Kenneth A. Jackson

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Crystal Growth, Diffusion, and Phase Transitions in Materials

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Kenneth A. Jackson
Arizona Materials Laboratory
Department of Materials Science
and Engineering
University of Arizona
3675 East Via Alcalde
Tucson, AZ 85718
USA
kaj@aml.arizona.edu

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Contents

Preface *XIII*

1 **Introduction** *1*
1.1 Arrhenius Plot *1*
1.2 The Relationship between Kinetics and Thermodynamics *2*
1.3 The Boltzmann Distribution *4*
1.4 Kinetic Theory of Gases *6*
1.5 Collisions *7*

2 **Diffusion in Fluids** *11*
2.1 Diffusion in a Gas *11*
2.2 Diffusion in Liquids *12*
2.2.1 Diffusion Distances *13*
2.2.2 Molecular Dynamics Simulations of Diffusion in Liquids *13*
2.2.3 Measurement of Diffusion Coefficients in Liquids *16*

3 **Diffusion in Amorphous Materials** *19*
3.1 Amorphous Materials *19*
3.2 Network Glass Formers *20*
3.2.1 Silica *20*
3.2.2 Silicon and Germanium *20*
3.3 The Glass Transition *22*
3.4 The Free-Volume Model *23*
3.5 Fictive Temperature *23*
3.6 Diffusion in Polymers *24*
3.7 The Stokes–Einstein Relationship *25*

4 **Diffusion in Crystals** *27*
4.1 Diffusion in a Crystal *27*
4.2 Diffusion Mechanisms in Crystals *28*
4.2.1 Vacancy Diffusion *28*
4.2.2 Interstitial Diffusion *30*

4.4 Equilibrium Concentration of Vacancies *30*
4.4.1 Thermodynamic Analysis *30*
4.4.2 Kinetic Analysis *32*
4.5 Simmons and Balluffi Experiment *34*
4.6 Ionic and Covalent Crystals *34*
4.7 Stoichiometry *36*
4.8 Measurement of Diffusion Coefficients *36*
4.9 Surface Diffusion *37*
4.10 Diffusion in Grain Boundaries *38*
4.11 Kirkendall Effect *38*
4.12 Whisker Growth *39*
4.13 Electromigration *40*

5 Diffusion in Semiconductors *45*
5.1 Introduction *45*
5.2.1 Vacancy Diffusion in Silicon *47*
5.2.2 Diffusion of Phosphorus in Silicon *49*
5.2.3 Diffusion of Arsenic in Silicon *50*
5.2.4 Diffusion of Boron in Silicon *50*
5.3 Diffusion of Zinc in GaAs *51*
5.4 Recombination-enhanced Diffusion *52*
5.5 Doping of Semiconductors *53*
5.6 Point-Defect Generation in Silicon during Crystal Growth *53*
5.7 Migration of Interstitials (and Liquid Droplets) in a Temperature Gradient *56*
5.8 Oxygen in Silicon *57*
5.9 Gettering *57*
5.10 Solid-State Doping *58*

6 Ion Implantation *61*
6.1 Introduction *61*
6.2 Ion Interactions *62*
6.3 Implantation Damage *64*
6.4 Rutherford Backscattering *67*
6.5 Channeling *69*
6.6 Silicon-on-Insulator *71*

7 Mathematics of Diffusion *75*
7.1 Random Walk *75*
7.2 The Diffusion Equation *77*
7.3 Solutions to the Diffusion Equation *79*
7.3.1 Gaussian Concentration Distribution *79*
7.3.2 Error Function Concentration Distribution *82*
7.3.3 p/n Junction Depth *84*
7.3.4 Separation of Variables *85*

7.4 Numerical Methods 90
7.4.1 Finite Difference Method for Diffusion 91
7.4.2 Initial Surface Concentration Boundary Conditions 91
7.4.3 Implanted Concentration Profile 92
7.4.4 Zero Flux Boundary Condition 93
7.5 Boltzmann–Matano Analysis 93

8 Stefan Problems 97
8.1 Steady-State Solutions to the Diffusion Equation 97
8.2 Deal–Grove Analysis 100
8.3 Diffusion-Controlled Growth of a Spherical Precipitate 102
8.4 Diffusion-Limited Growth in Cylindrical Coordinates 105

9 Phase Transformations 109
9.1 Transformation-Rate-Limited Growth 109
9.2 Diffusion-Limited Growth 111
9.3 Thermally Limited Growth 111
9.4 Casting of Metals 113
9.5 Operating Point 114

10 Crystal Growth Methods 117
10.1 Melt Growth 117
10.1.1 Czochralski Growth 117
10.1.2 Floating Zone 121
10.1.3 Bridgman Method 123
10.1.4 Chalmers Method 123
10.1.5 Horizontal Gradient Freeze 124
10.2 Solution Growth 124
10.2.1 Growth from Aqueous Solutions 125
10.2.2 Flux Growth 125
10.2.3 Hydrothermal Growth 125
10.3 Vapor-Phase Growth 126
10.4 Stoichiometry 126

11 Segregation 129
11.1 Segregation during a Phase Change 129
11.2 Lever Rule 130
11.3 Scheil Equation 131
11.4 Zone Refining 133
11.5 Diffusion at a Moving Interface 134
11.5.1 Steady-state Diffusion at a Moving Interface 134
11.5.2 Initial and Final Transients 137
11.6 Segregation in Three Dimensions 139
11.7 Burton, Primm and Schlicter Analysis 139

12 **Interface Instabilities** *143*
12.1 Constitutional Supercooling *143*
12.2 Mullins and Sekerka Linear Instability Analysis *149*
12.3 Anisotropic Interface Kinetics *152*

13 **Chemical Reaction Rate Theory** *155*
13.1 The Equilibrium Constant *155*
13.2 Reaction Rate Theory *155*
13.3 Reaction Rate Constant *157*
13.4 Transition State Theory *157*
13.5 Experimental Determination of the Order of a Reaction *158*
13.6 Net Rate of Reaction *160*
13.7 Catalysis *162*
13.8 Quasi-Equilibrium Model for the Rate of a First-Order phase Change *163*

14 **Phase Equilibria** *165*
14.1 First-Order Phase Changes *165*
14.2 Second-Order Phase Changes *169*
14.3 Critical Point between Liquid and Vapor *172*

15 **Nucleation** *175*
15.1 Homogeneous Nucleation *175*
15.1.1 Volmer Analysis *176*
15.1.2 Turnbull's Droplet Experiment *179*
15.1.3 Surface Free Energy *181*
15.1.4 Becker–Döring Analysis *183*
15.1.5 Nucleation Rate *187*
15.1.6 Limitations of the Becker–Döring Analysis *188*
15.1.7 Assumptions in the Classical Nucleation Theory *188*
15.1.8 Nucleation of a Precipitate Particle *189*
15.2 Heterogeneous Nucleation *190*
15.2.1 Heterogeneous Nucleation Theory *191*
15.2.2 Nucleation Lore *192*
15.2.3 Cavitation *193*
15.2.4 Re-entrant Cavities *194*
15.2.5 Cloud Seeding *195*
15.2.6 Industrial Crystallization *195*
15.2.7 Grain Refiners *196*
15.2.8 Residues *196*
15.3 Johnson–Mehl–Avrami Equation *197*
15.3.1 Johnson–Mehl Equation *197*
15.3.2 Johnson–Mehl–Avrami *199*

16 **Surface Layers** *203*
16.1.1 Langmuir Adsorption *203*
16.1.2 CVD Growth by a Surface-Decomposition Reaction *204*

16.1.3 Langmuir–Hinshelwood Reaction *205*
16.2 Surface Nucleation *206*
16.2.1 Nucleation on a Surface during Vapor Deposition *206*
16.2.2 Cluster Formation *207*
16.2.3 Rate Equations *209*
16.3 Thin Films *210*
16.3.1 Epitaxy *210*
16.3.2 Deposited Surface Layers *212*
16.4 Surface Reconstruction *213*
16.5 Amorphous Deposits *214*
16.6 Surface Modification *217*
16.7 Fractal Deposits *217*
16.8 Strain Energy and Misfit Dislocations *219*
16.9 Strained-Layer Growth *223*
16.9.1 Surface Modulation *223*
16.9.2 Strained-Layer Superlattice *223*
16.9.3 Graded-Strain Layers *224*

17 Thin-Film Deposition *227*
17.1 Liquid Phase Epitaxy *227*
17.2 Growth Configurations for LPE *228*
17.3 Chemical Vapor Deposition *229*
17.4 Metal-Organic Chemical Vapor Deposition *233*
17.5 Physical Vapor Deposition *234*
17.6 Sputter Deposition *235*
17.7 Metallization *235*
17.8 Laser Ablation *236*
17.9 Molecular Beam Epitaxy *237*
17.10 Atomic Layer Epitaxy *238*

18 Plasmas *241*
18.1 Direct Current (DC) Plasmas *241*
18.2 Radio-Frequency Plasmas *243*
18.3 Plasma Etching *245*
18.4 Plasma Reactors *247*
18.5 Magnetron Sputtering *249*
18.6 Electron Cyclotron Resonance *251*
18.7 Ion Milling *252*

19 Rapid Thermal Processing *253*
19.1 Rapid Thermal Processing *253*
19.2 Rapid Thermal Processing Equipment *254*
19.3 Radiative Heating *254*
19.4 Temperature Measurement *256*
19.5 Thermal Stress *257*
19.6 Laser Heating *258*

20 Kinetics of First-Order Phase Transformations *259*
20.1 General Considerations *259*
20.2 The Macroscopic Shape of Crystals *261*
20.3 General Equation for the Growth Rate of Crystals *262*
20.4 Kinetic Driving Force *263*
20.5 Vapor-Phase Growth *264*
20.5.1 Equilibrium *264*
20.5.2 Kinetics of Vapor-Phase Growth *265*
20.6 Melt Growth *267*
20.6.1 Early Models for Melt Growth *268*
20.6.2 Melt Growth Rates *269*
20.7 Molecular Dynamics Studies of Melt Crystallization Kinetics *269*
20.8 The Kossel–Stranski Model *272*
20.9 Nucleation of Layers *273*
20.10 Growth on Screw Dislocations *275*
20.11 The Fluctuation Dissipation Theorem *277*
20.11.1 Determination of the Kinetic Coefficient *277*
20.11.2 Experimental Determination of Surface Tension *281*

21 The Surface-Roughening Transition *283*
21.1 Surface Roughness *283*
21.2 The Ising Model *284*
21.3 Cooperative Processes *285*
21.4 Monte Carlo Simulations of Crystallization *287*
21.5 Equilibrium Surface Structure *288*
21.5.1 Thermodynamic Model for Surface Roughness *288*
21.5.2 Application of Surface Roughening to Materials *291*
21.5.3 Snow Flakes *294*
21.5.4 Rate-Theory Analysis of Surface Roughness *295*
21.5.5 Surface Roughness in the Ising Model *297*
21.6 Computer Simulations *298*
21.6.1 Determination of the Kinetic Coefficient *301*
21.6.2 Simulations of Silicon Growth *302*
21.7 Growth Morphologies *304*
21.8 Kinetic Roughening *306*
21.9 Polymer Crystallization *308*

22 Alloys: Thermodynamics and Kinetics *311*
22.1 Crystallization of Alloys *311*
22.2 Phase Equilibria *313*
22.3 Regular Solution Model *314*
22.4 Near-Equilibrium Conditions *316*
22.5 Phase Diagrams *317*
22.6 The DLP Model *320*

23 Phase Separation *323*
23.1 Ordering versus Phase Separation *323*
23.2 Phase Separation *324*
23.3 Analytical Model for Spinodal Decomposition *326*
23.4 Microstructure Resulting from Phase Separation *328*

24 Non-Equilibrium Crystallization of Alloys *331*
24.1 Non-Equilibrium Crystallization *331*
24.2 Experiment *331*
24.3 Computer Modeling *333*
24.4 Analytical Model *335*
24.5 Comparison with Experiment *336*
24.6 Crystallization of Glasses *338*

25 Coarsening, Ripening *341*
25.1 Coarsening *341*
25.2 Free Energy of a Small Particle *341*
25.3 Coarsening in a Solution *342*
25.4 Coarsening of Dendritic Structures *344*
25.5 Sintering *345*
25.6 Bubbles *346*
25.7 Grain Boundaries *347*
25.8 Scratch Smoothing *348*

26 Dendrites *351*
26.1 Dendritic Growth *351*
26.2 Conditions for Dendritic Growth *351*
26.3 Simple Dendrite Model *353*
26.4 Phase Field Modeling *358*
26.5 Faceted Growth *358*
26.6 Distribution Coefficient *358*

27 Eutectics *361*
27.1 Eutectic Phase Diagram *361*
27.2 Classes of Eutectic Microstructures *362*
27.2.1 Class I Eutectics *362*
27.2.2 Class II Eutectics *365*
27.2.3 Class III Eutectics *367*
27.3 Analysis of Lamellar Eutectics *367*
27.3.1 Curvature of the Interface *368*
27.3.2 Diffusion *370*
27.3.3 Calculation of Eutectic Interface Shape *372*
27.4 Off-Composition Eutectics *373*
27.5 Coupled Growth *374*
27.6 Third-Component Elements *378*

28 **Castings** *381*
28.1 Grain Structure of Castings *381*
28.2 Dendrite Remelting *382*

Subject Index *by Page* *387*

Subject Index *by Chapter Sections* *403*

Preface

This book is based on a course on Kinetic Processes which I taught for several years in the Materials Science Department at the University of Arizona. This is a required course for first year graduate students, although some of the material contained in the book would be suitable for a lower level course. The course initially derived from a series of lectures which I gave at Bell Labs, augmented by course notes from a similarly titled course at MIT. The content of the book has a highly personal flavor, emphasizing those areas to which I have made scientific contributions. I have concentrated on developing an understanding of kinetic processes, especially those involved in crystal growth, which is, perhaps, the simplest form of a first order transformation. The book assumes a basic understanding of thermodynamics, which underlies all kinetic processes and can be used to predict transformation kinetics for simple cases. The understanding of the complexities of crystal growth has developed significantly over the past several decades, but it is a wonderfully complex process, with still much to be learned. I have tried to present a coherent account of these processes, based on my view of the subject, which is available at present only in a dispersed form in the published literature, but it has not been assembled and coordinated as I have attempted to do here.

The book concentrates on atomic level processes and on how these processes translate into the microscopic and macroscopic descriptions of kinetic processes. It is aimed at a level appropriate for practitioners of materials processing. I have kept the mathematics at the minimum level necessary to expose the underlying physics. Many of my mathematically inclined friends will cringe at the simplified treatments which I present, but nevertheless, I suspect that non-mathematically inclined students will struggle with them. My colleagues in the crystal growth community, on the other hand, will cringe at my over-simplified descriptions of how single crystals and thin films, the basic materials for high-tech devices, are produced.

There are two streams of context in this book. One concentrates on basic kinetic processes, and the other on modern applications, where these kinetic processes are of critical importance. These two streams are interleaved. The book starts with an introduction to the basis of classical kinetics, the Boltzmann distribution. The following four chapters deal with diffusion processes in fluids, in amorphous materials, in simple crystals, and in semiconductors. This is followed by Chapter 6, on ion implantation, the important method for doping semiconductors, and includes a discussion of Rutherford backscattering. The next chapter introduces the diffusion equation, and some standard solutions. Chapter 8 deals with Stefan problems which are moving boundary problems encountered in phase transformations. Chapter 9 contains a general description of the kinetic processes involved in phase transformations, and is followed by Chapter 10 which contains a brief description of the methods used for growing single crystals. This is not intended to teach anyone how to grow crystals: there are individual books on several of these methods. Chapter 11 describes segregation at a moving interface, and is followed by Chapter 12, on the interface instabilities which can result from this segregation. These instabilities are described by non-linear equations which have been studied extensively, but are far beyond the scope of this book. Chapter 13 outlines some aspects of chemical kinetic theory, and is followed Chapter 14 on the formal aspects of phase transformations. Chapter 15 treats the initial formation of a new phase by a nucleation process. The next few chapters are on atomic processes at surfaces. Chapter 16 outlines adsorption, surface nucleation and epitaxial growth. This treatment only scratches the surface of the knowledge which has been accumulated by surface scientists. Chapter 17 discusses methods for the deposition of thin films, and Chapter 18 is on plasmas, which are used for both deposition and etching. Chapter 19 discusses rapid thermal processing, which is used to control and fine tune thermal annealing. The next few chapters return to fundamental considerations. Chapter 20 discusses the kinetics of first order phase transformations, and the following chapter discusses the important role of the surface roughening transition in these processes. The final chapters are on kinetic processes in alloys. Chapter 22 is on equilibrium in alloys and on growth processes in alloys near equilibrium. It is followed by a discussion, in Chapter 23, of phase separation, also known as spinodal decomposition. Chapter 24 is on rapid phase transformations, where kinetic processes modify the usual equilibrium segregation; where the rate of motion of the interface is comparable the rate of diffusive motion of the atoms. Chapter 25 contains a brief account of coarsening, sintering and grain growth, which applies not only to alloys. Again, much more is known about these processes than could be included here. Chapter 26 presents a discussion of dendritic growth, including a simple mathematical model. This growth mode is an extreme version of interfacial instabilities as discussed in Chapter 12, and has been the focus of extensive mathematical modeling, including the development of the phase field method. Chapter 27 discusses the formation of a two phase solid from a single phase liquid. The final chapter, 28, discusses an important aspect of the formation of the grain structure in metal castings. It is by no means an introduction to the computer models of segregation and fluid flow which are used to design castings today.

Most of what I know about this subject I have learned from my colleagues over the years. I would like to take this opportunity express the enjoyment I have experienced working with them, especially John Hunt and George Gilmer, without whose contributions this book would be a lot thinner. Colleagues at Bell Labs, including Harry Leamy, Kim Kimerling, John Weeks, Rudy Voorhoeve, Ho-Sou Chen, Bill Pfann, Richard Wagner, Bob Batterman, Jim Patel, John Hegarty, Kurt Nassau, Chuck Kurkjian, Ben Greene, Ray Wolfe, Ken Benson, Dennis Maher, David Joy, Helen Farrell, George Peterson, Walter Brown, Charlie Miller, Reggie Farrow, ... , (the list is endless) have all been involved in my education. I began my interest in this area under the tutelage of Bruce Chalmers, and I owe much to fellow students Bill Tiller, Dick Davis, Don Uhlmann, Jacques Hauser, Bob Fliescher, and Jim Livingston, as well as to discussions with leaders in the field, David Turnbull and Charles Frank. My other great source of inspiration has been my colleagues in the field of crystal growth, Bob Sekerka, Bob Laudise, Franz Rosenberger, John Wilkes, Alex Chernov, Dave Brandle, Vince Fratello, Joe Wenkus, Don Hurle, Brian Mullen, ... (another endless list). I would also like to acknowledge the direct and indirect contributions of my graduate students at the University of Arizona, Kirk Beatty, Don Hilliard, Katherine Gudgel, Mollie Minke, and Dan Bentz.

I would like to express my appreciation of the extensive and important contributions in the areas of crystal growth, phase transformations and materials processing, including some of my efforts, which have been made possible by the sponsorship of NASA.

I would like to thank Russell Linney for a critical reading of the manuscript, and Harry Sarkas, Franz Rosenberger, and Joe Simmons, as well as many of those mentioned above, for encouragement on this project.

This book would not have been possible without the continued support and understanding of a very special person, Gina Kritchevsky.

Kenneth A. Jackson,
Prescott, Arizona
June 26, 2004

Chapter 1
Introduction

The aim of this book is to provide an understanding of the basic processes, at the atomic or molecular level, which are responsible for kinetic processes at the microscopic and macroscopic levels.

Many of the rate processes dealt with in this book are classical rate processes described by Boltzmann statistics. That is, the rate at which a process occurs is given by an expression of the form:

$$R = R_0 \exp(-Q/kT) \tag{1.1}$$

The exponential term is known as Boltzmann factor, k is Boltzmann's constant and Q is called the activation energy. The Boltzmann factor gives the fraction of atoms or molecules in the system that have an energy greater than Q at the temperature T. So the rate at which the process occurs depends on a prefactor, $R_{0,}$ which depends on geometric details of the path, the atom density, etc., times the number of atoms that have enough energy to traverse the path.

1.1
Arrhenius Plot

Taking the logarithm of both sides of Eq. 1.1:

$$\ln R = \ln R_0 - Q/kT \tag{1.2}$$

Plotting ln R vs 1/T gives a straight line with slope –Q/k, as illustrated in Fig. 1.1. This kind of plot is known as an Arrhenius plot.

If the rate process has a single activation energy, Q, over the range of the measurement, this suggests strongly that the mechanism controlling the rate is the same over that range. If the slope changes, or if the curve is discontinuous, the mechanism controlling the rate has changed.

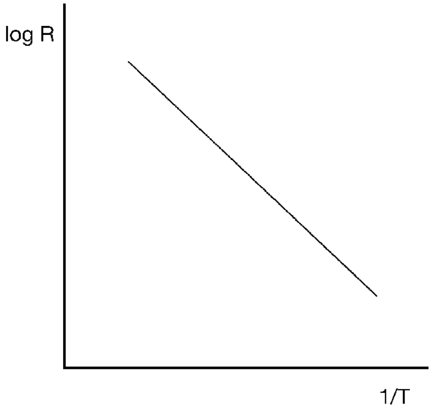


Figure 1.1 Arrhenius plot.

1.2
The Relationship between Kinetics and Thermodynamics

There is a simple relationship between the rate equation above and thermodynamics, which can be written:

$$G = -kT \ln R = Q - kT \ln R_0 \tag{1.3}$$

This implies that the rate at which atoms leave a state depends on their properties in that state. Comparing Eq. 1.3 with $G = H - TS$, it is evident that Q is related to the enthalpy, and the entropy, S, is $k\ln R_0$. If two states or phases are in equilibrium, their free energies are equal, which is equivalent to the statement that rates of transition back and forth between the two states are the same.

The relationship between thermodynamics and kinetics will be a recurring theme in this book. The thermodynamics formalism was developed during the last century based on the understanding of steam engines. If it were being developed today by materials scientists, it would be done in terms of rate equations, which are formally equivalent, but much more amenable to physical interpretation.

The origin of the Boltzmann factor will be outlined below, but first, we will attempt to answer the question:

What is temperature?

We all know what temperature is: it is something that we measure with a thermometer. The temperature scales that we use are defined based on fixed temperatures, such as the melting point of ice and the boiling point of water. We use the thermal expansion of some material to interpolate between these fixed points. But what is the physical meaning of temperature? What is being measured with this empirical system?

The simplest thermometer to understand is based on an ideal gas, where we can relate the temperature to the pressure of a gas in a container of fixed volume. The pressure on a wall or a piston derives from the force exerted on it by atoms or mo-

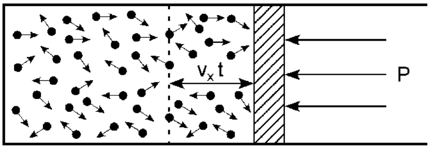


Figure 1.2 The change in momentum of the molecules striking a piston creates pressure on the piston.

lecules striking it. The pressure is due to the change of momentum of the atoms or molecules that hit the piston. The force, F, on the piston is the change in momentum per second of the atoms or molecules striking it.

So we can write:

F = (change in momentum per molecule) × (number of molecules per second striking the piston)

If v_x is the component of the velocity of a molecule in the x direction, then the change in momentum when the molecule makes an elastic collision (an elastic collision is one in which the molecule does not lose any energy) with the piston is $2mv_x$, since the momentum of the incident molecule is reversed during the collision.

As illustrated in Fig. 1.2, only the molecules within a distance $v_x t$ of the wall will strike it during time t, so the number of molecules hitting the wall per second is given by the number of molecules per unit volume, n, times the area of the piston, A, times $v_x/2$, since half of the molecules are going the other way. The force on the piston is thus:

$$F = (2mv_x)\left(\frac{1}{2}nv_x A\right) \tag{1.4}$$

And the pressure on the piston is:

$$P = \frac{F}{A} = nmv_x^2 \tag{1.5}$$

Writing n = N/V, and using the ideal gas law, we can write:

$$PV = Nmv_x^2 = NkT \tag{1.6}$$

This indicates that the thermal energy of an atom, kT, is just the kinetic energy of the atom. A more refined analysis relating the pressure to the motion of atoms in three dimensions gives:

$$kT = \frac{1}{3}mv_{rms}^2 = \frac{1}{2}m\bar{v}^2 \tag{1.7}$$

where v_{rms} is the root mean square average velocity of the atoms, and $\bar{v}$ is the most probable velocity.

A familiar form of the ideal gas law uses the gas constant R, rather than Boltzmann's constant, k. The two are related by $R = N_0 k$, where N_0 is Avagadro's number, which is the number of molecules in a mol. RT is the average thermal energy of a mol of atoms, kT is the average thermal energy of one atom.

Gas constant: $R = 1.98$ cal/mol.deg
$= 0.00198$ kcal/mol.deg
$= 8.31$ J/mol.deg
$= 8.31 \times 10^7$ ergs/mol.deg

Boltzmann's constant: $k = 8.621 \times 10^{-5}$ eV/atom.deg.
$= 1.38 \times 10^{-16}$ ergs/atom.deg.
$= 1.38 \times 10^{-23}$ J/atom.deg.

$$1\text{eV/atom} = 23\text{kcal/mol}$$

$$\frac{R}{k} = \frac{8.31 \times 10^7}{1.38 \times 10^{-16}} = 6.023 \times 10^{23}\ \text{molecules/mol} = \text{Avagadro's number}$$

The important point from the above discussion is that the temperature is a measure of the average **kinetic** energy of the molecules. Not the total energy, which includes potential energy and rotational energy, just the kinetic energy. Temperature is a measure of how fast the atoms or molecules are moving, on average.

1.3
The Boltzmann Distribution

Where does $N = N_0 \exp(-E/kT)$ come from?

We saw above that kT is a measure of the average kinetic energy of the atoms or molecules in an assembly. The Boltzmann function gives the fraction of atoms that have enough energy to surmount an energy barrier of height E, in an assembly of atoms with an average energy kT.

Let us look at an atom in a potential field. Gravity is a simple one.

The force of gravity on an atom is:

$$F = mg \tag{1.8}$$

The associated gravitational potential is:

$$\int_0^h F dx = mgh \tag{1.9}$$

which is the energy required lift an atom from height 0 to height h in gravity. mgh is the potential energy of an atom at height h.

For N atoms in a volume V at temperature T, the ideal gas law says:

$$PV = NRT \tag{1.10}$$

or

$$P = nkT \tag{1.11}$$

where $n = N/V$, the number of atoms per unit volume.

The change in pressure, dP, which will result from a change in atom density, dn, is

$$dP = kTdn \tag{1.12}$$

In a gravitational field, the number of atoms per unit volume decreases with height, and ndh is the number of atoms between heights h and h+dh.

The change in pressure between h and h+dh due to the weight of the atoms in dh is:

$$dP = P_{h+dh} - P_h = -mgndh \tag{1.13}$$

Combining Eqs. 1.12 and 1.13 gives:

$$\frac{dn}{n} = -\frac{mg}{kT}dh \tag{1.14}$$

or:

$$n = n_0 \exp\left(-\frac{mgh}{kT}\right) \tag{1.15}$$

which is the variation of atom density with height in the atmosphere due to the earth's gravitational field.

mgh is the potential energy of an atom at height h. This analysis is similar for a generalized force field, and the distribution of the atoms in the force field has the same form:

$$n = n_0 \exp\left(-\frac{P.E.}{kT}\right) \tag{1.16}$$

where P.E. is the potential energy of the atoms in the force field.

The kinetic energy distribution of the atoms can be derived by examining the kinetic energy that an atom at height zero needs to reach a height h (ignoring scattering).

In order to reach a height h, an atom must have an upwards kinetic energy equal to or greater than the potential energy at height h. It must have an upwards velocity greater than u, given by:

$$\frac{1}{2}mu^2 \geq mgh \tag{1.17}$$

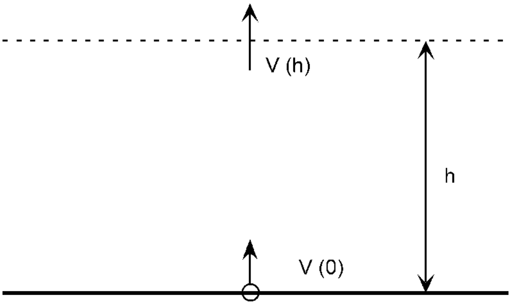


Figure 1.3 An atom with enough kinetic energy at height 0 can reach height h.

With a velocity less than u, the atom will not get to height h. In Fig. 1.3, the number of atoms passing through the plane at h is the number moving upwards at height zero with velocity greater than u, so

$$n_{v>0}(h) = n_{v>u}(0) \tag{1.18}$$

Assuming that the temperature is the same at zero and at h, the distribution of velocities will be the same, and the only difference will be the density of atoms, so:

$$\frac{n_{v>u}(0)}{n_{v>0}(0)} = \exp\left(-\frac{mgh}{kT}\right) = \exp\left(-\frac{mu^2}{2kT}\right) \tag{1.19}$$

or

$$n_{v>u} = n_0 \exp\left(-\frac{K.E.}{kT}\right) \tag{1.20}$$

where K.E. is the kinetic energy of the atom. This is the Boltzmann distribution of velocities. It says that the fraction of atoms with velocity (or kinetic energy) greater than some value is given by a Boltzmann factor with the average kinetic energy of the atoms in the denominator of the exponent.

Recalling that kT is the average kinetic energy of the atoms, the exponent is just the ratio of two kinetic energies. The Boltzmann factor describes the spread in the distribution of energies of the atoms. Given an average kinetic energy kT per atom, the Boltzmann factor tells us how many of the atoms have an energy greater than a specific value.

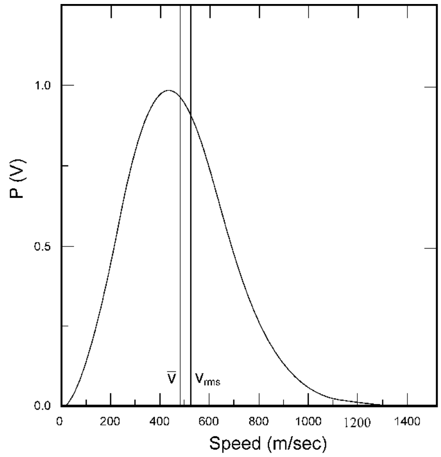
In general, if there is a potential energy barrier of height Q, the Boltzmann factor says that a fraction of the atoms given by $\exp(-Q/kT)$ will have enough kinetic energy to get over the barrier. This is independent of how the potential varies along the path. The atoms just have to have enough kinetic energy at the start to surpass the barrier. So, in general, if there is a potential barrier along a path, the atoms that are going in the right direction take a run at it, and those atoms that are going fast enough will make it over the barrier. And the fraction of the atoms that will make it over the barrier is given by a Boltzmann factor.

The original derivation of Boltzmann was concerned with atomic collisions between gas atoms, and the distribution of velocities and the spread in energy that the collisions produce. This is a very complex problem, but the result is remarkably simple. We have derived it crudely from Newton's laws and our practical definition of temperature, which is based on the ideal gas law.

1.4
Kinetic Theory of Gases

From statistics based on Newton's laws, Boltzmann derived that the probability P(v) that an atom of mass m will have a velocity v at a temperature T is given by:

Figure 1.4 Typical velocity distribution, P(v), of atoms in a gas at room temperature.



$$P(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \tag{1.21}$$

where k is Boltzmann's constant. This distribution is illustrated in Fig. 1.4.

The average velocity is given by:

$$\bar{v} = \int_0^\infty vP(v)dv = \sqrt{\frac{8kT}{\pi m}} \tag{1.22}$$

On average, the velocity of an atom in any one direction is $\bar{v}_x = \bar{v}_y = \bar{v}_z = \sqrt{\frac{2kT}{\pi m}}$. The root mean square velocity is slightly larger than the average velocity, and is given by $v_{rms} = \sqrt{\frac{3kT}{m}}$. kT is a measure of the average *kinetic* energy of the atoms in the gas. This is also true in liquids and solids. At room temperature, $\bar{v}_x$ is about $480\,\mathrm{ms}^{-1}$, or about 1060 mph.

1.5
Collisions

Two atoms of diameter d will collide if their centers pass within d of each other. We can imagine a cylinder with a diameter 2d, twice the diameter of an atom. The length of the cylinder, l, is such that the volume of the cylinder is the average volume per atom in the gas, 1/n, where n is the number of atoms per unit volume in the gas. We then have: $l\pi d^2 = 1/n$. When an atom traverses a distance l, it is likely to collide with another atom. The average distance between collisions is thus given approximately by l, which is equal to $1/\pi d^2 n$. A rigorous treatment for the average distance between collisions in a gas, which is known as the mean free path, λ, gives:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \tag{1.23}$$

For an ideal gas, $n = P/kT$, where P is the pressure, so that the mean free path can be written:

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P} \tag{1.24}$$

The diffusion coefficient (which will discussed in more detail in the next chapter) is given by:

$$D = \frac{\bar{v}\lambda}{3} \tag{1.25}$$

The viscosity of a gas is given by:

$$\eta = \frac{mn\bar{v}\lambda}{3} \tag{1.26}$$

The thermal conductivity of a gas is given by the specific heat times the diffusion coefficient:

$$K = \frac{C_v\bar{v}\lambda}{3} \tag{1.27}$$

where C_V is the specific heat of the gas at constant volume. A surprising result is obtained by inserting the value of the mean free path, Eq. 1.23, into Eq. 1.26 for the viscosity: the viscosity is independent of the pressure of the gas at a given temperature.

The flux of atoms through unit area in unit time is given by:

$$J = \frac{n\overline{v_x}}{2} = n\sqrt{\frac{kT}{2\pi m}} = \frac{P}{\sqrt{2\pi mkT}} \tag{1.28}$$

which is an expression we will use later for the flux of gas atoms to a surface. For one atmosphere pressure of nitrogen gas at room temperature, the flux is about 6×10^{23} atoms/cm^2 s.

Further Reading

The definition of temperature and the derivation of the Boltzmann function are taken from:

R. P. Feynman, R.B. Leighton, M. Sands, *The Feynman Lectures on Physics*, Vol. 1, Addison-Wesley, Reading, MA, **1963**, Ch. 40.

K. Huang, *Statistical Mechanics*, Wiley, New York, NY, **1963**.

C. H. P. Lupis, *Chemical Thermodynamics of Materials*, North-Holland, New York, NY, **1983**.

Problems

1. The specific heat of a monatomic gas is 3Nk. What are the thermal conductivities of helium and argon at room temperature?
2. How many atoms of argon at a pressure of one atmosphere are incident on a square centimeter of surface at room temperature in one microsecond?

Chapter 2
Diffusion in Fluids

2.1
Diffusion in a Gas

Diffusion describes the motion of atoms, so let us examine the net flux of atoms, J, across a plane in space.

In Fig. 2.1, the density of gas atoms to the left of the plane is n^-, and the density to the right is n^+. The average velocity of the atoms crossing a plane perpendicular to the x-axis is v_x. Denoting the average distance that an atom travels between collisions, which is known as the mean free path, to be λ, and denoting the average time between collisions, which is called the mean free time, to be τ, then the average velocity, v_x, is given by:

$$\bar{v}_x = \lambda/\tau \tag{2.1}$$

The number of atoms crossing the plane from left to right in time Δt is one half of the number within a distance $v_x\,\Delta t$ of the boundary, and similarly from right to left. And so the net flux is:

$$J_x = \frac{\frac{1}{2}n^-\bar{v}_x\Delta t - \frac{1}{2}n^+\bar{v}_x\Delta t}{\Delta t} = \left(\frac{n^- - n^+}{2}\right)\bar{v}_x \tag{2.2}$$

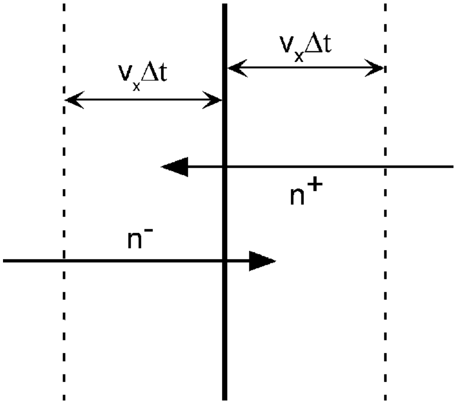


Figure 2.1 Flux of atoms across a plane.

The densities of atoms on the two sides of the plane, n^- and n^+, should be taken as the densities within a mean free path of the plane, and the difference between these two densities can be written in terms of the gradient in the density of atoms:

$$n^+ - n^- = \frac{dn}{dx}\Delta x = \frac{dn}{dx}2\lambda \tag{2.3}$$

where the densities are taken to be within a distance λ of each side of the plane.

The net flux can then be written:

$$J = -\bar{v}_x\lambda\frac{dn}{dx} = -\frac{1}{3}\bar{v}\lambda\frac{dn}{dx} \tag{2.4}$$

where $\bar{v}$ is the average velocity in three dimensions. Comparing this equation with Fick's first law, which is an empirical equation describing the diffusion flux in a concentration gradient in terms of the diffusion coefficient, D:

$$J = -D\frac{dn}{dx} \tag{2.5}$$

results in a diffusion coefficient given by:

$$D = \frac{1}{3}\lambda\bar{v} \tag{2.6}$$

The expression for the average velocity of the atoms in a gas, Eq. 1.22, and for the mean free path, λ, Eq. 1.23 can be substituted into this equation to express the diffusion coefficient in terms of the gas pressure, atom density, and so on. Since the average velocity of an atom is proportional to $\sqrt{1/m}$, Eq. 2.6 indicates that light atoms will diffuse much more rapidly than heavy ones. Since heat is carried by the diffusive motion of the atoms in a gas, the thermal conductivity of a gas is also much larger for gases that are composed of light atoms.

It is worth noting that gases can move very quickly by flow or convection, and this is usually much faster than diffusion.

2.2
Diffusion in Liquids

Diffusion in a liquid is similar to that in a gas, but different. The atoms are also randomly distributed, but they are much closer together. As a result, the collisions are much more complicated many-body interactions, rather than simple two-body collisions. These complex collisions are amenable to computer simulation, but not to mathematical analysis. The atoms or molecules in a liquid are surrounded by other atoms or molecules, which form a cage. An atom or molecule moves within its cage, at thermal velocities, and many of the properties of the liquid can be described by the atom or molecule bumping off its neighbors in its cage. This process is dominated by the repulsive part of the atomic potential. For diffusion, however, the cage must move. And this motion will depend on the differences in momenta and velocity between