Appendix 2A. Physical Examples of the Equations of Mechanics

1. From d'Alembert to Lagrangian Equations

The Lagrangian equations do not closely resemble the Newton equation, [Eq. (1)]. Therefore we shall follow Goldstein[1] to explain the differences. We shall derive Eq. (7) for a non-conservative system. In terms of the q_i's we can write

$$\mathbf{v}_i = \sum_j \frac{\partial \mathbf{r}_i}{\partial q_i} \dot{q}_j j + \frac{\partial \mathbf{r}_i}{\partial t} \tag{A1}$$

$$\delta \mathbf{r}_i = \sum_j \frac{\partial \mathbf{r}_i}{\partial q_j} \delta q_j \tag{A2}$$

With these definitions, the virtual work of the $\mathbf{F}_i$, i.e. $\sum_i \mathbf{F}_i \cdot \delta \mathbf{r}_i$, can be written

$$\sum_i \mathbf{F}_i \cdot \delta \mathbf{r}_i = \sum_i \sum_j \mathbf{F}_j \cdot \frac{\partial \mathbf{r}_i}{\partial q_j} \delta q_j = \sum_j Q_j \delta q_j \tag{A3}$$

where the quantity

$$Q_j = \sum_i \mathbf{F}_i \cdot \frac{\partial \mathbf{r}_i}{\partial q_j}$$

are called generalized forces. With some algebra, we can start from Eq. (A3) and write a relation between the generalized forces and the kinetic energy T

$$\sum_j Q_j \delta q_j = \sum_j \left(\frac{\partial T}{\partial q_j} - \frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} \right) \tag{A4}$$

or

$$\sum_j \left[\left\{ \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j} \right\} - Q_j \right] \delta q_j = 0 \qquad (A5)$$

This set of equations is valid only if the coefficients of the δq_i vanish, (since the latter are independent of δq_k) and we can therefore write

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j} = Q_j \qquad (A6)$$

which are the Lagrangian equations for a non-conservative system. For a conservative system, $F_i = -\nabla V_i$ and using Eq. (A3) Q_j becomes

$$Q_j = -\frac{\partial V}{\partial q_j} \qquad (A7)$$

and Eq. (A6) becomes

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial (T - V)}{\partial q_j} = 0 \qquad (A8)$$

Because the potential V is not a function of time, and therefore independent of the $\dot{q}_j$ it follows that

$$\frac{\partial V}{\partial \dot{q}_j} = 0 \qquad (A9)$$

and therefore we can add this to the first term in Eq. (A8), obtaining the Lagrangian expression for a conservative system

$$\frac{d}{dt}\left(\frac{\partial (T - V)}{\partial \dot{q}_j} - \frac{\partial (T - V)}{\partial q_j}\right) = 0 \qquad (A10)$$

2. The Lagrange Equations

A concise and clear account of the meaning of the Lagrange equations has been provided by many authors, including Landau and Lifshitz. In the simple case of a particle moving in an external field, the Lagrangian L is

$$L = \frac{1}{2}mv^2 - U(\mathbf{r}, t) \qquad (A11)$$

and the equation of motion is

$$m\dot{\mathbf{v}} = -\frac{\partial U}{\partial \mathbf{r}} \tag{A12}$$

which is Newton's equation.

In molecular dynamics simulation, and in other problems, it is often necessary to deal with interactions between different bodies which take the form of constraints, which are restrictions on their relative positions. To determine the motion of this system, the Lagrangian is used with a set of independent generalized coordinates equal in number to the actual degrees of freedom. This is illustrated later in this appendix with reference to small oscillations, important in the theory of normal modes of vibration in molecules and proteins.

3. Hamilton's Equations

The equations of Hamilton, the canonical equations, are first order, and therefore can be solved if we know the generalized coordinates and generalized momenta for t = 0. Taking the simple example of a particle moving in a plane with potential energy V(x, y), the Lagrangian is

$$L = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2) - V(x, y) \tag{A13}$$

and the generalized momenta are

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \qquad p_y = \frac{\partial L}{\partial \dot{y}} = m\dot{y} \tag{A14}$$

from the above we can easily derive the Hamiltonian and canonical equations of motion:

$$H = T + V = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2) + V(x, y) \tag{A15}$$

and

$$\dot{x} = \frac{\partial H}{\partial p_x} = \frac{1}{m}p_x \qquad \dot{p}_x = -\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x} \tag{A16}$$

with the same equations in y.

4. Vibrational Motion and the Harmonic Oscillator

Chapter 5 of Landau and Lifshitz's[34] well known text on mechanics is a clear introduction to the theory of oscillations and normal modes of vibration in molecules. This section is based on the treatment by Landau and Lifshitz.

The theory of harmonic oscillation is based on retaining only the first term in the expansion of the difference U(q) - U(q_0) where the potential energy U is expressed as a function of the coordinat q, whose equilibrium value is q_0. Using $x = q - q_0$ the first term is usually

$$U(x) = \frac{1}{2}kx^2 \tag{A17}$$

where k is a positive coefficient, known as the force constant. If the mass of the particle is m the Lagrangian is

$$L = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2 \tag{A18}$$

and Newton's equation becomes

$$\ddot{x} + \omega^2 x = 0; \qquad \omega = \sqrt{\left(\frac{k}{m}\right)} \tag{A19}$$

whose solution is

$$x = a\cos(\omega t + \alpha) \tag{A20}$$

The system executes harmonic oscillations near equilibrium, and so to a first approximation do the bonds vibrating in a molecule. The coefficient a is the amplitude and α the phase of the vibration. The quantity ω is the angular frequency. The latter can be simulated and this is discussed further in Chapter 8. The energy of the system is proportional to the square of the amplitude.

When the system has more than one degree of freedom, say i, then the potential energy is a function of q_i with a minimum at q_{i0}. Defining $x_i = q_i - q_{i0}$ we have

$$U = \frac{1}{2}\sum_{i,k} k_{ik}x_i x_k \tag{A21}$$

and the Lagrangian of this system, for example a molecule with i degrees of freedom, can be written as

$$L = \frac{1}{2}\sum_{i,k}(m_{ik}\dot{x}_i\dot{x}_k - k_{ik}x_i x_k) \tag{A22}$$

Taking the total differential of the Lagrangian provides the Lagrange equations for the system

$$\sum_k m_{ik}\ddot{x}_k + \sum_k k_{ik}x_k = 0; \qquad (i = 1,2,.....,s) \tag{A23}$$

a set of s linear differential equations with constant coefficients.

The s unknown functions are sought in the assumed form

$$x_k = A_k \exp(i\omega t) \tag{A24}$$

Substituting Eq. (A24) in Eq. (A23) gives

$$\sum_k (-\omega^2 m_{ik} + k_{ik})A_k = 0 \tag{A25}$$

and for non zero solutions the determinant of the coefficients vanishes:

$$|k_{ik} - \omega^2 m_{ik}| = 0 \tag{A26}$$

This is known as the characteristic equation with s different real positive roots in general:

$$\omega_\alpha^2 (\alpha = 1,2,....,s) \tag{A27}$$

The ω's are the characteristic, or eigen-frequencies of the system.

The roots of Eq. (A26) must be real and positive, otherwise the Hamiltonian is not constant. The general solution of the characteristic equation takes the form

$$\Theta_\alpha = Re(C_\alpha \exp(i\omega_\alpha t)) \tag{A28}$$

and the time variation of each coordinate of the system is a superposition of s simple periodic oscillations Θ_1, Θ_2,.. and so on, with arbitrary amplitudes and phases but well defined frequencies.

Normal coordinates are generalized coordinates chosen such that each one of them executes only one simple oscillation. In the same way we arrive at the normal vibrational modes of a diffusing molecule in a simulation. The normal coordinates Θ_α satisfy the equation

$$\ddot{\Theta}_\alpha + \omega_\alpha^2 \Theta_\alpha = 0 \tag{A29}$$

so that there are s independent equations of motion in the normal coordinates, and the normal oscillations of the system are also independent.

The Lagrangian expressed in terms of normal coordinates is a sum of expressions each of which corresponds to oscillation in one dimension, and is of the form:

$$L = \sum_{\alpha} \frac{1}{2} m_{\alpha} (\dot{\Theta}_{\alpha}^2 - \omega_{\alpha}^2 \Theta_{\alpha}^2) \qquad (A30)$$

where the kinetic and potential energies are both in diagonal form.

The use of normal coordinates, defining normal vibrational modes in diffusing molecules, makes possible the reduction of a problem of forced oscillations of a system with more than one degree of freedom to a series of problems of forced oscillations in one dimension. The Lagrangian includes the variable external force:

$$L = L_0 + \sum_{k} K_k(t) x_k \qquad (A31)$$

where L_0 is the Lagrangian for free oscillations. In normal coordinates the equations of motion contain only one unknown.

These normal mode techniques are the basis for the treatment of molecular vibration and its simulation.

5. Classical Anharmonic Oscillation

When dealing with the vibration of polyatomic molecules the change introduced by the consideration of anharmonicity is fundamental. The potential energy, Eq. (A17), is no longer purely quadratic in displacement, and the resolution just described into normal modes of vibration is no longer possible. Lack of symmetry in the governing potential energy leads to very complicated motions as soon as we depart from harmonicity. If the anharmonicity is small, the vibration will at first be approximately harmonic but will gradually evolve into motion of great complexity, there is a transition from deterministic to chaotic motion. The smaller the amplitude and anharmonicity, the greater the time during which the motion is approximately a simple vibration of the type already described.

In anharmonic motion we replace Eq. (A11) with

$$2V = \sum_{i}\sum_{j} k_{ij} x_i x_j + \sum_{i}\sum_{j}\sum_{k} f_{ijk} x_i x_j x_k + \sum_{i}\sum_{k}\sum_{j}\sum_{l} g_{ijkl} x_i x_j x_k x_l + \ldots\ldots\ldots \qquad (A32)$$

which introduces cubic and higher cross terms into the normal coordinates and the total energy is no longer the sum of independent oscillators. In the case of slightly anharmonic vibrations, the normal coordinates may be expressed as a generalized Fourier series.

In spectral terms anharmonicity introduces extra frequencies in the infrared and Raman which can be observed experimentally. These often show that the har-

monic approximation to bond vibration is poor, even in proteins. Anharmonicity splits degenerate vibrational levels and shifts the energies (frequencies) of other vibrational modes of motion. However this is the domain of quantum mechanics, where the Hamiltonian of anharmonic oscillation is used in the Schrödinger equation (Chapter 3).

Chaotic Motion — The development of chaotic motion can be discerned from the complexity of the finite oscillation of a simple circular pendulum. In this case the period always depends on the amplitude of the oscillation, because we are essentially solving a non-linear equation of the type

$$\ddot{\theta}(t) + \frac{g}{a} \sin \theta(t) = 0 \tag{A33}$$

where a is the radius of the described arc and g the acceleration due to gravity. Transition to chaotic motion occurs when considering two or more linked pendula, when the bob trajectories become extremely complicated, and very sensitive to minute changes in the initial conditions. This "transition to chaos" has recently given rise to a whole new science of dynamics.

6. Lagrangian Multipliers

The variation process involved in Hamilton's principle is one in which the time, for each point on the path, is held constant. The virtual displacements occurring in the variation must satisfy equations of constraint of the form

$$\sum_k a_{lk}\, \delta q_k = 0 \tag{A34}$$

The index l indicates there may be more than one such equation.

We now use Eq. (A34) to reduce the number of virtual displacements to independent ones. The procedure for eliminating these extra virtual displacements is the method of *Lagrange undetermined multipliers.*

If Eq. (A34) are true, then so are:

$$\lambda_l \sum_k a_{lk}\, \delta q_k = 0 \tag{A35}$$

where λ_l are, in general, unknown functions of time.

Using Hamilton's Principle, as described in Goldstein, it may be shown that

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_k} - \frac{\partial L}{\partial q_k} = \sum_i \lambda_l a_{lk}; \quad k = 1, 2, \ldots, n \qquad (A36)$$

which are the complete set of Lagrange equations for non-holonomic systems. The r.h.s. of Eq. (A36) can be identified with Q_k, *generalized forces of constraint.*

The Lagrange multiplier method can therefore be used to obtain the forces of constraint and when it is inconvenient to reduce all the q's to independent coordinates.

7. Statistical Mechanics, the Boltzmann and Kramers Equations

The Boltzmann equation represents one of the most elegant attempts made to understand the subtleties of statistical mechanics, and its detailed interface with classical mechanics. A clear account has recently been given by Coffey. The Boltzmann equation is derived from the rate of change of the probability distribution due to collisions, when only two body interactions are important, such as in a dilute gas. The Kramers equation is derived in the limit of small collisions in liquids, and deals with Brownian motion in a potential well. In this limit the positions are unchanged but the velocities are altered infinitesimally by collisions. Between these two limits, numerical methods and computational techniques must be used for solution of the basic equations of statistical mechanics.

The Boltzmann equation is derived on the assumption that collisions that result in uncorrelated changes in molecular velocity are balanced by reverse collisions so that the probability distribution functions are balanced at equilibrium

$$f_i^* f_j^* = f_i f_j \qquad (A37)$$

This implies a detailed balancing of the collisions specified by the velocity exchanges from which the Maxwell distribution follows from Boltzmann's H Theorem, Eq. (A37).

In general the Boltzmann equation is a non-linear integro-differential equation derived from the Hamilton equations and Liouville's equation by assuming that there is collisionless motion ("streaming") and that there are collisions. The latter mean that the D operator of the Liouville equation is no longer zero. It may be written as

$$\frac{\partial f_j}{\partial t} + \mathbf{v}_j \cdot \nabla_{\mathbf{r}} + \frac{1}{m_j}\mathbf{X}_j \cdot \nabla_{\mathbf{v}} f_j = 2\pi \sum_i \int\int \{f_i^* f_j^* - f_i f_j\} g_{ij} b db d\mathbf{v}_i \qquad (A38)$$

where

$$2\pi f_i(\mathbf{r}, \mathbf{v}_i, t) g_{ij} b db dt \qquad (A39)$$

is the probable number of i molecules in a cylindrical shell of radius b. The equation deals with collisions of molecules of type i with molecules of type j. A molecule of type j is located at r and the velocities of each type are denoted v. The probability distribution functions are denoted $f$in each case. Finally X_j denotes an external force.

The Kramers equation is useful for the description of Brownian motion in a potential well, and in its simplest form is equivalent to the Langevin (i.e. Newton type) equation:

$$m\frac{d^2x(t)}{dt^2} + \zeta\frac{dx}{dt} + \frac{\partial V}{\partial x} = F(t) \tag{A40}$$

for one dimensional Brownian motion in a potential V. Here m is the mass of the Brownian particle and F the stochastic force. The equivalent Kramers equation is for the phase space distribution function:

$$f(x, v, t \mid x(0), v(0), 0) = f(x, v, t) \tag{A41}$$

which measures the probability of finding the particle at x with velocity v at time t given its position and velocity at the initial t = 0. It is:

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} - \frac{1}{m}\frac{\partial V(x)}{\partial x}\frac{\partial f}{\partial v} = \frac{\zeta}{m}\frac{\partial}{\partial v}\left(vf + \frac{kT}{m}\frac{\partial f}{\partial v}\right) \tag{A42}$$

It is also known as the Klein and Kolmogorov equation.

8. The Equations of Motion of a Compressible Viscous Fluid

In the general case of three dimensional flow in a compressible, viscous, Newtonian fluid the flow field is given by

$$\mathbf{w} = \mathbf{i}u + \mathbf{j}v + \mathbf{k}w \tag{A43}$$

which is the velocity vector, the pressure, and the density, all as functions of the coordinates x, y, z and of the time t. For the determination of these five quantities there exist five equations, the continuity equation (conservation of mass), the three equations of motion, and the thermodynamic equation of state.

The continuity equation is:

$$\frac{D\rho}{Dt} + \rho\,\mathbf{div}\,\mathbf{w} = 0 \tag{A44}$$

where ρ is the density. The symbol D represents the hydrodynamic derivative, made up of a local and convective contributions.

These equations are derived from Newton's equation [Eq. (1)], but in fluid motion it is necessary to consider gravitational forces, acting throughout the mass

of the body, and forces acting on the boundary, pressure and friction. The surface forces depend on the rate at which the fluid is strained by the velocity field present in it. The system of forces determines a state of stress, and the relation between stress and strain in Newtonian hydrodynamics is linear.

There is considerable practical utility in being able to merge computational techniques with the Newton equation of motion [Eq. (1)] and his linear relation between stress and strain in a fluid environment. After three hundred years the former can be used to investigate the validity of the latter with sufficiently powerful computer systems. If we are able to understand the rheology of simple liquids we are also able to forecast what will happen in situations of interest to engineers in an every day environment. It is possible to extrapolate from picosecond and angstrom scales to those of the laboratory and the industrial engineer. The investigation by Newtonian computer simulation of atomic liquids will lead to results of use with the structurally more complex liquids using master curves and the methods of extrapolative interpolation.

Newton's linear relation between stress and strain is a limiting behavior, and more generally, sheared liquids are "non-Newtonian" showing shear thinning and thickening, structural and convective turbulence and other phenomena characterized by dimensionless numbers, such as the Deborah, Reynolds, and Mach numbers.

9. The Deborah Number

The numerical challenge is to reproduce these phenomena with computer simulation, and Clementi and co-workers have shown how this can be achieved with about a quarter of a million particles. There are several distinct phases in the development of non Newtonian behavior, and these can be classified conveniently by the Deborah number

$$D = \tau_r \dot{\gamma} \tag{A45}$$

where τ_r is the structural relaxation time and $\dot{\gamma}$ the shear rate, so that the product is dimensionless. Newtonian behavior occurs when D is small and the viscosity is a constant, but a variety of other behaviors occurs when D increases.

10. The Reynolds Number

The condition under which flows of different fluids about two geometrically similar bodies display geometrically similar streamlines is given by the Reynolds number

$$R = \frac{\rho v d}{\mu} \tag{A46}$$

where ρ is the density, v the streaming velocity, v a characteristic dimension of the body, such as a diameter of a spherical body, and μ is the frictional force. Thus two flows are similar when the Reynolds number is similar for both, which is Reynolds's principle of similarity. The Reynolds number is dimensionless because ρ has the dimensions of lbf sec^2 / ft^4; v of ft / sec; v of ft.; and μ of lbf sec / ft^2.

11. The Mach Number

This is the ratio of the velocity of flow to the velocity of sound. It is therefore the ratio of two velocities and dimensionless. The velocity of sound is defined as

$$v_s = \sqrt{\left(\frac{E}{\rho}\right)} \tag{A47}$$

where E is the modulus of elasticity and ρ the density.

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