other things."

- **PC:** Just stepping back a bit. In 1988, you work together on the actual joint paper between you, Dave Thirumalai, and Ted Kirkpatrick on "Scaling concepts for the dynamics of viscous liquids near an ideal glassy state"⁸⁰. What led you to join forces at that stage?
- PGW: [0:44:23] The interaction with Ted just continued, if you look at the notes which I sent you. (I was in Japan, so I had to write. Everything was being done by writing. I guess there was email but we called it BITNET⁸¹. I don't think Ted used BITNET; I hardly used BITNET.) Directly in those notes, we went back and forth on different scaling ideas. We wanted to have something that was instanton-like from our previous paper. Then, the question was what's the exponent for what we now would call the mismatch energy. Ted thought it had to be less than d-1/2, because of an argument of Danny Fisher⁸². I said I'm agnostic about it, at first, so I'll let it be a coefficient y, but then I said: "If you insist that there's only one length, which is what you need for a scaling theory, then you end up with fixing the value of y so that the length exponent turns out to be 2/d, and then the Vogel-Fulcher law⁸³ follows." I remember the moment, literally, where I found that, which was in Japan. In Japan, I remember playing around with the numbers, like little bits of algebra, and I saw that you came with the exact Vogel-Fulcher law." Then, I said: "That's it." The rest of the regular mail goes back and forth arguing about this. Ted oscillated back and forth over the next year like, because d/2 is bigger than (d-1)/2. Although, I don't think you can completely rule it out just on experiment; (d-1)/2 would kind of be okay. I don't know about the conversations he was having with Dave. I do know that at some point after we got back, when we were writing the paper up, we debated whether Dave should be part of the paper. I had no knowledge of Dave being involved really, other than sort of someone for Ted to talk to. Then [Ted] argued that his interaction with Dave was critical to him, and that he should therefore be a co-author of the paper.
- PC: So, you never went to visit to Maryland and never worked or exchanged with Dave?

⁸³ Vogel-Fulcher-Tammann equation:

 ⁸⁰ T. R. Kirkpatrick, D. Thirumalai and P. G. Wolynes, "Scaling concepts for the dynamics of viscous liquids near an ideal glassy state," *Phys. Rev. A* 40, 1045 (1989). <u>https://doi.org/10.1103/PhysRevA.40.1045</u>
 ⁸¹ BITNET: https://en.wikipedia.org/wiki/BITNET

⁸² Daniel S. Fisher: https://en.wikipedia.org/wiki/Daniel S. Fisher

https://en.wikipedia.org/wiki/Vogel%E2%80%93Fulcher%E2%80%93Tammann_equation

- **PGW:** [0:47:16] Right. Well, I mean, it's possible. I know there was an email or something in there. It's possible that I might have talked to him on the phone or something, but in general my conversations were with Ted.
- PC: What was the reaction to that work? Did you present this at a Gordon Research Conference on the Physics and Chemistry of Liquids? Did you go around and gave many seminars?
- **PGW:** [0:47:46] I I did talk about it—but that's of course in a completely weird place, it would have had to be '87—but with the wrong value of the exponent at the Hans Frauenfelder festschrift in Urbana⁸⁴. Just before I went to Japan, I talked about it there. So, I wrote the article in Japan with the new scaling argument in the speculation part of the paper⁸⁵.

I gave a talk about it when I got back from Japan. One of the first seminars after [I came] back was at UT Austin. I do remember a thing that was interesting about a fellow you may know from another part of your life, a guy called Rich Friesner⁸⁶. Rich Friesner, I met with him after my seminar, which is unusual. He said: "Oh, that was really a nice seminar. It's probably the last interesting seminar with analytical results I'll ever see." I do remember that, so he liked it. But overall, I would say, I didn't hear too much about that work. We used things from this in other papers on proteins. The protein work is what I mostly would talk about. In more or less the middle of the '90s, there was something that caused me to really go back to this a little bit, which was Phil Anderson⁸⁷, who I still greatly respect. (I think he's a real hero of 20th century physics.) They asked him: "What is the most important unsolved problem?" This is quoted a lot. He said this thing in Science⁸⁸: "The most important unsolved problem is the problem of the glass transition." I remember reading that and going like: "Well, that pisses me off." I remember. Obviously, I haven't impressed Anderson because the problem is solved. I kind of re-entered the field around the year 1999 with this paper with Xiaoyu Xa in PNAS⁸⁹. I had always held that the problem with this scaling argument is that things never get very big in terms of the distance that you go in correlation length.

⁸⁴ International Symposium on Frontiers in Science: On the Occasion of the 65th Birthday of Professor Hans Fraunfelder, 1-3 May 1987, Urbana, IL, USA. Proceedings: AIP Conference Proceedings **180**(1) (1988). https://pubs.aip.org/aip/acp/issue/180/1

⁸⁵ P. G. Wolynes, "Aperioidic crystals: Biology, Chemistry and Physics in a fugue with stretto," AIP Conf. Proc. **180**, 39–65 (1988). <u>https://doi.org/10.1063/1.37862</u>

⁸⁶ Richard A. Friesner: <u>https://en.wikipedia.org/wiki/Richard A. Friesner</u>

⁸⁷ Philip W. Anderson: <u>https://en.wikipedia.org/wiki/Philip W. Anderson</u>

⁸⁸ P. W. Anderson, "Through the glass lightly," *Science* **267**, 1615-1616 (1995). <u>https://doi.org/10.1126/science.267.5204.1615.f</u>

⁸⁹ X. Xia and P. G. Wolynes, "Fragilities of liquids predicted from the random first order transition theory of glasses." *Proc. Nat. Acad. Sci. U. S. A.* **97**, 2990-2994 (2000). <u>https://doi.org/10.1073/pnas.97.7.2990</u>

So, the only way to test a theory like this, to my mind, is to calculate things microscopically, in my opinion. This view is not held by anyone else these days, but to my mind the only way to test a theory like this would be to be able to calculate some experimental number for a real thing that actually exists in the laboratory, in three dimensions. I remember thinking that what we now call RFOT theory had an advantage when I compared that to everything else that was going on: "It's the only theory that even lets you start to do a microscopic calculation. No other theory says how to start and carry out a calculation starting from fundamental forces."

My student, Xiaoyu Xia⁹⁰, didn't want to work on proteins, so I said: "Well, why don't we look at this problem?" I thought he was going to have to do a very elaborated calculation. He's a really brilliant guy, a big hedge fund guy, now, made a lot of money. He only wanted to write three papers. He was doing a finance degree at the same time. I tried to persuade him that the calculation would be easier than it seemed. One of the weird ideas I had was this idea that if the interface were sharp, that you could calculate the surface tension by an argument that's more or less the analog of how we calculate the surface tension of a liquid, by saying you lose half the bonds. So, we did that calculation. Then, when I did it, I said: "Oh my God! If this is true, the coefficient is purely entropic, and you can calculate it for any substance." So, that paper allowed us to say, even though it's a microscopic calculation, that there's a general way to map it onto specific materials. That's what we did in that paper a little bit, and then later in the PRL⁹¹ for calculating the stretching exponent beta and for other things. Again, it was one of those moments of revelation. There was no reason why the calculation should turn out nice, but it turned out that when you did the calculation, within that sharp interface approximation, you ended up with a very universal result. Not universal like critical phenomenology, but universal like the way the Van der Waals equation works for all the rare gases and alkanes pretty well.

PC: I'd like to go back a bit to the protein work before we move to that second period, and tie in some of the loose ends we left. You mentioned Dan Stein, with whom, as a friend, you organized the ITP workshop. When you first started working on protein folding and its relationship with glasses with

⁹⁰ Xiaoyu Xia, *A random first order theory of liquid-glass transition*, PhD Thesis, University of Illinois at Urbana-Champaign (2001). <u>https://i-share-</u>

uiu.primo.exlibrisgroup.com/permalink/01CARLI_UIU/gpjosq/alma99453911812205899 (Accessed November 7, 2023.)

⁹¹ X. Xia and P. G. Wolynes, "Microscopic theory of heterogeneity and nonexponential relaxations in supercooled liquids," *Phys. Rev. Lett.* **86**, 5526 (2001). <u>https://doi.org/10.1103/PhysRevLett.86.5526</u>

Joe Bryngelson⁹², you sort of built on the work of Dan Stein⁹³. How did you get interested in this idea? Was it through interacting with Frauenfelder or Dan Stein?

- [0:54:03] Mostly through Frauenfelder. I wouldn't have said I built on the PGW: work of Stein at all, actually. I knew about it. I think that Dan got his motivations from interacting with Hans indirectly as well, which was to try to explain the glassy dynamics of the already folded protein, which was what was showing up in Hans's kinetic experiments. I think in discussions with Hans we started really [talking] that there must be some relationship to whatever is going on in spin glasses with this hierarchical energy landscape. Hans always liked the hierarchical nature of the landscape a great deal. That was one thing. I also felt, however, that the folding problem was different. [For] the folding problem, the problem isn't just where do you put the side chains as in Stein's model. It's how do you even organize the polymer in the first place. So, it really has to do with bringing things in contact that are not even on a lattice or anything like that. Then, Joe and I tried seven or eight different kinds of approximations. They were all some sort of replica-type thing for a polymer with random interactions. Then, we said: "Well, everything seems like it's just coming out like a random energy model." So, we said: "Why don't we just assume it's a random energy model?" Then, when you calculate that, you see that the random energy model transition isn't like folding at all, that it doesn't have a significant latent heat. That's why we postulated that it's really the competition of the glass transition of a random hetero polymer with [what] you might call the crystallization transition of the evolved sequences that matter. So, it's really the Turnbull story in reverse. Turnbull was trying to find materials that have a hard time crystallizing. Evolution was trying to find things that have an easy time crystallizing. That sort of analogy between what makes something crystallizable or freezable, as opposed to glassy, that was what was on our mind in that paper.
- **PC:** At about the same time, people like Thomas Garel and Henri Orland were also working on similar approaches⁹⁴, broadly speaking. Were you at all in touch with these groups?

 ⁹² See, *e.g.*, J. D. Bryngelson and P. G. Wolynes, "Spin glasses and the statistical mechanics of protein folding," *Proc. Nat. Acad. Sci. U.S.A.* 84, 7524-7528 (1987). <u>https://doi.org/10.1073/pnas.84.21.7524</u>
 ⁹³ See, *e.g.*, D. L. Stein, "A model of protein conformational substates,"

Proc. Nat. Acad. Sci. U.S.A. **82**, 3670-3672 (1985). <u>https://doi.org/10.1073/pnas.82.11.3670</u> ⁹⁴ See, *e.g.*, T. Garel and H. Orland, "Chemical sequence and spatial structure in simple models of biopolymers," *Europhys. Lett.* **6**, 597 (1988). <u>https://doi.org/10.1209/0295-5075/6/7/005</u>

- **PGW:** [0:56:59] I didn't know of their work. Another person who was doing things at a similar time was Eugene Shakhnovich⁹⁵. I think both Orland and Garel did things with the full replica technology. Like I said, at first, I was still always somewhat skeptical of those as a technology, in my hands anyway. Later, we have done things with replicas, but we always tried to do things with lesser means.
- **PC:** This brings the question. How did you become acquainted with replicas? How were you teaching yourself?
- **PGW:** [0:57:54] I read the literature. I knew about replicas from the Edwards-Anderson papers. I also remember at some point coming across the lectures of Anderson⁹⁶. This might be where I started to hear about [it]. An article that made a big impact on me anyway was this article by Anderson in Les Houches *La Matière mal condensée*. He has a lot of side issues in there, where he actually does deal a little bit with structural glasses, and probably even mentions the entropy problem. He certainly mentioned something which I think has been ignored by most people but was a keystone for me. It's one of the things... I've only met Anderson a couple of times. I was very impressed with him partly because of his style, which I really like. He actually knows things. He's not just a technique guy.

One of the things that he points out is if you take the two-level systems that you have in glasses and you integrate up their heat capacity up to the glass transition, they give you only about 1/100th of the residual entropy. So, a lot of people who are trying—I would say even today—to make the theory of glasses be exactly the same as the theory of some two-level system entities that then interact, let's say—people who will remain nameless here—I would say that that struck me as very interesting, that the things that you see in the two level systems may be related to the glass transition, but they're not the objects which are finally loosened up [or] whatever at T_g , at least in a simple way.

PC: Getting back to heteropolymers. As you said, there's many groups who were coming to these ideas at roughly the same time. How was the community structured? Were there conferences where you all met?

⁹⁵ See, *e.g.*, E. I. Shakhnovich and A. M. Gutin, "Formation of unique structure in polypeptide chains: theoretical investigation with the aid of a replica approach," *Biophys. Chem.* **34**, 187-199 (1989). <u>https://doi.org/10.1016/0301-4622(89)80058-4</u>; "Frozen states of a disordered globular heteropolymer," *J. Phys. A* **22**, 1647 (1989). https://doi.org/10.1088/0305-4470/22/10/019

⁹⁶ P. W. Anderson, "Course 3. Lectures on amorphous system," In: *La Matière mal condensée/III-Condensed Matter*, R. Balian, R. Maynard, G. Toulouse eds. (Amsterdam: North-Holland Publishing, 1979): 159-262.

- [1:00:35] No. Not for me. I don't mean there were no conferences. I PGW: mentioned this conference in Copenhagen. There was this workshop we had in in Santa Barbara. At least some of these people were there, like Danny Fisher. I think [he] came to our meeting in Santa Barbara and Sethna was there. I used to say that I was a mid-Atlantic theorist in this. More or less the people in Europe believed in replicas, and more or less the people in the United States didn't believe anything that came from replicas. I was sort of in between. I felt like there were some things you could use from replicas, but that it wasn't the full answer. But usually, it was formulated by the Americans as what's really wrong with this replica method, and how it misses everything. That was sort of how it was presented in most conferences that I went to that involved people on disordered systems. Danny was very much against them. He knew the techniques very well, and he has a few papers where he does replica calculations for, I think, the interface problem or something like that⁹⁷. It's not that he doesn't know them, but he just doesn't like them. Or didn't like them at that time, anyway.
- **PC:** As part of that effort, you eventually collaborated with Dave Thirumalai in that field as well. You have a paper together⁹⁸. Had you kept in touch since the glass work?
- **PGW:** [1:02:30] That paper is a strange paper. The paper you're thinking about is a short paper. It's a one-page paper in *Science*, I believe. That's the only other paper I've written with Dave Thirumalai. The origin of this was that Dave appreciated what Joe and I had said fairly early. He wrote a couple of simulational papers. They may or may not have been lattice models, but they're highly simplified models, where he mentions those ideas and sort of mentioned something about the gap in the energy spectrum, which is of course the same idea as there being a high T_f to T_g , what we would call the minimal frustration principle. So, he definitely mentioned that. He was aware of that.

Around this time, these ideas started to become more interesting to people. The experts really knew about the stuff quite well, but they didn't necessarily talk about it in that way. I was a very much again kind of annoyed with some of these papers, because there was a study of these lattice models and they would use them as a way of talking about real things, but they never tried to map things onto real systems. Already in

⁹⁸ P. G. Wolynes, J. N. Onuchic and D. Thirumalai, "Navigating the folding routes," *Science* **267**, 1619-1620 (1995). <u>https://doi.org/10.1126/science.7886447</u>

⁹⁷ See, *e.g.*, D. S. Fisher, "Random fields, random anisotropies, nonlinear σ models, and dimensional reduction," *Phys. Rev. B* **31**, 7233 (1985). <u>https://doi.org/10.1103/PhysRevB.31.7233</u>

1989, I was writing simulation papers using machine learning to get potentials to fold real proteins that have names and pictures and stuff⁹⁹. Not on the lattice, we worked off-lattice. Then, this lattice stuff kind of got in, and I thought that one of the ways to bring these things together was to try to see how you could map the lattice problem onto a real protein. Part of the key idea was that there was some structure formation to start with that was very local in sequence, the formation of secondary structure. We had a theory of how much entropy that removes. Again, since entropy is the main story of all of this, we were able to make a mapping of the lattice model onto a real protein through calculation of the amount of entropy that was lost. So, we came to this idea that the lattice model that everyone was studying, the so-called 27 cube¹⁰⁰, really was not bad as a model of maybe a 60-mer that was helical. The nice thing about the 27 cube was all of its compact states could be enumerated. You didn't have to simulate things. The Wolynes theorem that you can't learn anything by simulation is still true, but you don't have to simulate it. You just know what the energy spectrum is. José Onuchic¹⁰¹ had taken up some of this stuff and had written some lattice simulations. So, we started an interaction again, José and me. (José had worked with me in Santa Barbara when he was a student still at Caltech¹⁰².) We said: "Oh, we'll write a paper that maps the lattice problem onto the real problem." That's what led to this picture of the funnel¹⁰³.

How Thirumalai was involved was that Thirumalai somehow contacted someone at *Science* or was contacted by people at *Science*. They said: "Well, shouldn't you write some paper on all these lattice things, or some short news brief thing on that." He contacted us, and we basically wrote that one page paper, which was kind of a summary of the previous paper with José as well as a simulation that Dave had done separately with his simplified model. So, there's a picture in there of his simplified model

https://doi.org/10.1103/PhysRevLett.67.1665; P. E. Leopold, M. Montal and J. N. Onuchic, "Protein folding funnels: a kinetic approach to the sequence-structure relationship," *Proc. Nat. Acad. Sci. U.S.A.* **89**, 8721-8725 (1992). https://doi.org/10.1073/pnas.89.18.8721

⁹⁹ M. S. Friedrichs and P. G. Wolynes, "Toward protein tertiary structure recognition by means of associative memory Hamiltonians," *Science* **246**, 371-373 (1989). https://doi.org/10.1126/science.246.4928.371

¹⁰⁰ See, *e.g.*, E. Shakhnovich, G. Farztdinov, A. M. Gutin and M. Karplus, "Protein folding bottlenecks: A lattice Monte Carlo simulation," *Phys. Rev. Lett.* **67**, 1665 (1991).

¹⁰¹ José Onuchic: <u>https://en.wikipedia.org/wiki/Jos%C3%A9_Onuchic</u>

¹⁰² J. N. Onuchic and P. G. Wolynes, "Classical and quantum pictures of reaction dynamics in condensed matter: Resonances, dephasing, and all that," *J. Phys. Chem.* **92**, 6495-6503 (1988). <u>https://doi.org/10.1021/j100334a007</u>

¹⁰³ J. N. Onuchic, P. G. Wolynes, Z. Luthey-Schulten and N. D. Socci, "Toward an outline of the topography of a realistic protein-folding funnel," *Proc. Nat. Acad. Sci. U.S.A.* **92**, 3626-3630 (1995). <u>https://doi.org/10.1073/pnas.92.8.3626</u>

protein. Those were the ingredients of that paper. Then, we sent it in. I would say it was very key paper, because first of all it was short—people could read it. The figure is more or less the same figure as in the OWLSS paper, as we call it. (I chose that title because it was supposed to be clever. The order of authors is so that it spells out Onuchic, Wolynes, Luthey, Schulten, Socci, so it's OLWSS, the wise guys. (I didn't know I was going to move to Rice, where the emblem of the school is owls¹⁰⁴. So, that's the OWLSS paper.) But the *Science* drawing staff redrew it, and they just did such a brilliant job with all the colors.

I'm actually very proud of the first figure, because most people draw these funnel pictures, and they just draw something that looks like funnel. But I had just read this book by Tufte on the visual presentation of quantitative data¹⁰⁵, and he said: "You should really try to put as much information in the figure that's quantitative as you can." It turns out that that figure has many things shown on it, like this is how big the entropy is, this is how much the energy loss is, this is how a big the barriers are. All those are the results of theories. They are real numbers. They may not be exact numbers—they're far from exact, in fact—but they're numbers that are meant to be taken seriously on the figure. It's not just a hand-drawn figure. That's why I was very proud of that being real science, and not just a drawing. The *Science* guys did a better job drawing it than the first one, but still preserved most of the numbers right, so it came out very nicely. That's why the paper is so well cited, I think.

- **PC:** A couple of years later you wrote a review for the Annual Reviews of *Physical Chemistry* with José Onuchic and Zen Schulten¹⁰⁶, in which you stated "that an extremely important statistical mechanical tool for investigating the connection between the macroscopic forces and the energy landscape of proteins and hetero polymers has been the replica methods for spin glass theory." You mentioned earlier that in the spin glass and the structural glass world, there were different views across the Atlantic about replicas. Were somehow ideas of replicas better accepted in the hetero-polymer world?
- **PGW:** [1:09:38] I don't think so. First of all, like I said, Eugene Shakhnovich wrote some things with replicas, although I think one of the issues with his way of doing it was that he made some really [unnecessary] additional

¹⁰⁴ "Rice traditions," *Rice University* (n.d.). <u>https://www.rice.edu/rice-traditions</u> (Accessed January 21, 2024.)

 ¹⁰⁵ E. R. Tufte, *The Visual Display of Quantitative Information* (Cheshiere, Conn.: Graphics Press, 1983).
 ¹⁰⁶ J. N. Onuchic, Z. Luthey-Schulten and P. G. Wolynes, "Theory of protein folding: the energy landscape perspective," *Annu. Rev. Phys. Chem.* 48, 545-600 (1997).
 https://doi.org/10.1146/annurey.physchem.48.1.545

approximations that made it very hard to compare it to actual proteins. But the ideas are there for sure. On the other hand, with Masaki Sasai, we started to do replicas and we tried to do a little bit better approximation on the polymer physics, and also apply it to our associative memory Hamiltonian that we started to use as a practical tool to predict structure¹⁰⁷. Actually, we wrote this paper with replicas where we use a variational approximation for the assumed ansatz of the replica symmetry breaking and it's basically the same thing that Mézard and Parisi did essentially at the same time for the random interface problem¹⁰⁸. That's a place where we used it. I think that that result made us feel confident of the random energy model-style results we continued to use.

With Shoji Takada we also looked at instantons in the replica method first, before we had ever applied it to structural glasses¹⁰⁹. There'd been the TAP equation use of the instantons in that 1987 paper, but this was the first one where we used replica instantons. Although you can make an argument that that the fully connected model is a good thing, because proteins aren't all that big. It also turns out to be true that whole proteins are not all that big, but they're not all that little either. So, in fact, the mechanism of folding only involves a finite part of even a 60-mer. A 60-mer, and 80-mer maybe a third of it really is involved in the transition state for folding. That's why we needed to have a sort of nucleation-like picture to understand things. But I would say all those papers had very little impact on the experimentalists in protein folding or other theorists, who worked on folding at the time. Most of the community was simulation-based. Those sorts of questions didn't seem to excite them very much.

PC: That brings us back to where we were a little before, the late '90s, early 2000s, when you go back to issues of problems of structural glasses. You had two PhD students, Vassily Lubchenko¹¹⁰ and Xiaoyu Xia working on the

¹⁰⁷ M. Sasai and P. G. Wolynes. "Molecular theory of associative memory Hamiltonian models of protein folding," *Phys. Rev. Lett.* **65**, 2740 (1990). <u>https://doi.org/10.1103/PhysRevLett.65.2740</u>; "Unified theory of collapse, folding, and glass transitions in associative-memory Hamiltonian models of proteins," *Phys. Rev. A* **46**, 7979 (1992). <u>https://doi.org/10.1103/PhysRevA.46.7979</u>

 ¹⁰⁸ M. Mézard and G. Parisi, "Interfaces in a random medium and replica symmetry breaking," *J. Phys. A* **23**, L1229 (1990). <u>https://doi.org/10.1088/0305-4470/23/23/008</u>; "Replica field theory for random manifolds," *J. Physique I* 1, 809-836 (1991). <u>https://doi.org/10.1051/jp1:1991171</u>

¹⁰⁹ See, *e.g.*, S. Takada and P. G. Wolynes, "Statics, metastable states, and barriers in protein folding: A replica variational approach," *Phys. Rev. E* **55**, 4562 (1997). <u>https://doi.org/10.1103/PhysRevE.55.4562</u>; "Microscopic theory of critical folding nuclei and reconfiguration activation barriers in folding proteins," *J. Chem. Phys.* **107**, 9585-9598 (1997). <u>https://doi.org/10.1063/1.475256</u>

¹¹⁰ Vassiliy Lubchenko, *Quantum theory of glasses*, PhD Thesis, University of Illinois at Urbana-Champaign (2002). <u>https://i-share-</u>

uiu.primo.exlibrisgroup.com/permalink/01CARLI_UIU/gpjosq/alma99457887912205899

topic, I think, in parallel. What drew you back to the problem at that particular point?

PGW: [1:13:08] I think they're not quite in parallel. Xiaoyu is a little bit earlier, although I'd have to be a little bit careful. I think they overlapped. What Vas was supposed to work on originally was a completely different thing related to the two-level systems. So, let's come back [to that]. Xiaoyu was working on it because he didn't want to do anything on biological stuff. I said: "I still would like to just show people that you can do this microscopic calculation." He was very good with that. He did the calculation, and then he did the calculation where we added in-for the first time-the fluctuations, so that one could explain the stretched exponential¹¹¹. The stretched exponentials were of course a big deal in all of the glassy physics. It was the kind of thing that attracted Hans to saying there was a landscape. I would say the stretched exponential is the clearest proof there's a landscape since it shows there's something that's heterogeneous. But none of the previous work on the RFOT theory paid any attention to that as far as I could tell. It turned out to be a very nice theory that you could show how the stretching exponent was related to the heat capacity. That works reasonably well. Xiaoyu, I wanted to have come to San Diego, but he said: "Oh, you know, I've been taking this these classes in finance. I have a job arranged at McKinsey. I want to just get out of here." I said: "Okay!" He had three papers—very good papers—so he passed my minimal standards. He turned out to be a very rich guy on the basis of this. He has his own hedge fund and so on. I often joke; I guess it's a bad one. My group once brought to me this information. They said: "Oh, we just saw Xiaoyu Xia in the news. He just paid a three million dollar fine to the Securities Exchange Commission¹¹²." I said: "That shows he's very successful because he's able to pay the three million dollars fine." Anyway, he's actually a very nice guy.

What we were doing with Vas was kind of an interesting story. It was connected with glasses but not related to the glass transition originally. What had happened was that I had heard of a puzzle from Tony Leggett¹¹³. A few people who had studied the two-level systems in glasses, one of the major experimental groups was a guy named Ansel Anderson¹¹⁴, who was

¹¹¹ Ref. 89; X. Xia and P. G. Wolynes, "Diffusion and the mesoscopic hydrodynamics of supercooled liquids," *J. Phys. Chem. B* **105**, 6570-6573 (2001). <u>https://doi.org/10.1021/jp004616m</u>

 ¹¹² "LITIGATION RELEASES: Xiaoyu Xia and Yanting Hu," U.S. Securities and Exchange Commission, LR-23249 (2015). <u>https://www.sec.gov/litigation/litreleases/lr-23249</u> (Accessed November 7, 2023.)
 ¹¹³ Anthony Leggett: <u>https://en.wikipedia.org/wiki/Anthony_James_Leggett</u>

¹¹⁴ "Ansel C. Anderson," *AIP Physics History Network* (n.d.). <u>https://history.aip.org/phn/11409004.html</u> (Accessed November 8, 2023.). See, *e.g.*, M.W. Klein, B. Fischer, A. C. Anderson and P. J. Anthony, "Strain interactions and the low-temperature properties of glasses," *Phys. Rev. B* **18**, 5887 (1978).

a head of the UIUC physics department. So, a lot of experiments had been done on this. Tony, first of all, told me he had independently proposed the two-level system idea for low-temperature properties of glasses¹¹⁵, maybe slightly earlier than Anderson, Halperin and Varma¹¹⁶. [Leggett] was very interested in this. He noticed that there was this weird universality of the measured properties. If you simply sprinkle in some two-level systems, [then] why should they have any universal properties at all. He pointed this out. Then, he tried to say: "Well, this must be because it's really the case that the two-level systems interact with each other, and they've got to be renormalized in some way, so that you end up with a universal result." He did a calculation with Clare Yu of this¹¹⁷. It's a very interesting but obscure to me calculation. It ends up suggesting there's universality, but it's off by a factor of at least 100.

In talking to Vas, who had worked on some tunneling in bath problems when he was a master's student¹¹⁸, I said: "Look, I know how to do tunneling in a bath much better than Tony, actually. In the '80s, we wrote more papers with Monte Carlo. I'm sure he just made some mistakes, and we should just do the calculation right." So, I had Vas start on various, better approximations for in baths made up of two-level systems. And he would always get the same answer as Clare and Tony. Then, I said, "Why don't you try this approximation?", and he tried another approximation. And he also got more or less their answer again. He kept doing this about five or six times, and he got very discouraged. He just wasn't getting anywhere. I said: "You've just got to write up your calculation. We know it gives the wrong answer, but if it gives the wrong answer and you've done this calculation so many times, it still will get you a thesis, so just finish the goddamn thing." So, I said: "Why don't you come out with me to San Diego." (I was moving to San Diego.) "And I'm going to sit on you until you finish this." He still kept doing more approximations, always getting the

https://doi.org/10.1103/PhysRevB.18.5887; J. J. Freeman an A. C. Anderson, "Thermal conductivity of amorphous solids," *Phys. Rev. B* **34**, 5684 (1986). <u>https://doi.org/10.1103/PhysRevB.34.5684</u> ¹¹⁵ W. A. Phillips, "Tunneling States in Amorphous Solids," *J. Low Temp. Phys.* **7**, 351 (1972). <u>https://doi.org/10.1007/BF00660072</u>

 ¹¹⁶ P. W. Anderson, B. I. Halperin and C. M. Varma, "Anomalous low-temperature thermal properties of glasses and spin glasses," *Philo. Mag.* 25, 1-9 (1972). <u>https://doi.org/10.1080/14786437208229210</u>
 ¹¹⁷ C. C. Yu and A. J. Leggett, "Low Temperature Properties of Amorphous Materials: Through a Glass Darkly" *Comments Cond. Mat. Phys.* 14, 231 (1988). <u>https://ps.uci.edu/~cyu/publications/TLS_AJL.pdf</u> (Accessed November 8, 2023.)

¹¹⁸ Prof. Lubchenko obtained a MSc in Chemistry from Carnegie Mellon University in 1995. See, *e.g.*, Y. Dakhnovskii, V. Lubchenko and P. G. Wolynes, "False tunneling" and multirelaxation time nonexponential kinetics of electron transfer in polar glasses," *J. Chem. Phys.* **104**, 1875-1885 (1996).

https://doi.org/10.1063/1.470943; Y. Dakhnovskii, V. Lubchenko and R. D. Coalson, "Light Absorption in Strongly Irradiated Long Range Polar Electron Transfer Systems," *Phys. Rev. Lett.* **77**, 2917 (1996). https://doi.org/10.1103/PhysRevLett.77.2917

same answer to that Tony did, but he still wouldn't write anything up. I said [to myself]: "Oh, he's just getting bored. I've got to make this problem more interesting." So, I said [to him]: "What if the two-level systems lived on the boundaries of the mosaic?" That would give him some spatial order in there and then the problem would be more fun. I calculated how many borders there would be, what fraction of them would have a low enough energy to tunnel, and the answer came out to be the experimental number. That's how the paper then changed completely to just say that those are the two-level systems¹¹⁹. The quantum active ones are only a fraction of the guys which are at the borders of the mosaic. That's how he did this. Originally, it was not supposed to be connected to the glass transition problem at all. It was supposed to be a tunneling in the bath problem, but it didn't turn out to be that way.

- **PC:** The way you frame it, it sounds like this revival of interest had nothing to do with the advances made in the meantime by Jean-Philippe Bouchaud¹²⁰, Marc Mézard and Giorgio Parisi, who had started to look at replicated liquids¹²¹. Did you follow at all the work that had happened in the replica world?
- **PGW:** [1:20:12] I probably knew the replicated liquid. I definitely know it now. I probably knew it by the year 2000 or so. I think that paper is like [1996]. I remember that the problem with the paper was that it used the hypernetted-chain equation¹²², which had a very bad reputation in liquid state theory for things that had hard spheres. Also, the original papers didn't really seem to try to get accurate transition densities or anything, so I didn't pay a lot of attention to it. The first calculation we did with a non-random system with replicas was with Jörg Schmalian. Jörg Schmalian, I met at either Aspen¹²³ or ICAM.¹²⁴ Jörg had been a postdoc of David Pines¹²⁵, but I'd never met him at Illinois. He came from a polymer background.

¹²² Hypernetted-chain (HNC) equation: <u>https://en.wikipedia.org/wiki/Hypernetted-chain_equation</u>

¹²³ Aspen Center for Physics: <u>https://en.wikipedia.org/wiki/Aspen Center for Physics</u>
 ¹²⁴ Institute for Complex Adaptive Matter:

¹¹⁹ V. Lubchenko and P. G. Wolynes, "Intrinsic quantum excitations of low temperature glasses," *Phys. Rev. Lett.* **87**, 195901 (2001). <u>https://doi.org/10.1103/PhysRevLett.87.195901</u>

¹²⁰ See, *e.g.*, J.-P. Bouchaud and M. Mézard, "Self induced quenched disorder: a model for the glass transition," *J. Physique I* **4**, 1109-1114 (1994). <u>https://doi.org/10.1051/jp1:1994240</u>

¹²¹ See, *e.g.*, M. Mézard and G. Parisi, "A tentative replica study of the glass transition," *J. Phys. A* **29**, 6515 (1996). <u>https://doi.org/10.1088/0305-4470/29/20/009</u>; "A first-principle computation of the

thermodynamics of glasses," *J. Chem. Phys.* **111**, 1076-1095 (1999). <u>https://doi.org/10.1063/1.479193</u>; "Thermodynamics of glasses: A first principles computation," *J. Phys.: Cond. Matt.* **11**, A157 (1999). <u>https://doi.org/10.1088/0953-8984/11/10A/011</u>

https://en.wikipedia.org/wiki/Institute for Complex Adaptive Matter

¹²⁵ David Pines: <u>https://en.wikipedia.org/wiki/David_Pines</u>

- **PC:** Didn't you co-author a paper together with David Pines and him¹²⁶?
- **PGW:** [1:21:42] Later, I did a paper with David Pines, which I can tell you a story about, but it's a think-piece paper. I've never written a real research paper with David.
- **PC:** So, did you not interact with Jörg Schmalian at that point?
- [1:21:59] No. But then he was at that Aspen meeting—probably Aspen or PGW: ICAM meeting or something, a meeting probably organized by David Pines¹²⁷—he said: "I think this glass stuff might be really relevant for the high temperature superconductors. There are all these stripes. There's also this other stuff that goes on. "Do you think that could be playing a role?" I said: "Yeah, maybe so." I would say he took the lead really and sort of with my just holding his hand, saying: "Maybe we could try using these replicas techniques for the for the striped Hamiltonian." He came up with the using the Monasson-style analysis¹²⁸ for that system. That's probably the only paper where we officially used replicas for a non-random system. The paper is titled something like self-generated randomness in striped glasses or something like that¹²⁹. Technically it's almost the same as the HNC paper, I guess, but the Hamiltonian is a Landau-style field-theoretic Hamiltonian. Also later, there were several other glass things that came from talking with Jörg.

¹²⁶ R. B. Laughlin, D. Pines, J. Schmalian, B. P. Stojković and P. G. Wolynes, "The middle way," *Proc. Nat. Acad. Sci.* U.S.A. **97**, 32-37 (2000). <u>https://doi.org/10.1073/pnas.97.1.32</u> **PC:** Prof. Schmalian was then already at the University of Iowa.

¹²⁷ Likely the second ICAM meeting. See, *e.g.*, "Chaired by Robert Laughlin, Peter Wolynes, David Pines, and Alexander Balatsky (Los Alamos), a second ICAM workshop brought together thirty-three senior scientists, three postdocs, and three graduate students for an in-depth discussion of "Mesoscopic Organization in Matter [...] Immediately after the workshop a group of us spent four days at my home working on the draft of a paper that would tell a PNAS audience about what we had learned at the workshop." (290-291) D. Pines, "Emergence," In: *The Routledge Handbook of Emergence*, Sophie Gibb, Robin Findlay Hendry, Tom Lancaster, eds. (New York: Routledge, 1999): 287-297. https://doi.org/10.4324/9781315675213-24

¹²⁸ See, *e.g.*, R. Monasson, "Structural Glass Transition and the Entropy of the Metastable States," *Phys. Rev. Lett.* **75**, 2875 (1995). <u>https://doi.org/10.1103/PhysRevLett.75.2847</u>

¹²⁹ J. Schmalian and P. G. Wolynes, "Stripe glasses: Self-generated randomness in a uniformly frustrated system," *Phys. Rev. Lett.* **85**, 836 (2000). <u>https://doi.org/10.1103/PhysRevLett.85.836</u>; H. Westfahl Jr, J. Schmalian and P. G. Wolynes, "Self-generated randomness, defect wandering, and viscous flow in stripe glasses," *Phys. Rev. B* **64**, 174203 (2001). <u>https://doi.org/10.1103/PhysRevB.64.174203</u>. See also comment and response: M. Grousson, G. Tarjus, and P. Viot, "Comment on 'Stripe Glasses: Self-Generated Randomness in a Uniformly Frustrated System'," *Phys. Rev. Lett.* **86**, 3455 (2001). <u>https://doi.org/10.1103/PhysRevLett.86.3456</u>

- **PC:** One of these, in particular, actually computed instantons in a field-theoretic description of RFOT¹³⁰. What was the driving force? Was this again his ideas and you helped him along? Or did you have a particular interest in this topic?
- **PGW:** [1:23:44] I liked the instantons. I don't remember exactly who said we should do some instantons there. The first paper on the striped glass certainly is aware that what you needed to see in the experiment was something having to do with time scales. When we put in the numbers with the Landau sort of starting Hamiltonian for a real glass, I would say they don't work really as smoothly or as nicely as when you say matter is made up of atoms, which can only vibrate about one tenth of a particle spacing before they find a new kind of minimum. The Landau Hamiltonian for crystallization is really not very good. That's why I would say quantitatively we don't use the replica instantons too much.

The other thing I did with Jörg was more exciting. I think we all became very fascinated with this question of the of the spinodal behavior, the T_{A} . There are all kinds of arguments about that. Really solving mode-coupling equations, as you know, you have to sort of know lots of liquid state values, and then you still end up with questions [like] should I really take a factor of two difference of temperatures as being meaningful or not, for example. So, we were interested in that. We had some discussions, and I think he may have been the one who brought to mind—although I knew the work—this work of Klein on the metastability of an ordinary first order transition. I translated that into an argument for the barriers. It's kind of there in the Klein thing¹³¹. That turned out to work very well for understanding what the crossover phenomenon where they would occur in terms of the numbers for real glasses. So, that led to a whole series of papers on that, starting with Jörg and Jake Stevenson¹³².

PC: By the early 2000, you were in much more regular contact with the European Community working on disordered systems. What sort of meetings would you attend?

library.ucsd.edu/permalink/01UCS_SDI/Id412s/alma991002276639706535

¹³⁰ See, *e.g.*,; M. Dzero, J. Schmalian and P. G. Wolynes, "Activated events in glasses: The structure of entropic droplets," *Phys. Rev. B* **72**, 100201 (2005). <u>https://doi.org/10.1103/PhysRevB.72.100201</u>; "Replica theory for fluctuations of the activation barriers in glassy systems," *Phys. Rev. B* **80**, 024204 (2009). <u>https://doi.org/10.1103/PhysRevB.80.024204</u>

¹³¹ W. Klein and C. Unger, "Pseudospinodals, spinodals, and nucleation," *Phys. Rev. B* **28**, 445 (1983). <u>https://doi.org/10.1103/PhysRevB.28.445</u>

 ¹³² J. D. Stevenson, J. Schmalian and P. G. Wolynes, "The shapes of cooperatively rearranging regions in glass-forming liquids," *Nat. Phys.* 2, 268-274 (2006). <u>https://doi.org/10.1038/nphys261</u>; Jacob D. Stevenson, *Cooperative motions in supercooled liquids and glasses*, PhD Thesis, University of California, San Diego (2009). <u>https://search-</u>

PGW: [1:26:34] I wouldn't say it was in 2000. The XW calculations started to take numbers very seriously, and I gave a talk about the XW theory at Berkeley. David Chandler, [with whom] I had bad interactions for about 20 years, invited me to give a talk at the at the Berkeley Statistical Mechanics Meeting¹³³. I gave a talk on the XW things. Everything was all fine, I would say.

About five months later, I get this email from David Chandler saying: "Here's what I think you meant to say in your talk." It was a description of this kinetically facilitated model that he had a preprint on¹³⁴. I wrote back to him, I said: "No. That isn't what I wanted to say at all." Anyway, there were a lot of emails from him with lots of capital letters. I've got to say I'm very proud of myself I don't use capital letters too much in emails. So, he had this story. This is where we get into the interaction with Europe.

Somehow, Bouchaud and Biroli were aware—you should ask them directly—of Chandler's work. They wrote a paper that pointed out that... Chandler's main story was that these are kinetic effects, they have nothing to do with thermodynamics. Therefore, any correlation with the heat capacity is just silly, which is a key result of RFOT, to my way of thinking certainly, to the entropy crisis, but also to the heat capacity. So, Chandler turned his models around, and he calculated. He said: "Look, depending on how fragile things are in his model, [you] would also find that the heat capacity would go more or less the same way as in experiment." The more fragile it was, the more the heat capacity was, and he wrote down a formula for that, which was a formula with lots of proportionality signs. What Bouchaud and Biroli did was they calculated the actual result of Chandler and showed that it was possibly true for his model, but that the heat capacity was 100 times larger than what it is in real life¹³⁵. It's hard to make a mistake on the heat capacity by that much in that direction for sure. They sent in a paper to JCP, and I was a referee of the paper. I said it's a great paper. Then, I waited. Some—maybe nine—months later, I said: "Whatever happened to that paper of Bouchaud and Biroli." I wrote them and I said: "You realized I was the referee of your paper, could you tell me where it appeared? I'd like to cite it." They said: "It's never appeared." Then, they showed me the correspondence they had with the editor of JCP,

¹³³ Second Berkeley Statistical Mechanics Meeting, University of California Berkeley, David Chandler, January 2001. <u>https://berkeleystatmech.org/home-2-3/</u> (Accessed November 8, 2023.)

¹³⁴ J. P. Garrahan and D. Chandler, "Coarse-grained microscopic model of glass formers," *Proc. Nat. Acad. Sci. U.S.A.* **100**, 9710-9714 (2003). <u>https://doi.org/10.1073/pnas.1233719100</u>

¹³⁵ G. Biroli, J.-P. Bouchaud and G. Tarjus, "Are defect models consistent with the entropy and specific heat of glass formers?" *J. Chem. Phys.* **123**, 044510 (2005). <u>https://doi.org/10.1063/1.1955527</u>

who was actually a great guy, Marshall Fixman¹³⁶. (He passed away. He was a good person.) For some reason he had decided that even though the paper was a paper, that he viewed it as a comment on Chandler's paper and had sent it to him to referee also. Then, Chandler wrote an incredibly scathing review saying it should not be published blah blah blah blah. So, they compromised on having back-to-back papers¹³⁷, where Chandlers sort of says: "I never meant equals. I just meant there's a proportionality." So, that's how I ended up having interactions with Biroli and Bouchaud, because I commiserated with them about how that happened. I'm sorry American journals treat you this way, but what can I do?

I think that's around the time they came up with this point-to-set correlation paper¹³⁸, which has a lot of parallels with the paper I had just written with Vas Lubchenko on aging¹³⁹, because we used this idea that you think about ever larger regions and how what are the states in those regions and stuff. So, they published that paper. I think that paper had a very big influence on people. First of all, it made much clearer that the length scale question was a key question.

There's an also an experimental paper by Biroli, Bouchaud and several other people, the experimentalists, [I've forgotten who is the first author], where they sort of get these inequalities on length scale¹⁴⁰. That, I think, brought out [that] the length scale question was under some degree of control, let's say.

PC: In an interview published in 2010¹⁴¹, you're cited as saying that "results from the prior 20 years or so should already be part of the curriculum". What have you done to include this material in the curriculum. In particular, do you ever teach about spin and/or structural glasses and replica symmetry breaking?

¹³⁶ Marshall Fixman: <u>https://en.wikipedia.org/wiki/Marshall_Fixman</u>

¹³⁷ D. Chandler and J. P. Garrahan, "Thermodynamics of coarse-grained models of supercooled liquids," *J. Chem. Phys.* **123**, 044511 (2005). <u>https://doi.org/10.1063/1.1955528</u>

 ¹³⁸ J.-P. Bouchaud and G. Biroli, "On the Adam-Gibbs-Kirkpatrick-Thirumalai-Wolynes scenario for the viscosity increase in glasses," *J. Chem. Phys.* **121**, 7347-7354 (2004). <u>https://doi.org/10.1063/1.1796231</u>
 ¹³⁹ V. Lubchenko and P. G. Wolynes, "Theory of aging in structural glasses," *J. Chem. Phys.* **121**, 2852-2865 (2004). <u>https://doi.org/10.1063/1.1771633</u>

¹⁴⁰ L, Berthier, G. Biroli, J-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu and M. Pierno, "Direct experimental evidence of a growing length scale accompanying the glass transition," *Science* **310**, 1797-1800 (2005). <u>https://doi.org/10.1126/science.1120714</u>

 ¹⁴¹ J. Kurchan, J. S. Langer, T. A. Witten and P. G. Wolynes, "Scientific interview," In: *Dynamical Heterogeneities in Glasses, Colloids, and Granular Media*, L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, W. van Saarloos, eds. (Oxford: Oxford University Press, 2011), 1-38.

https://doi.org/10.1093/acprof:oso/9780199691470.003.0001, arXiv:1010.2953 [cond-mat.stat-mech].

- PGW: [1:33:05] Sort of. Since about 2010, I've taught typically courses that were on biomolecules. I did a course that's called Biomolecular Concepts. In Biomolecular Concepts, about a third of the way through, we start to talk about folding, and therefore we introduce the random energy model and how that interplays with the ordinary folding transition, and then use those ideas quite a lot. That was a mixed undergrad-grad course. The last three years, I've been teaching a new class for me, which is called Chemical Kinetics, which is a mixed undergrad-grad course that used to be gas phase reaction dynamics. As I say, we start with the Greeks and end with my papers, literally. It turns out one of the nice things about Rice is when you enter the campus there's a small inscription that most of the students have never read because it's in Greek. But I came across this, and the inscription says: "Democritus, it is said, would rather discover a single law of physics than become the Emperor of Persia¹⁴²," which I think is a great place to start. Then, we end with nucleation in glasses and protein folding on the last few lectures of that course. Basically, through more or less the random energy model for the protein folding and something like the simple parts of nucleation and the RFOT argument, but not really the full-blown replica technology.
- **PC:** When did you start teaching them about the REM? Was this around 2010 or was it before?
- **PGW:** [1:35:35] I'm sure I've taught about that. I did that in San Diego in probably 2005. The REM is so easy. It's actually easier than most things we teach in a statistical mechanics class. I think the problem with the REM is it looks so incredibly easy you go like: "I've been swindled." You feel swindled. I'm sure that's what Derrida thought. If you read the Derrida paper¹⁴³, [it's] quite complicated, but I think it's because he's trying to convince himself the simple answer was right. Of course, to some extent, that's maybe where other people see the value of his paper. My viewpoint was: "Well, that's more or less fine and simple." Then, the connection between the REM and the Potts system is basically just that you first have to establish that you have minima. Then, once you have minima that are unrelated to each other then it's the REM all over again. That's why I think at that level that's easy enough to teach to people.
- **PC:** In that same interview you expressed some exasperation at the fact that in the '90s people told you "they would be happy if there was a theory of

 ¹⁴² See, *e.g.*, Fredericka Meiners, *A history of Rice University: the Institute years, 1907-1963* (Houston: Rice University Studies, 1982):42-43. <u>https://archive.org/details/historyofriceuni00mein/page/42/mode/2up</u>
 ¹⁴³ B. Derrida, "Random-energy model: An exactly solvable model of disordered systems," *Phys. Rev. B* 24, 2613 (1981). <u>https://doi.org/10.1103/PhysRevB.24.2613</u>

a structural glasses that would reproduce the macroscopic experimental trends the more remarkable strange behaviors and be exact in some limit. Those desires have since been satisfied, yet it seems that the ideas remain challenging for some." What do you think underlies such refraction?

PGW: [1:37:31] First of all, I would still say unfortunately that statement remains true, which is a little exasperating to me. I would say there's been a slight change. Since that was written in 2010 you more often now have people say about RFOT something like: "It's the leading theory of glasses", or something like that, "but we need to do something more." I don't mean that there's nothing more to do, but I just mean that I think that that way of viewing things is a little strange. The same is true of BCS theory¹⁴⁴, for example. There still were things to do in BCS theory long after it was being used to calculate lots of stuff. Some of it is maybe just some kind of social inertia. I think there are two fundamental problems that couple. I would say that barrier crossing seems to be considered a mystery to most people who come from condensed matter physics background. I can even trace this back to Feynman. Feynman in his lectures, in volume 1¹⁴⁵, talks about chemical reaction rates, and he has actually a pretty good description of chemical reaction rates. But he says the problem with chemical reaction rates is they depend exponentially on these energies, and because of that, it's probably not even worth thinking about anything more than figuring out what the activation barrier is. Even then, you're not likely to be able to get very good experimental results because it's so sensitive. So, you could argue Feynman already told you [that] you should avoid this problem. But I would say in general even though Kramers is well-known to chemical physicists, that work is very only lightly known in the rest of the physics community. I think the fact that there's an activated event going on here, there's this sense of that makes glasses a mystery. I think that's at least one of the reasons.

> The other reason is there's this intense fascination with universality, and the only type of universality that is completely kosher is the universality of large length scales that comes from the renormalization group. First of all, that problem is quite interesting, but resolving it is to my mind not important for understanding any experiment today because the length scales never get that big. Maybe there's some regimes, some other kind of one-step replica symmetry breaking system where you will be able to access huge length scales. So, I think it's not a wrong thing to think about,

¹⁴⁴ BCS theory: <u>https://en.wikipedia.org/wiki/BCS theory</u>

¹⁴⁵ R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics, Vol. 1: Mainly Mechanics, Radiation, and Heat* (Reading, Mass: Addison-Wesley, 1977). See, Chapter 1-4: Chemical Reactions. <u>https://www.feynmanlectures.caltech.edu/l_01.html#Ch1-S4</u> (Accessed November 8, 2023.)

but I think that's one of the problems. Many of the objections to the renormalization group treatments of the dynamics of random first order transitions are equally valid for nucleation theory of liquids out of gases, or crystals out of liquids. If you really want to be a purist, you can say we don't understand nucleation at all despite the fact that we calculate things and use ideas from it all the time to make actual materials because there's no infinite length scale involved in nucleation, and once you come to the critical point it's spinodal again. I think that that's one of the reasons why socially these [concerns are there].

First of all, I agree, I don't know whether there will be a system that you can actually take down to T_{K} and see that there's a sub extensive number of aperiodic structures that have essentially the same energy per particle. I don't know if such a system actually exists. For real materials made of single substances, I tend to agree with Anderson. They will crystallize. The unit cell might have three hundred particles in it, but they'll probably crystallize. Thus there may be an issue there. I think those are the reasons why it still stays active. In a way, like I said, this sense that the actual physical system just isn't something that we can say anything about, because it has too many details.

- **PC:** We're nearing the end of this interview. Is there anything else you would like to share with us about this era that we may have missed and would be germane to our conversation?
- **PGW:** [1:43:22] It sounds to me like these are the things that are most relevant. There are many things that haven't come up in this this two-hour [conversation] that show why the problem is still quite rich, despite this sense that I have that the basic ideas are probably sound. There have been a lot of new phenomena found in the last 20 years, like the ultrastable glasses that Mark Ediger found¹⁴⁶. They've led to the ability to see if there's actual front propagation and such things¹⁴⁷.

There's a huge amount of other ways to transform one glass into another glass. I've spent a lot of time on the connection of glasses with soft matter and the cytoskeleton and biology and stuff like that¹⁴⁸. That's still an area

¹⁴⁶ See, *e.g.*, L. Berthier and M. D. Ediger, "Facets of glass physics," *Physics Today* **69**(1), 40-46 (2016). <u>https://doi.org/10.1063/PT.3.3052</u>

¹⁴⁷ See, *e.g.*, C. Rodríguez-Tinoco, M. Gonzalez-Silveira, J. Rafols-Ribe, A. F. Lopeandía, M. T. Clavaguera-Mora and J. Rodriguez-Viejo, "Evaluation of growth front velocity in ultrastable glasses of indomethacin over a wide temperature interval," *J. Phys. Chem. B* **118**, 10795-10801 (2015). <u>https://doi.org/10.1021/ip506782d</u>

¹⁴⁸ See, *e.g.*, S. Wang and P. G. Wolynes, "Microscopic theory of the glassy dynamics of passive and active network materials," *J. Chem. Phys.* **138**, 12A521 (2013). <u>https://doi.org/10.1063/1.4773349</u>

that's got a lot of activity in it, but I would say nobody's reaching a full consensus on active matter there.

I guess the one thing [that] frustrates me is it's not so much to sort of go like "Yes, we should just celebrate the great thing of the past", it's that understanding that some stuff is already understood gives you tools to do new problems. I think it's a little bit frustrating to see that there's all sorts of frontiers for us to explore, but we spend a lot of our time worrying about the past rather than about the future. (That's a bad thing to say to somebody who's doing a historical study of this. I love the past. My middle daughter is a professor of medieval history¹⁴⁹, so we like the past in our family.) The thing that's a little bit exasperating is that there's a lot of new things to do, and new things that had been done that aren't explored enough because of this sort of fixation on asymptotia.

- **PC:** I know you have notes that you've kept from that epoch. Do you have a plan to deposit them in an academic archive at some point?
- **PGW:** [1:45:57] I haven't. I certainly don't have a plan. I assumed when I died somebody might go through these things, especially from this era before email. Before email, we have lots of notes and so on. I don't keep lab notebooks, but I do have correspondence. There's a lot of correspondence on various problems in these periods. Unfortunately, a lot of science, especially in proteins, we did it with people who were actually around. So, the stuff is found in the papers and such. This was sort of a weird case where a lot of it was done when two of us were really different places. So, we did have letters going back and forth for a part of it. I'm not sure quite I'm up to the level [at which] people want to keep all my correspondence, but I'm keeping it in case that sometimes it's [helpful] for someone.
- **PC:** Prof. Wolynes, thank you very much for this conversation.
- **PGW:** [1:47:27] Thank you. Bye.

¹⁴⁹ Eve Wolynes is currently Assistant Librarian and a Special Collections Curator at Kenneth Spencer Research Library of the University of Kansas. See, *e.g.*, E. Wolynes, "Meet the KSRL Staff: Eve Wolynes," *Inside Spencer: The KSRL Blog* (2023). <u>https://blogs.lib.ku.edu/spencer/meet-the-staff-eve-wolynes/</u> (Accessed November 8, 2023.)