Basic Statistical Mechanics
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Lecture - 01
Why Study Statistical Mechanics?

Welcome, everybody. The basic idea, you know well statistical mechanics is very big in physics department and chemistry department. Across India it is hardly taught and my motivation came from once I was visiting the Central College in Bangalore University and I was going through their syllabus, I was giving some valedictory lecture, then I went to their syllabus and they have statistical mechanics, irreversible thermodynamics so I said what is.

But they said they do not have anybody to teach it and then I tried to talk with the physical chemist one quantum chemist and they said you know, that they have never been taught and it is difficult for them to pick it up. So then it occurred to me and I noticed one thing, in undergraduate colleges, that, Indian students not that every IIT's and other places but across the board in the state universities and even JNU, they like to read books written by Indian authors.

That is a very important observation. So I said okay we do not have a single statistical mechanics book in neither by physicists nor by a chemist really in the sense of a textbook. So I already had written two books and this was a herculean task to get this done and involved a lot of help from the students and it took a very long time.

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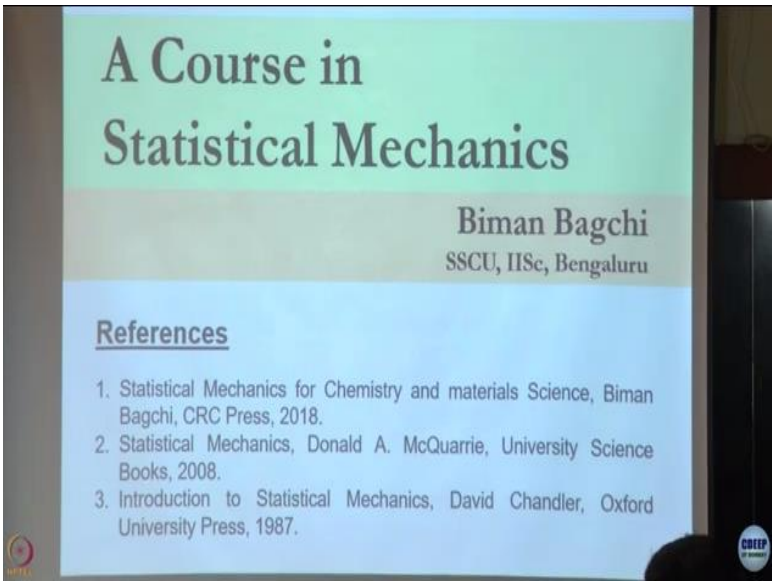

A Course in Statistical Mechanics

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References

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2. Statistical Mechanics, Donald A. McQuarrie, University Science Books, 2008.
3. Introduction to Statistical Mechanics, David Chandler, Oxford University Press, 1987.

So this is the standard book that we read, all read. The first edition, now it is I think second or third edition. This is the statistical mechanics by David Chandler. But this book is somewhat different in the sudden sense that I will go through. Though the course will be kind of a mixture and not from any one book and I would like to have put an elementary here but I thought that will lessen the appeal.

Because we will do many things which are not elementary, Okay? And I will go on doing it for some time and I think those who are present here you will enjoy it and it will take you through many things which usually you do not think about. Now let me start by saying the following thing.

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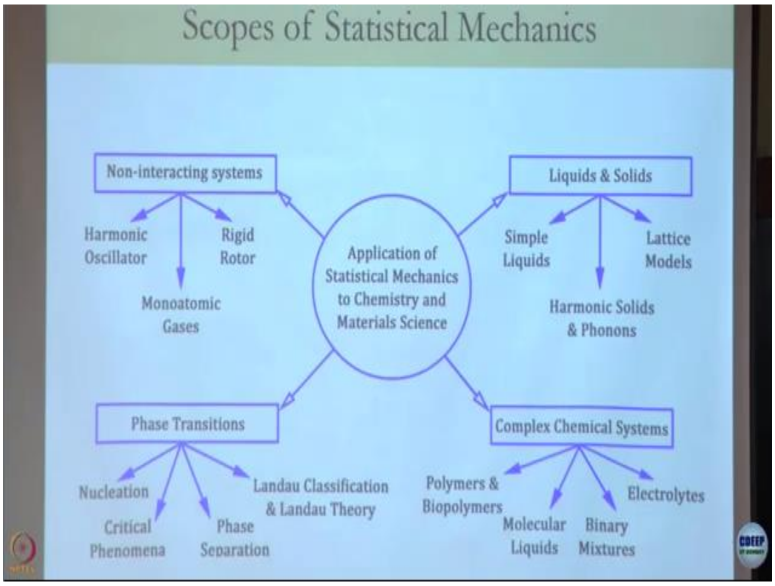

Scopes of Statistical Mechanics

Application of Statistical Mechanics to Chemistry and Materials Science

Non-interacting systems
- Harmonic Oscillator
- Rigid Rotor
- Monoatomic Gases

Liquids & Solids
- Simple Liquids
- Lattice Models
- Harmonic Solids & Phonons

Phase Transitions
- Nucleation
- Critical Phenomena
- Phase Separation
- Landau Classification & Landau Theory

Complex Chemical Systems
- Polymers & Biopolymers
- Molecular Liquids
- Binary Mixtures
- Electrolytes

That when you go through, take out the textbook you know, you will go back even take the Walter Moore or Castellan or Glasstone or even Atkins. Atkins of late has done some amount of more modernization but if you take the undergraduate textbook you will see there is electrochemistry, there will be binary mixtures, and the eutectic diagram. You have liquid molecule, liquids like water, ethanol, you have polymers.

And then you have the liquid-solid transitions. The huge number of things,that you will study in undergraduate physical chemistry. Almost except spectroscopy and atomic structure all the chapters, essentially come as a phenomenology. For example, take the ionic motion in water. You have read and about the solvent bulk model that means the water forms an ice-like structure and that reduces the mobility of lithium ion.

Again and again that kind of structure breaking and structure making is observed. When you do binary mixtures we say okay this is structure making and this is structure breaking like water, ethanol or water DMSO and they have a dependence on the whether they are structure breaking or structure making, you have a composition dependence of viscosity which of this curve, going up with the composition and going down.

I am spending so much time on this, essentially to bring home the point that, what we read is essentially statement of facts. They are observations and there hardly any explanations there. Okay, but that does not help you. You can memorize the fact and you will forget. What stays with you is you have a certain amount of understanding because then you can use it later. This is one that I will come back, this particular slide.

That, because we hope to do quite a bit of that earlier part, we will do non-interacting systems then we do interacting systems. Ultimately we want to touch on this very important thing for a chemistry particularly in modern days of nanomaterial synthesis and understanding. .

Now I will do something a little bit which is very important and profoundly important.

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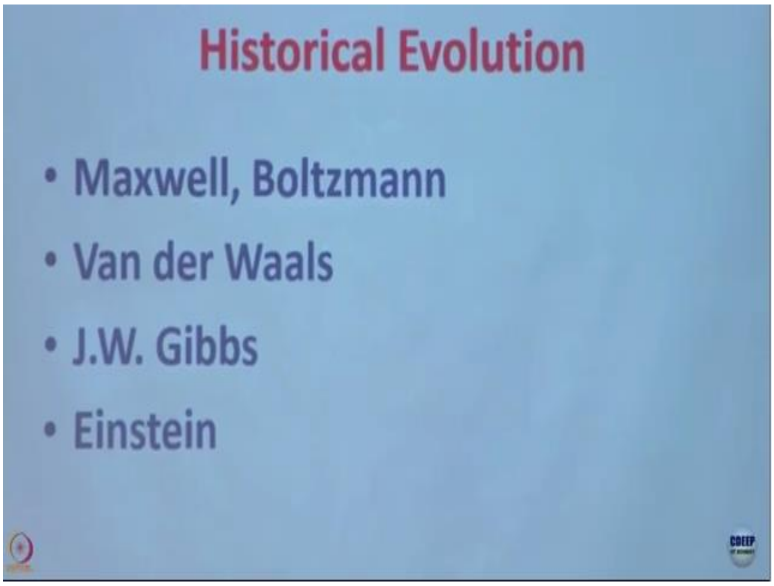

Historical Evolution

- Maxwell, Boltzmann
- Van der Waals
- J.W. Gibbs
- Einstein

See when we do quantum mechanics we start with blackbody radiation and Planck's introduction of quanta and quantum theory. Then you go to Einstein Photoelectric effect. Then we go to Niels Bohr's theory of atomic structure, electrons, and stationary orbits. Then it comes to the very important, de Broglie wave particle duality. Then, it was Peter Debye who said that is stupid to talk of it is silly actually to talk of wave equation or wave-particle duality or waves without a wave equation, which means only prompted Schrodinger to do his work.

Then, of course Heisenberg and all these things and Dirac. So these evolution of quantum mechanics is folklore. Most of us knew it when we were doing BSc and by MSc we certainly knew, such does not exist in the historical evolution of statistical mechanics, though it is very well known and you all know quite a bit of that, how did it start? So I will do a little bit of the historical evolution of statistical mechanics.

Which will, allow you to think and put the things in the perspective. So it is all started around 1850, there are several people though Maxwell who gave the clearest exposition we were thinking of the distribution of velocity of a gas particles. The very idea that people were thinking of distribution was quite unusual because that time it was a days of deterministic which you again know from quantum mechanics.

Everything was kind of deterministic perspective that people were doing. I am not going to go into very detail because I will just want to give you the history now. Maxwell came up with his famous Maxwell velocity distribution which is the Gaussian distribution. So now suddenly people know like Maxwell proposed that you might not know the velocity of an individual particle.

It does not make any sense anymore, because when there are so many particles are moving around.

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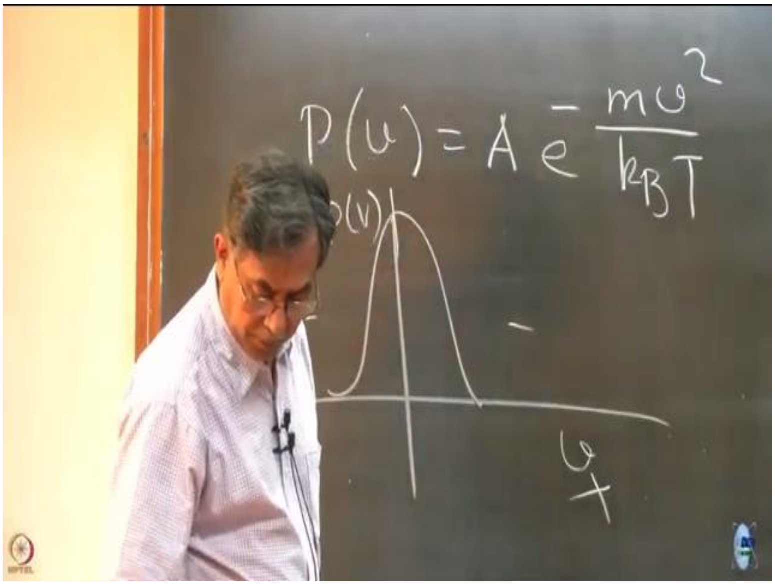

Instead of that, we should be able to talk of a velocity distribution and this is the normalization constant.

$$p(v) = Ae^{-\frac{mv^2}{k_BT}}$$

So this distribution we all know is the Gaussian distribution does this path velocity, if it is v_x and then positive and negative and this is the P(v). Now that impressed Boltzmann so much that all his life rest of his life he carried that paper of Maxwell with him.

So he was obsessed and he realized that this distribution is a very fundamental way can explain many things in nature starting from very corpuscular it was called the corpuscular view of the matter. And so Boltzmann then went on trying to develop theories and Boltzmann suffered an enormous amount of criticism, Maxwell died early. So this distribution- related criticism he did not quite suffer as was that Boltzmann suffered.

To the extent he probably committed suicide and that is even further mystery there in 1906. Another very important thing happened around that time which all of you know is the Van der Waals equation. Why it is so significant? I am now trying to tell you and again I am repeating that I am giving you right now the history, how statistical mechanics was developed and it is very important to establish the history and the chronology of evolution.

Van der Waals came up with that equation his famous equation and which is you know

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

Now what was interesting and very interesting was that, Maxwell and Boltzmann they already derived the equation from a molecular view a particle view the equation

$$PV=RT$$

the universal gas law. You know if you look at that, that was a very significant.

Actually we cannot overemphasize the importance of that the way they derived. In the whole kinetic theory of gases you do not see any name because all are done by Maxwell, maybe a little bit by Boltzmann. Similarly when you do quantum mechanics all the way up to a hydrogen molecule you do not hear any name.

Because it was all done by Schrodinger everything was done by Schrodinger. Particle in the box, harmonic oscillator, rigid rotator, hydrogen atom, hydrogen molecule and I had that collection of Schrodinger seven papers you know; one and all by picked up on a college street second-hand bookstore and I was just impressed that here is a guy and he did not do the way you do quantum mechanics.

Berry, Rice, and Ross in their first edition did the way Schrodinger derived Schrodinger equation. Okay? Not the operator thing that you did, no that is not the way he did went from de Broglie, Okay? This is very, very important that you know the history and the chronology, because that gives you much, much deeper insight.
Van der Waals at those terms pressure P.

But Van der Waals introduced one more thing which they did not have, he had. Maxwell did not have, Boltzmann had later, and I will come to that. The size of the molecule remember.

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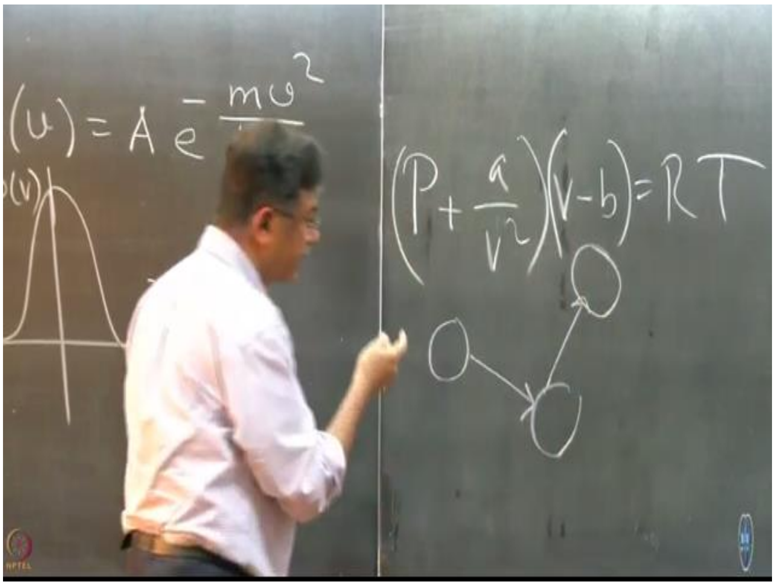

This one

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

if I take V going to infinity then I get

$$PV = RT$$

So Van der Waals introduced the interaction which gives ‘a’ and this size which is ‘b’ yes it is some approximate way and we all know the criticism of Van der Waals equation. But this equation was a kind of a thermodynamic equation, but it was used Maxwell’s essential method that a particle is going to hit the wall and it is drawn back the way we all know the derivation of Van der Waals.

So interaction in the atoms and molecules were beginning to come, though classical mechanics and continuum people were quite a bit against and very critical of the Maxwell Boltzmann approach. Van der Waals was a thermodynamic equation it was an equation of state which was verified in a very spectacular way by law of corresponding states. I will talk a lot about law of corresponding states.

The beauty of that and the universality of law of corresponding states, the whole critical phenomena originated from law of corresponding states. Now comes this one of a genius Willard Gibbs. He realized something very, very interesting. He was absolutely again obsessed with Van der Waals equation and he set out to develop a statistical mechanical the approach.

Now again a bit of history, Maxwell did with the ideal gas law. Boltzmann now tried to put in interaction between atoms and molecules that there is a size and he assumed hard sphere. He did not have an ideal gas law, does not need any interaction, but here there is a ballistick collision between two particles. So Boltzmann introduced this important collisional event that one molecule going and hitting another molecule and then, getting deflected.

The scattering event or binary collision event was taken into account by Boltzmann. But Boltzmann could not go very far what Boltzmann tried to do, they evolved the distribution function of such event of binary collision, probability distribution, that one particle at a position R1 as velocity V1 and another particle at position R2 as velocity V2.

This joint probability distribution was a very formidable thing that Boltzmann tried to tackle and he had to make certain big, big approximations. One is that, a molecular chaos and when Boltzmann made he was heavily criticized not only that he remembered the whole concept of entropy in a molecular definition

$$S = k \ln w$$

that k comes from Boltzmann. You know wherever there is a statue of Boltzmann I saw in the University of Vienna, Austria on his vast that famous equation is written.

So much further was developed. So it is important to realize that Boltzmann tried to develop a time-dependent approach to statistical mechanics he added a molecular definition of entropy he tried to go as far as he could. But he could not go very far, because things were exceedingly complicated . On the other side of the Atlantic there was great fan of Maxwell and Maxwell was great fan of Willard Gibbs.

And Willard Gibbs looked at very carefully the approach of Boltzmann. Then he realized one thing that even if I could solve what Boltzmann was trying to do, Boltzmann could not go beyond two particles but we are inadequate or in gas phase, we have many particles, the Avogadro number at least we need to discuss in a locally few hundred or thousand molecules interacting.

So Boltzmann approach as Boltzmann tried was too ambitious it will not work. But what is the brilliant thing Willard Gibbs realized that if I have a glass of water, then that glass of water and I put water in the another glass that is standing there at equilibrium, the property we take density 1gm/cm^3 ,specific heat in our older unit one, all these properties are time independent.

They are time independent they are not time dependent but Boltzmann tried with a clue from Maxwell developed a time dependent which ultimately after 100 years bore enormous fruit, but that is much later. Willard Gibbs realized that, then I should be able to develop an equilibrium approach. That means I do not have to solve the equation of motion. Boltzmann tried to solve Newton’s equation.

Could not do, even now nobody has been able to solve the 3-body problem, Okay? And Gibbs realized that then I would be able to do something if I assume I create many, many glasses of water, millions in my mind frame and then at a given instant all the water molecules in each glass are in. different positions. They are moving at different velocities they are occupied a little bit of different positions.

So he realized if I now go back kind of Maxwellian way of thinking, that if I can think of a distribution and equilibrium distribution not the time-dependent distribution which poor Boltzmann tried and could not do I can do an equilibrium distribution of my millions and millions of glasses, in each glass of water molecules are occupied in different positions. If
I have a distribution of the locations and positions of the water molecules I should be able to use Boltzmann distribution, Boltzmann distribution

$$P(E) = e^{-\beta E}$$

So now he combined Maxwell Boltzmann and his brilliant mental construction.

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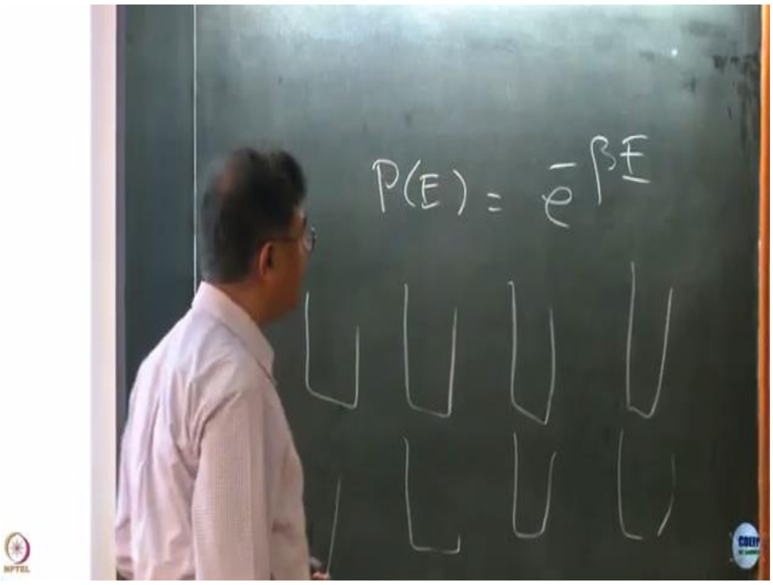

So we all know Boltzmann, so now he said if I have this millions of glasses and with water molecules millions of them, each of them at a given time by water molecules are located differently each of them has a different energy, but that essentially obey this kind of a distribution then I will be able to calculate the properties, So he avoided and this is extremely important that Willard Gibbs avoided the construction of Boltzmann.

He avoided by this brilliant which is called ensemble picture, he avoided the whole difficulty Boltzmann faced and Willard Gibbs is considered along with Boltzmann as the father of statistical mechanics. He is the one who created this ensembles picture and he is the one who created this (Boltzmann did micro-canonical) a canonical, grand-canonical. All these things are done by Willard Gibbs, and why Willard Gibbs did that?

One thing you should really know when you are doing science that we are no different from carpenter in certain sense. Science is a very pragmatic thing very practical thing it is nothing to do with any philosophy. Science is science. We had a great teacher Sadhan Basu who used to come like this with the pant dis-organized and he was a wonderful teacher. You know we wish that we had way of, those days could video his thing.

And he was talking of free will and all these things in context of Bohr's theory. And he was saying in context of famous line we all used to say that science is science, philosophy is philosophy and science is not philosophy. So Willard Gibbs really did something lot of philosophical discourse went into it but he had nothing no philosophy in mind. He just wanted to calculate he wanted to calculate this thing.

He wanted to calculate Van der Waals equation states, and he wanted a formulation. The starting with atoms and molecules starting with the intermolecular interaction; how do I go there? Not the heuristic derivation of Van der Waals and on top of that you know that Van der Waals had this loop which all again Maxwell corrected. It called Maxwell tie line getting the correct pressure out of Van der Waals.

So these three guys or four guys are just hand in gloves. They together created the whole statistical mechanics. Now, so now I have said that it was started by Maxwell but I should emphasize again Maxwell was not the only person some other people also had the Maxwell distribution but Maxwell gave a very clear exposition. Maxwell motivated Boltzmann and Boltzmann went to develop. They solved Newton's equation for many-body problem introduced the definition of entropy.

And Boltzmann could not do beyond binary collision even that he could not do very well. Then, Gibbs was trying to develop and understand Van der Waals equation and phase diagram and phase transition. Van der Waals is again the guy who did the first theory of interface surface tension. All these things were done by Van der Waals, which we will do a little bit of that.

Another very important area that you have faced in your BSc and MSc is surface phenomena, but again that was not done in a very systematic way in your undergraduate or MSc degree, but this is a beautiful subject. The surface phenomena and surface tension which is again connected with nucleation as some of you know, a Cahn-Hilliard theory. Now Einstein played an amazing role in statistical mechanics. He played an outsider role.

He created the theory of Brownian motion, which we use to do the diffusion. Einstein, contemporary when they were doing the great work. He was senior to Einstein. Around the same time, Einstein came up with what is called the theory of fluctuation. Einstein realized one thing, that many, probably from Boltzmann, the thing we call specific heat, the thing conductivity, viscosity.

These are all what in today’s language we call response function, like when you get the first thing we got the rock from the moon, what do you think we calculated? What is the thing we would not calculate? We measured the density and specific heat. Any rock that is what we do? What is the specific heat? It is a response function. What is the conductivity? It is a response.

What is the isothermal compressibility? That is a response function. Einstein realized that response functions are actually natural property of the system. They are mean square fluctuations. If I have an energy, energy of a system interacting with surrounding medium is always fluctuating, moving up and down. You now take the average and then you can take the delta e energy flux different at any given time.

And then you square it and take an average over a long time that is your specific heat. Then take the volume and take the fluctuation of the volume that gives you the isothermal compressibility. This was done by Einstein that you know, that is why he really showed the path in certain way, that how to calculate the things Gibbs was trying to develop in certain sense.

So just like, as I said in quantum mechanics all of us know very well the tree of development. In statistical mechanics, however I have not seen that tree of development not even the great book of Tolman. Okay? Or any of the books that we say so this pathway that I traced here is the way statistical mechanics was developed and that is not the way it is told in the books, but that is the way it should be told.

When you try to explain statistical mechanics, the beauty of it is through these things. Okay!