

A Course on the INTRODUCTION TO THE MOLECULAR THEORY OF THERMODYNAMICS

H. TED DAVIS

*University of Minnesota
Minneapolis, Minnesota 55455*

WHAT IS DESCRIBED IN this paper is the first quarter of a three quarter graduate course on the molecular theory of thermodynamics and transport phenomena. The course material of the first quarter is designed for the general chemical engineering student. In the subsequent two quarters there is increasing specialization, suited primarily for students with at least some research interest in molecular theoretical subjects. A book on the equilibrium part of the course sequence is in preparation and will perhaps be published next year.

In the course we try to focus on those subjects of traditional importance to chemical engineers, such as bulk fluid phase behavior and transport properties, as well as those subjects rapidly being incorporated into the mainstream of chemical engineering, such as colloid and interfacial phenomena, fluid microstructures (e.g., thin films, liquid crystals, and micellar solutions), and the auto-correlation function theory of transport and relaxation processes.

The structure of the theory is developed at two levels: first concepts are introduced heuristically and their utility established by examples, and then the rigorous basis of the theory is laid. For example, the barometric formula, well-known to chemical engineering students, is used to invent

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H. Ted Davis received his B.S. from Furman Univ. (1959) and his Ph.D. from the Univ. of Chicago (1962). He joined the ChE department at the University of Minnesota in 1963 and is the author of over 100 publications in scientific and engineering journals and edited books. His research interests include statistical mechanics of equilibrium and transport processes, experimental and theoretical investigation of the physico-chemical processes in flow in porous media as related to petroleum recovery, interfacial and colloid science, mathematical modelling of transport, reaction and mechanical properties of disordered media, liquid electronics, and heat and water movement in food systems.

the partition function which is then used to introduce the molecular origins of fluid behavior long before the full trappings of ensemble theory are unveiled in the course.

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The following sections, which appeal more to the heuristic than to the rigorous elements of the course, are chosen to try to exemplify the spirit and substance of the course.

DILUTE GAS KINETICS

THE KINETIC BEHAVIOR OF a dilute gas derives directly from the fact that molecules have non-zero velocities. Effusion or leakage through a small hole in a containing vessel and pressure exerted on a confining wall of a vessel are probably the most familiar manifestations of the existence of

molecular velocity. In 1845, Waterston [1] had correctly recognized the connection between molecular velocity and Dalton's law of partial pressures, Avogadro's law of equal molecular density of gases at equal pressure and temperature, and Graham's law of effusion. However, conservatism of the Royal Society prevented publication of Waterston's work, so that it remained for Maxwell [2] (1860) to rediscover these things along with his Gaussian distribution of velocities, according to which

$$\phi(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{mv^2}{2kT}\right], \quad (2.1)$$

where $\phi(v)d^3v$ represents the probability that a gas molecule has a velocity between v and $v + dv$. The absolute temperature T of the gas and the mass m of a molecule of the gas characterize the dispersion of molecular velocities about a mean value of zero. k is Boltzmann's constant and equals the gas constant divided by Avogadro's number. Maxwell's velocity distribution has been verified experimentally and is predicted from ensemble theory as well as the kinetic theory of gases.

The pressure P exerted by a dilute gas calculated from the momentum exchange between a wall and particles rebounding from the wall is

$$P = \frac{2}{3} n \left\langle \frac{1}{2} mv^2 \right\rangle, \quad (2.2)$$

where $\left\langle \frac{1}{2} mv^2 \right\rangle$ is the average kinetic energy

and n the number density of gas molecules. The empirical ideal gas law is

$$P = nkT. \quad (2.3)$$

The combination of Eq. (2.2), with the average $\left\langle \frac{1}{2} mv^2 \right\rangle$ predicted from a Gaussian distribution, and Eq. (2.3) enabled Maxwell to identify the mean square velocity dispersion as $kT/2m$, the value used in Eq. (2.1).

The Maxwell velocity distribution predicts an average molecular speed of $\langle v \rangle = \sqrt{8kT/\pi m}$, a result demonstrating the connection between the speed of sound, $c = \sqrt{(dP/mdn)_T} = \sqrt{kT/m}$, and the movement of molecules in a dilute gas.

The average flux of dilute gas molecules against a wall is

$$\langle F \rangle = \frac{1}{4} n \langle v \rangle = \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}}. \quad (2.4)$$

This result is the origin of Graham's law, according to which the rates of escape through a pinhole of different gases at the same temperature and pressure vary inversely as the square roots of the molecular weights or mass densities ($\equiv mn$). The ratio of times for equal volumes to escape through the same size pinhole of two different gases at the same temperature and pressure equals the ratio of the molecular weights or of the mass densities of the molecules of the two gases. This is the basis of the effusimeter devised by Bunsen [3] for measuring relative densities or molecular weights of dilute gases.

If two components are in a dilute gas at densities n_1 and n_2 , occupy the same container, and escape from the same pinhole, then the gas densities n_1' and n_2' of the escaping stream obeys the relation

$$\frac{n_1'}{n_2'} = \frac{n_1}{n_2} \left[\frac{m_2}{m_1} \right]^{1/2}. \quad (2.5)$$

Thus, the molecular component of lower molecular weight is enriched upon effusion. This effect is important for isotope separation processes, the most important example of which was the separation of U^{235} from U^{238} during World War II by

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staged gaseous effusion of the hexafluorides of uranium.

Molecules of a dilute gas collide with one another, even when obeying ideal gas equations of state. Collision rates determine the rates of chemical reactions in dilute gases. If the diameter of a molecule is d , then the frequency ν of intermolecular collisions and the mean free path λ (average distance travelled between collisions) are given by

$$\nu = \sqrt{2}\pi d^2 n \langle v \rangle \text{ and } \lambda = \langle v \rangle / \nu = \frac{1}{\sqrt{2}\pi d^2 n}. \quad (2.6)$$

The probability that a particle will travel a distance x (or time t) without collision is

$$q = e^{-x/\lambda} \text{ (or } e^{-\nu t} \text{)}. \quad (2.7)$$

The average particle separation $l \equiv n^{-1/3}$, mean free path, collision frequency, and width X of a vessel for which the probability is 0.95 that a

TABLE I
Dilute nitrogen at 300K. The molecular diameter d
is assumed to be 2×10^{-8} cm.

P(atm)	l (cm)	λ (cm)	ν (sec ⁻¹)	X (cm)
10^{-3}	3.46×10^{-6}	2.34×10^{-2}	2.03×10^6	1.20×10^{-3}
1	3.46×10^{-7}	2.34×10^{-5}	2.03×10^9	1.20×10^{-6}

particle can cross without collision are illustrated in Table I for dilute nitrogen.

Although the mean free path is large compared to the average separation of particles in a dilute gas, the molecules of the gas collide frequently with one another by the time they traverse a system of macroscopic size. Thus, the concept of particle equilibrium (and therefore temperature) makes sense even though the ideal gas law holds for pressure and average energy.

THERMODYNAMIC FUNCTIONS AND THE PARTITION FUNCTION

If an isotropic fluid is subject to a conservative external force, whose potential energy is $u(\mathbf{r})$, then the equation of hydrostatics is

$$\nabla P = -n \nabla u. \quad (3.1)$$

In an isothermal ideal gas, $P = nkT$, so that Eq. (3.1) can be integrated to yield the barometric formula $P(\mathbf{r}) = P(\mathbf{r}_0) \exp(-[u(\mathbf{r}) - u(\mathbf{r}_0)]/kT)$. Or, eliminating pressure in favor of density, we obtain

$$n(\mathbf{r}) = n(\mathbf{r}_0) e^{-[u(\mathbf{r}) - u(\mathbf{r}_0)]/kT}. \quad (3.2)$$

The density $n(\mathbf{r})$ can be interpreted statistically: $n(\mathbf{r})d^3r$ is the probable number of particles in the volume d^3r , so that if $p(\mathbf{r})d^3r$ is the probability that a particle is located in the volume d^3r fixed on \mathbf{r} , then $p(\mathbf{r}) = n(\mathbf{r})/N$, N being the total number of particles in the system. According to Eq. (3.2), $p(\mathbf{r})$ is proportional to the "Boltzmann factor", $\exp -u(\mathbf{r})/kT$.

Combining the results of the preceding paragraph with Maxwell's law of velocity distribution, we conclude that the probability that a particle is in a volume element centered on \mathbf{r} and having velocity between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$ is proportional to

$$e^{-\epsilon/kT} d^3v d^3r, \quad (3.3)$$

where $\epsilon = \frac{1}{2} m v^2 + u(\mathbf{r})$ is the energy of the par-

ticle. Thus, the probability that particle 1 of the gas is in d^3r with velocity in the range \mathbf{v}_1 to $\mathbf{v}_1 + d\mathbf{v}_1$, particle 2 is in d^3r_2 with velocity in the range \mathbf{v}_2 to $\mathbf{v}_2 + d\mathbf{v}_2$, etc., is

$$p_N(\mathbf{r}_1, \dots, \mathbf{v}_N) d^3v_1 d^3r_1 \dots d^3v_N d^3r_N \\ = \frac{e^{-E/kT}}{\widetilde{Q}} d^3v_1 d^3r_1 \dots d^3v_N d^3r_N, \quad (3.4)$$

where $E = \sum_{i=1}^N \left[\frac{1}{2} m v_i^2 + u(\mathbf{r}_i) \right]$ is the

total energy of the particles of the medium and \widetilde{Q} is the normalization constant for p_N , i.e.,

$$\widetilde{Q} = \int \dots \int e^{-E/kT} d^3v_1 \dots d^3v_N d^3r_1 \dots d^3r_N \\ = \left(\frac{m}{2\pi kT} \right)^{3N/2} \int \dots \int e^{-u/kT} d^3r_1 \dots d^3r_N \\ \equiv \left(\frac{m}{2\pi kT} \right)^{3N/2} Z. \quad (3.5)$$

\widetilde{Q} is called the partition function and Z is called the configuration partition function. In Eq. (3.5),

$$u^N \equiv \sum_{i=1}^N u(\mathbf{r}_i).$$

The formula for p_N given above is rigorously established by the equation of hydrostatics for ideal gases. The heuristic step allowing us to treat real fluids is to assume that p_N is of the same form for interacting particles, i.e., that the external force on a particle is that exerted on it by the other molecules in the fluid. Thus, for pair,

$$\text{central forces } u^N = \sum_{i=1}^N u(\mathbf{r}_i) = \frac{1}{2} \sum_{i,j} u(\mathbf{r}_{ij}).$$

With this generalization, the thermodynamic energy of the system is

$$U \equiv \langle E \rangle = \int e^{-E/kT} E \frac{d^3v_1 \dots d^3r_N}{\widetilde{Q}} \quad (3.6)$$

and the pressure is

$$P = \langle F_w \rangle / A, \quad (3.7)$$

where F_w is the force between a flat wall of area A and the particles of the fluid.

Comparing the statistical mechanical expressions for U and P with the thermodynamic expres-

sion $dU = TdS - PdV$, we can show $S = -k \langle \ln p_N \rangle + C(N)$, where $C(N)$ is a function whose N dependence can be determined from the extensivity of entropy. This formula for entropy brings out the relationship between entropy and disorder of a system—the more localized a system is in velocity and coordinate space the smaller is $-k \langle \ln p_N \rangle$. By combining the entropy and energy relation, we obtain the basic starting point of statistical thermodynamics, namely,

$$F = -kT \ln Q, \quad (3.8)$$

where F is the Helmholtz free energy and $Q = \tilde{Q}/N! h^{3N}$ for a pure system or

$$Q = \tilde{Q} / \prod_{\alpha=1}^{\nu} \pi^{\nu} (N_{\alpha}! h^{3N_{\alpha}}) \text{ for a system of } \nu \text{ com-}$$

ponents. From Eq. (3.8), all the thermodynamic functions of interest can be generated as appropriate derivatives of the partition function ($S = -\partial F/\partial T$, $P = -\partial F/\partial V$, etc.). The quantity h , Planck's constant, enters the classical theory only as an undetermined constant but is identified in later lectures on quantum ensemble theory.

With the connection provided by Eq. (3.8), prediction of the thermodynamic properties of classical fluids involves evaluation of the integrals of the configuration partition function Z . If the molecules have internal energies (rotational, vibrational, electronic) that contribute, this will only affect the temperature dependent multiplier of Z in Eq. (3.5) but not Z to a good approximation. In a later section of the course quantum mechanical ensemble theory allows incorporation of the internal energies. The partition function in the quantum mechanical limit is similar to the classical formula of Eq. (3.5) except that the integrations over velocity and configuration states are replaced by summation over energy levels. In the usual approximation for classical fluids, the partition function is expressed in the form $Q = [q_i(T)]^N Z/N!$, where $q_i(T)$ arises from kinetic, rotational, vibrational, and electronic energies of a single molecule and contributes only to the ideal gas part of the thermodynamic functions. The nonideal part is determined by Z .

PHASE EQUILIBRIA OF FLUIDS

ALMOST A CENTURY AGO Van der Waals [5] derived an equation of state that has provided ever since our simplest model for understanding the relation of phase behavior and molecular forces. Moreover, empirical extensions of Van der

Waals' equation, known variously as the Redlich-Kwong [6], Soave [7], Peng-Robinson [8], etc. equations, have provided in many cases quantitative descriptions of phase behavior.

In Van der Waals' model, one divides the pair potential into the sum of two parts, a short ranged repulsive part $u_R(r_{ij})$ and a long ranged attractive part $u_A(r_{ij})$. Then, supposing that the repulsive forces restrict the configurations allowed to the particle centers, one assumes that the total

attractive energy, $u_A^N = \frac{1}{2} \sum_{i,j} u_A(r_{ij})$, is never

far from its average value in the integrand of Z . Thus, the approximation

$$Z \cong e^{-\langle u_A^N \rangle / kT} \left\{ \dots \right\} e^{-u_R^N / kT} d^3r_1 \dots d^3r_N \quad (4.1)$$

is introduced. Since pair potentials are assumed,

$$\langle u_A^N \rangle = \frac{1}{2} N(N-1) \langle u_A(r_{12}) \rangle,$$

$N(N-1)/2$ being the number of interacting pairs and $u_A(r_{12})$ the potential of a typical pair.

Let $p(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2$ denote the probability of a pair of molecules being in a configuration such that one is in d^3r_1 and the other is in d^3r_2 . If \mathbf{r}_1 and \mathbf{r}_2 are far apart, then $p(\mathbf{r}_1, \mathbf{r}_2) = p(\mathbf{r}_1) p(\mathbf{r}_2)$, i.e., the particles are statistically independent. Since the molecules cannot overlap, $p(\mathbf{r}_1, \mathbf{r}_2)$ must go to zero as $|\mathbf{r}_1 - \mathbf{r}_2|$ becomes small. Thus, $p(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) p(\mathbf{r}_1) p(\mathbf{r}_2)$, where $g(\mathbf{r}_1, \mathbf{r}_2)$ is the pair correlation function which represents the deviation of local molecular structure from random packing. g has a first peak representing the nearest neighbor shell, a second peak representing next nearest neighbors, etc. In an isotropic fluid $p(\mathbf{r}) = 1/V$ and $g(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|)$ so that

$$\begin{aligned} \langle u_A^N \rangle &= \frac{1}{2} N(N-1) \int \int p(\mathbf{r}_1, \mathbf{r}_2) u_A(|\mathbf{r}_1 - \mathbf{r}_2|) d^3r_1 d^3r_2 \\ &= \frac{1}{2} \frac{N(N-1)}{V^2} \int \int g(|\mathbf{r}_1 - \mathbf{r}_2|) u_A(|\mathbf{r}_1 - \mathbf{r}_2|) d^3r_1 d^3r_2. \quad (4.2) \end{aligned}$$

Introducing the coordinate transformation $\mathbf{r}_1, \mathbf{r}_2 \rightarrow \mathbf{r}, \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, we can integrate over one of the volumes in Eq. (4.2) to obtain

$$\langle u_A^N \rangle = - \frac{N^2}{V} a; \quad a \equiv - \frac{1}{2} \int g(r) u_A(r) d^3r. \quad (4.3)$$

Van der Waals assumed that the constant a is independent of density and temperature. Since $g(r)$ depends on these quantities, this assumption is an approximation, but not a bad one as has been shown in model calculations.

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The integrals over positions in the repulsive part of Eq. (4.1) can be approximated by assuming that the repulsive forces are rigid sphere forces so that their only role is to exclude from the integration over V a volume Nb occupied by the molecular centers of the particles. Thus, the N -particle integral can be approximated as $(V-Nb)^N$, yielding with Eq. (4.3), the configuration partition function

$$Z = \exp\left(-\frac{N^2a}{VkT}\right) (V-Nb)^N, \quad (4.4)$$

and therefore the free energy expression

$$F = N\mu^+(T) - NkT \ln(V-Nb) + \frac{N^2a}{V}, \quad (4.5)$$

where $\mu^+(T)$ can be interpreted as the chemical potential of the fluid in an ideal gas reference state. The negative volume derivative of F yields the famous equation of Van der Waals (VDW)

$$P = \frac{NkT}{V-Nb} - \frac{N^2a}{V^2}. \quad (4.6)$$

In terms of the molecular diameter, d , the excluded volume is $b = \frac{2\pi}{3} d^3$, so that mean free path, solid density, and the VDW parameter b can be cross checked with one another. Rigorous derivations of Van der Waals theory have appeared in recent years. [9, 10]

From the conditions of the critical point, $(\partial P/\partial V) = \partial^2 P/\partial V^2$, the relations $a = 27k^2T_c^2/64P_c$ and $b = kT/8P_c$ can be obtained. Thus, the parameters of the VDW equation can be determined from the critical pressure and temperature. It also follows that the reduced pressure $P_r \equiv P/P_c$ obeys the equation

$$P_r = \frac{8T_r}{3V_r-1} - \frac{3}{V_r^2}, \quad (4.7)$$

where the reduced temperature and volume are $T_r \equiv T/T_c$ and $V_r = V/V_c$. Equation (4.7) implies that the reduced pressure of all fluids will be the same if they are compared at the same reduced temperature and equation of state. This **law of corresponding state**, being the basis of the so-called generalized charts, has been extremely useful for engineering estimation of thermodynamic properties.

The PVT diagram predicted by the VDW equation is shown in Fig. 1. Level pressure lines (Maxwell tie-lines) connecting coexisting liquid and vapor volumes are given in the figure. The liquid-vapor coexistence states are determined by requiring that the pressure and the chemical potential, $(\partial F/\partial N)_{T,V}$, of the liquid and vapor phases be equal. This is equivalent to finding the pressure such that $\int VdP = 0$, i.e., that the area the pressure isotherm makes with the Maxwell tie-line from below equals the area it makes from above.

The PVT state lying underneath the dashed dome in Fig. 1 are in what is called the spinodal region, where bulk fluid is unstable. These are sometimes called unphysical. This is not strictly true. Such states can be stabilized with density gradients and in fact play an important role in fluid microstructures such as interfaces, drops, bubbles, etc. [11]

The VDW model generalizes easily to multi-component fluids. The first term in the Helmholtz free energy function, Eq. (4.5), is replaced by

$$\sum_{\alpha=1}^{\nu} N_{\alpha} \mu_{\alpha}^+(T) \text{ and the parameters } b \text{ and } a \text{ be}$$

come composition dependent, $b = \sum_{\alpha=1}^{\nu} x_{\alpha} b_{\alpha}$

$$\text{and } a = \sum_{\alpha, \beta=1}^{\nu} x_{\alpha} x_{\beta} a_{\alpha\beta}.$$

x_{α} and b_{α} denote the mole fraction and excluded volume of species α . $a_{\alpha\beta}$ is defined as in Eq. (4.3) for the potential of interaction between particles of species α and β . The equation of state, Eq. (4.6), unchanged in form. A useful empiricism, $a_{\alpha\beta} = \sqrt{a_{\alpha\alpha} a_{\beta\beta}}$, allows one to predict mixture properties using only the critical point parameters of pure fluids.

Liquid-vapor, liquid-liquid, and liquid-liquid-liquid phase equilibria are easily investigated with the VDW equation. The qualitative features of the phase behavior are determined primarily by the relative magnitudes of the excluded volume and energy parameters b_{α} and $a_{\alpha\alpha}$. Liquid-vapor phenomena result largely from a balance between

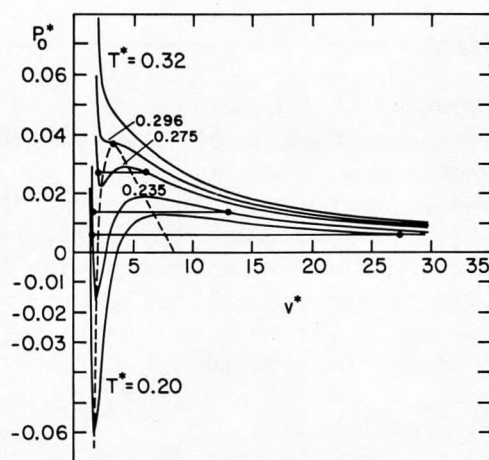


FIGURE 1. Pressure-volume isotherms of a Van der Waals fluid. $P^* \equiv Pb^2/a$, $V^* \equiv V/Nb$, and $T^* \equiv bkT/a$. At the critical point $T^* = 0.296$.

the effects of molecular repulsion (through b) and the effects of molecular attraction (through a). Liquid-liquid phenomena are also sensitive to the relative magnitudes of the attractive energy parameters ($a_{\alpha\alpha}/a_{\beta\beta}$).

In liquid-liquid equilibria one can often simplify the thermodynamic theory by assuming that the molecules are restricted to lattice sites. Such a restriction removes pressure from the problem, equates the Gibbs and Helmholtz free energies, and yields such well-known models as the regular solution model for low molecular weight molecules and the Flory-Huggins model for mixtures of low and high molecular weight molecules. [12] Most of the patterns of phase behavior observed in nature can be explained with the VDW theory and/or the lattice models. However, even with adjustable parameters in the models hydrogen-bonded fluids, unlike the others, are particularly resistant to quantitative predictions.

CONCLUDING REMARKS

AS ILLUSTRATED BY THE material outlined above, one of the key concepts of the course structure is the development of a molecular theoretical basis that not only leads to an understanding of the molecular origins of thermodynamic behavior but also to semiempirical formulas which can be exploited quantitatively to predict thermodynamic properties of real systems. In addition to the topics outlined in this article, we also discuss the molecular theory of fluid microstructures,* the theory of intermolecular forces, quantum princi-

ples, and statistical mechanical ensemble theory. Fluid structure is treated in an elementary fashion in the first quarter course, the advanced theory being reserved to the next quarter. We strive to balance the modern and the traditional elements of the subject, the rigorous and the useful results, and the mathematical and the physical understanding of the phenomena of the field. \square

*This will be the subject of a subsequent paper by Professor Davis in *CEE*. Editor

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ChE news

ZWIEBEL APPOINTED CHAIRMAN

Dr. Imre Zwiebel has been appointed Chairman of the Department of Chemical and Bio Engineering at Arizona State University, effective July 1, 1979.

RICE APPOINTED HEAD

Dr. Richard G. Rice has been appointed Professor and Head of the Chemical Engineering Department at Montana State University, effective August 1, 1979.